Synthèse et caractérisation de nanocomposites à base de nitrure de silicium et de bore comme support catalytique mesoporeux pour applications énergétiques

Abhijeet Lale

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SYNTHESIS AND CHARACTERIZATION OF SILICON AND
BORON-BASED NITRIDE NANOCOMPOSITES AS
CATALYTIC MESOPOROUS SUPPORTS FOR ENERGY
APPLICATIONS

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Le 04 Octobre 2017

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Abstract (English):
The thesis has been funded by a collaborative research partnership between Indian (Dr. Ravi Kumar, Department of Metallurgical and Materials Engineering, Indian Institute of Technology-Madras (IIT Madras), Chennai) and French institutes (Dr. Samuel Bernard, European Membrane Institute, CNRS, Montpellier), IFCPRA/CEFIPRA. It is focused on the synthesis, and characterization of binary (silicon nitride and boron nitride) and ternary (Si-M-N, B-M-N (M = Ti, Zr, Hf)) ceramics which are prepared through a precursor approach based on the Polymer-Derived Ceramics (PDCs) route. The idea behind the preparation of the ternary systems is to form nanocomposite structures in which metal nitrides (M = Ti, Zr, Hf) nanocrystals grow during the synthesis of silicon nitride and boron nitride. A complete characterization from the polymer to the final material is done. Then, these materials have been prepared as mesoporous monoliths coupling the PDCs route with a nanocasting approach to be applied as supports of platinum nanoparticles for the hydrolysis of liquid hydrogen carriers such as sodium borohydride. The performance as catalyst supports has been evaluated in terms of volume of hydrogen released and reproducibility. We showed that the very high specific surface area TiN/Si₃N₄ nanocomposites displayed the best performance because of the catalytic activity of amorphous Si₃N₄, the presence of nanoscaled TiN and the synergetic effect between Pt nanoparticles, nanoscaled TiN and amorphous Si₃N₄. Interesting, these materials are multi-functional as demonstrated as a proof of concept: they can be applied as electrocatalyst supports, electrode materials for fuel cells and supercapacitors, in particular those containing 2D layered materials and free carbon.
Résumé:

La présente thèse s’inscrit dans un projet collaboratif de type CEFIPRA entre l’Inde (Dr. Ravi Kumar, Department of Metallurgical and Materials Engineering, Indian Institute of Technology-Madras (IIT Madras), Chennai) et la France (Dr. Samuel Bernard, Institut Européen des Membranes, CNRS, Montpellier). Les travaux de thèses se sont consacrés à la synthèse de céramiques de type non-oxyde autour de systèmes binaires (nitrure de silicium et nitrure de bore) et ternaires (Si·M·N, B·M·N (M=Ti, Zr, Hf)) à partir de précurseurs moléculaires et polymères, i.e., la voie polymères précéramiques ou PDCs. L’idée principale de ce travail est de former des structures nanocomposites à partir des systèmes ternaires dans lesquelles des nanocristaux de nitrures métalliques (M=Ti, Zr, Hf) se développent pendant la synthèse du nitrure de silicium et du nitrure de bore. Une caractérisation complète allant des polymères aux matériaux finaux a été conduite. Ces matériaux ont ensuite été préparés sous forme de composés mésoporeux (monolithes) en couplant la voie des polymères précéramiques à une approche de nanomoulage. Ces monolithes à haute surface spécifique et mésoporosité interconnectée ont alors été appliqués comme support de nanoparticules de platine pour l’hydrolyse du borohydrure de sodium pour générer de l’hydrogène. Les performances en tant que support de catalyseur ont été évaluées en termes de volume d’hydrogène libéré et de reproductibilité. Nous avons montré que les nanocomposites TiN/Si₃N₄ de surface spécifique très élevée présentent les meilleures performances grâce à l’activité catalytique du Si₃N₄ amorphe, de la présence de TiN nanométrique et de l’effet syngénétique entre les nanoparticules Pt, le TiN nanostructuré et le Si₃N₄ amorphe. En preuve de concept, nous avons montré que ces structures nanocomposites étaient multifonctionnelles: elles peuvent être appliquées en tant que supports d’électro-catalyseurs et matériaux d’électrodes dans les piles à combustibles et les super-condensateurs, en particulier pour ceux contenant des matériaux lamellaires 2D et du carbone libre.
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I would like to dedicate this thesis to my late maternal grandfather Mr. Sharad Tiloo who was a philosophical guiding light in my life. His words of wisdom and faith in me have brought me to where I am today.
GENERAL INTRODUCTION
At the turn of the 21st century, the world population stood at a staggering 7 billion. In the past one century, human population has exploded by 3 fold to what it was in the early 1900’s. The figure 1 (NETL, National Energy Technology Laboratory, US DOE) below compares the growth of population to the energy consumption during the same period.

The demand for energy increases with increasing population and is expected to increase even further as we cross new frontiers of science. Thus finding new sources of energy has been one of the fundamental pursuits in science and technology. For the past few centuries, fossil fuels like coal and wood have been the mainstay of energy industry in powering the world. There was a shift from coal to crude oil in the second half of the 20th century. The attractive properties of crude oil and its relative abundance lead to its overuse and overexploitation in early years. The industrial revolution in the early 19th century and mass production methods in the mid 20th century pumped a lot of CO and CO₂ along with other harmful gases like (NO)ₓ in the atmosphere which have now led to change in climate and global warming. This exploitation of the nature led to environmental problems like deforestation, pollution of water bodies and air. Thus energy and environment are two sides of the same coin.

Figure 1 World population and Energy Requirement plotted versus time
To protect the environment and allow human race to grow at the same pace a solution is required which takes into account sustainability and renewability. There are various sources of energy in nature which follow these two principles. The most common example is our closest star ‘The Sun’. But we need to remember that these renewable sources have their own inherent problems like cost and operational limitations. These systems need to be coupled with each other to make efficient and sustainable use. One such technology which can be used in the coupling process is hydrogen economy. Nevertheless, the development of a hydrogen economy is hampered by three main issues that can be problematic: i) production, ii) storage and iii) purification. In this thesis we focus on the first problem and up till a certain extent on energy storage in general.

Hydrogen has the highest gravimetric energy density and can be produced from a variety of feedstock including fossil resources as well as renewable resources. It is mainly produced from natural gas at high temperature involving a severe evolution of carbon dioxide which requires separation methods to purify hydrogen. A simpler way to produce hydrogen is found in liquid-phase carriers which can be used in combination with fuel cells to produce electrical energy (for automobiles, stationary applications such as power generators and portable electronics) with zero emission except water. Based on the important opportunities offered by this new-born technology, we have been interested in the hydrogen generation through such processes. Chemical compounds like boranes, hydrides and organic acids are abundant sources of hydrogen which can be easily adapted for existing infrastructure used for liquid fuels. These sources generally require presence of catalyst to make the process of generation feasible. As a main focus of this thesis we develop materials which can be used for these catalytic processes as catalyst or as catalyst supports.

Common oxide ceramics such as silica and alumina have largely dominated the ceramic field, and the understanding of their chemistry, processing and properties has been well documented. In contrast, non-oxide ceramics have been significantly less investigated most probably because their strong and predominantly covalent atomic bonds impose high temperature solid-state sintering, thereby increasing their cost in comparison to oxides. However, ceramic processing techniques based on molecular engineering and polymer chemistry may significantly reduce the processing temperature and costs of these high-tech ceramics, while offering much more versatility in terms of shaping, structure and texture.
Within this context, we firstly focused our work on the design of precursor (molecular and polymeric)-derived binary nitrides such as boron nitride and silicon nitride to be explored as catalyst supports. Because the addition of other elements to these nitrides may extend and improve their performance, we focused secondly on the molecular design of multi-element boron- and silicon-based non oxide ceramics in the B-M-N and Si-M-N-C systems with \( M = \text{Ti, Zr, Hf} \) as catalyst supports.

The thesis has been funded by a collaborative research partnership between Indian (Dr. Ravi Kumar, Department of Metallurgical and Materials Engineering, Indian Institute of Technology-Madras (IIT Madras), Chennai) and French institutes (Dr. Samuel Bernard, European Membrane Institute, CNRS, Montpellier), IFCPRA/CEFIPRA.

The present manuscript is divided into five chapters.

The first chapter deals with the state of art in the field of energy conversion, energy storage and ceramic synthesis from polymer route.

The second chapter deals with the experimental techniques involved in synthesizing the material systems and the characterization tools.

The third chapter discussed on the synthesis and characterization of precursor-derived boron nitride (BN) and its nanocomposite derivatives by introducing transition metal such as Ti, Zr and Hf at molecular scale in BN precursors. We describe in the first part of the chapter the preparation of BN from ammonia borane and polyborazine, then we report in the second part the chemical modification of BN precursors with transition metal-based precursors and the complete structural characterization of the resulting metal-modified BN materials. A last part is focused on the control of the crystallinity of BN.

In the fourth chapter, we applied the concept and structure used in chapter 3 by changing the matrix from BN to silicon nitride (Si₃N₄). The role of the chemistry of the precursors behind the elaboration process of Si-M-N ceramics is highlighted.

In the fifth chapter, we explore the potential of the materials prepared in chapters 3 and 4 as mesoporous components to be used as catalyst supports of platinum nanoparticles for the hydrolysis of a liquid-based carrier, sodium borohydride.
The manuscript ends with a conclusion in which we summarize the results and discussions proposed in each chapter, and underlines its prospective future by evaluating some perspectives.
CHAPTER 1
LITERATURE SURVEY
1. Introduction

With the growing world population and impending climate change we face the challenge of meeting the increased energy requirements with cleaner and greener sources of energy and ways to keep our environment clean. The most promising technologies of clean energy being already used and being optimized for the future are electrochemical power sources including batteries, fuel cells and supercapacitors. Material science is the key to make these technologies commercially available for everyone. Within this context, the first part of the present chapter deals with the description of these technologies. We particularly focused on the fuel cell and supercapacitor systems and on the issues that still limit the commercialization of these technologies: the hydrogen source for fuel cells and the (electro)catalyst supports and electrode materials for both systems. Then, we described the state-of-the-art processes to produce hydrogen from solid hydrogen storage materials with a particular focus on the hydrolysis reaction of sodium borohydride and the ideal catalytic supports. This part is followed by the state-of-the-art electrocatalyst supports and electrode materials that are investigated in the context of fuel cells and supercapacitors. We briefly propose our objectives in terms of alternative materials in this first part to transition toward the second part of this chapter. In the second part, we particularly discuss on the polymer derived ceramic (PDC) route to prepare Si- and B-based ceramics with a particular focus on nanocomposites and porous materials to be used as catalyst support for the hydrolysis of sodium borohydride and electrocatalyst supports/electrode materials for fuel cells and supercapacitors.
2. Energy Context

Electrochemical power sources represent one of the next generation energy sources which can facilitate the transition from fossil fuels to renewable energy sources. The scientific and technological challenges of electrochemical power sources are mainly related to the emergence of new, advanced knowledge and fundamental understanding of materials. Below, we provide a state-of-the-art of three types of electrochemical power source-based technologies and the current key materials that are applied in such technologies. We discuss on their advantages/disadvantages and propose alternative materials that will be developed in the present manuscript.

2.1 Electrochemical Power Sources

Electrochemical cells and systems are important in a wide range of industrial sectors. These form the base of upcoming technologies like renewable energy, energy management conservation, and storage, pollution control/monitoring, and greenhouse gas reduction. A large number of electrochemical technologies have been developed in the past and these systems continue to evolve in terms of life cycle, performance and cost. Existing technologies are being retrofitted with emerging technologies like fuel-cells, large format lithium-ion batteries, electrochemical reactors, ion transport membranes and supercapacitors. This growing demand (multi billion dollars) for electrochemical energy systems along with the increasing maturity of a number of technologies is having a significant effect on the global research and development effort which is increasing in both in size and depth.

Although the energy storage and conversion mechanisms are different in batteries, fuel cell and supercapacitors; there are still some similarities in the three systems which are more detailed below; especially fuel cells and supercapacitors.
2.1.1. Batteries

Batteries are self-contained units that store chemical energy that on demand can directly convert it into electrical energy to power a variety of equipment. Batteries can be classified into three types: primary batteries that are discharged once and discarded; secondary rechargeable batteries that can be discharged and then restore to the original condition by reversing the current flow through the cell; and lastly specialty batteries that are designed to fulfil a specific purpose. These are closed systems, with the anode and cathode being the charge-transfer medium and taking an active role in the redox reaction (Figure 1.1) as “active masses”, i.e., energy storage and conversion occur in the same compartment (Table 1.1).

![Figure 1.1 a) Schematic of a Daniel cell; b) Typical I-V graph for a battery](image)

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>operate over a wide temperature range</td>
<td>low energy content compared to other fuels</td>
</tr>
<tr>
<td>choice of chemical system and voltage</td>
<td>expensive compared to coal and gasoline</td>
</tr>
<tr>
<td>variable in size /commonality of cell sizes</td>
<td>no single general purpose system</td>
</tr>
<tr>
<td>can deliver high current pulses</td>
<td></td>
</tr>
<tr>
<td>operate in any orientation</td>
<td></td>
</tr>
<tr>
<td>can choose best battery for a specific purpose</td>
<td></td>
</tr>
</tbody>
</table>
2.1.2. Fuel Cells

Fuel cells, like batteries, convert chemical energy residing in a liquid and gaseous fuel into electrical energy on demand. Earliest reference to the term “Fuel Cell” was made by German physical chemist Wilhelm Ostwald in 1894. He ideated the use of a device which utilized electrochemical mechanism instead of combustion (chemical oxidation) of natural fuels, such as those in power plants. He suggested that as in this case the reaction will bypass the intermediate stage of heat generation, this would be a “cold combustion”, and hence will not be subject to limitations placed by the Carnot cycle.

Ostwald, in his work had only considered the thermodynamic aspect of the fuel cell but had entirely left out the kinetic aspects of such reactions using natural fuels. The first experiments after the publication of his paper showed that it was very difficult to build such devices using electrochemical oxidation of natural fuels.

Around the mid-1980s, another application (apart from Ostwald's idea of powerful plants) of fuel cells which came up was its use an autonomous power source of intermediate or small capacity. These were intended for use in areas where the grid was inaccessible, such as in means of transport, in portable devices and in remote areas. This new application changed the meaning of the term “Fuel Cell” from a power source with current producing reaction involving natural fuels to an electrochemical power source which works as long as the reactants are provided and products are removed (Figure 1.2). The most widely used example of a fuel cell with gaseous reactants is hydrogen–oxygen (air) fuel cells. An example of a fuel cell with at least one liquid reactant is the methanol–oxygen (air) fuel cell in which methanol is supplied as an aqueous solution.
In modern fuel cells, electrical energy is generated by conversion of chemical energy via redox reactions. These reactions occur at the anode and cathode. As reactions at the anode usually take place at lower electrode potentials than at the cathode, the terms negative and positive electrode (indicated as minus and plus poles) are used. The more negative electrode is designated the anode, whereas the cathode is the more positive one. Thus according to the modern definition these are open systems where the cathode and anode are charge-transfer media and the active masses undergoing the redox reaction are delivered from outside the cell, either from the environment, for example, oxygen from air, or from a tank, for example, fuels such as hydrogen and hydrocarbons. This also is one of the main differences between a battery and a fuel cell.

Fuel cells are placed under the subheading of energy conversion technologies in the regime of electrochemical devices. They have a wide variety and their output can range from a few watts to a Megawatts range. There has a lot of study on their operating regimes and widely varying performance characteristics\(^2\)\(^-\)\(^4\). They can be categorized depending on the type of electrolyte used, the fuel used and fuel usage can be further divided on the operating temperature range (Figure 1.3).

One of the most common fuel cells in use today is the Proton-Exchange Membrane Fuel Cell (PEMFC). These operate at relatively low temperatures ranging from 60°C to 90°C, hence are well suited for both domestic as well as commercial applications. These were first developed by Grubb and Niedrach at General Electric in the 1960s for use as power source in the Gemini spacecrafts\(^1\)\(^,\)\(^5\)\(^,\)\(^6\). The polymeric proton exchange membrane serves as a solid electrolyte and the conductivity is due to the presence of water. The membrane swells leading
to dissociation of the acidic functional groups and formation of protons free to move about throughout the membrane. The following reactions occur in the PEMFC:

At hydrogen anode: $2H_2 + 4nH_2O \rightarrow 4H^+ . nH_2O + 4e^-$

At oxygen cathode: $O_2 + 4H^+ . nH_2O + 4e^- \rightarrow (n + 2)H_2O$

The membrane being currently used in most commercial PEMFC is called Nafion® and it is manufactured by Du Pont.

Due to their light weight and relatively mild operating conditions these are being looked at for use in commercial applications like cars and household uses. The current systems have a specific power of current of 600–800 mW.cm$^{-2}$.

### 2.1.3. Supercapacitors

These are electrochemical devices that use charge separation for storing energy. Generally these have same electrodes on both sides with the difference being the active material loading in each case$^7$. Figure 1.4 shows a schematic form of this symmetrical supercapacitor.

![Figure 1.4 Basic illustration of a common supercapacitor](image)

They typically store 10 to 100 times more energy per unit volume or mass than electrolytic capacitors, can accept and deliver charge much faster than batteries, and tolerate many more charge and discharge cycles than rechargeable batteries. When the electrodes are polarized by an applied voltage, ions in the electrolyte form electric double layers of opposite polarity to the electrode's polarity. For example, positively polarized electrodes will have a layer of negative ions at the electrode/electrolyte interface along with a charge-balancing layer of positive ions adsorbing onto the negative layer. The opposite is true for the negatively polarized electrode.
In our work, we are more focused on fuel cells and supercapacitors and in particular on the two major issues that limit the commercialization of fuel cells and supercapacitors: the hydrogen source for fuel cells and the electrode materials in fuel cells and supercapacitors. Our objectives are to propose alternative hydrogen sources like sodium borohydride as liquid hydrogen carriers for fuel cells and materials like catalyst supports for the hydrolysis of NaBH₄ and electrocatalyst supports/electrode materials for both fuel cells and supercapacitors.

### 2.2 Hydrogen storage materials

Around 50% of the hydrogen produced in the world is made via steam-methane reforming; a mature production process in which high-temperature steam (700–1000 °C) is used to produce hydrogen from a methane source, such as natural gas. In steam-methane reforming, methane reacts with steam under 3–25 bar pressure (1 bar = 14.5 psi) in the presence of a catalyst to produce hydrogen, carbon monoxide, and a relatively small amount of carbon dioxide. Subsequently, in what is called the "water-gas shift reaction," the carbon monoxide and steam are reacted using a catalyst to produce carbon dioxide and more hydrogen. In a final process step called "pressure-swing adsorption," carbon dioxide and other impurities are removed from the gas stream, leaving essentially pure hydrogen. Steam reforming can also be used to produce hydrogen from other fuels, such as ethanol, propane, or even gasoline. However, this is a complex energy-consuming process and methane is also a major contributor to rising CO₂ levels and thus climate change.

The search for hydrogen storage materials capable of efficiently storing hydrogen in a compact and lightweight package and delivering hydrogen on demand is one of the most difficult challenges for the upcoming hydrogen economy. Hydrogen storage is a key enabling technology for the advancement of hydrogen and fuel cell technologies in applications including stationary power, portable power, and transportation. Hydrogen has the highest energy per mass of any fuel; however, its low ambient temperature density results in a low energy per unit volume, therefore requiring the development of advanced storage methods that have potential for higher energy density.

There are mainly two ways to store hydrogen, namely, physical storage and material based storage. Figure 1.5 gives a brief overview of the storage options.
2.2.1. **Physical-based storage**
Hydrogen can be stored physically as either a gas or a liquid. Storage of hydrogen as a gas typically requires high-pressure tanks (350–700 bar [5,000–10,000 psi] tank pressure). Storage of hydrogen as a liquid requires cryogenic temperatures because the boiling point of hydrogen at one atmosphere pressure is −252.8°C. Although physical storage is the most mature hydrogen storage technology as of now, storing it physically for onboard operation can be risky owing to the highly flammable nature of hydrogen.

2.2.2. **Material-based storage**
To avoid the risks related to physical storage of hydrogen it is imperative to develop materials which can store hydrogen via adsorption or as chemical units within themselves. Chemical hydrogen storage materials with high gravimetric and volumetric hydrogen densities have the potential to overcome the challenges associated with hydrogen storage. Moreover, the liquid-phase nature of these hydrogen storage systems provides significant advantages of easy recharging, and the availability of the current liquid fuel infrastructure for recharging.

The chemical hydrides can be divided into two types: organic hydrogen carriers and inorganic hydrogen carriers. The following flowchart (Figure 1.6) lists the major compounds in this series.
Hydrogen release through suitable dehydrogenation reactions has been particularly described for a variety of compounds, such as cycloalkanes, N-heterocycles, 1,2-BN-heterocycles, methanol, formic acid, hydrous hydrazine and ammonia borane (AB). In these categories, we focused on boron-based compounds. As a reference in the category of boron-based compounds Ammonia Borane (AB) is a stable solid at room temperature which is easily dissolvable in polar solvents like water and tetrahydrofuran (THF). Due to its high theoretical volumetric (146 g. L\(^{-1}\)) and gravimetric (19.6 wt\%) hydrogen capacities it is promising candidate for meeting the standards set by U.S. DOE\(^{10,12,13}\). Its thermolysis under nitrogen generates H\(_2\) but also toxic gases like ammonia, diborane and borazine\(^{14-26}\). Hence an aqueous catalytic hydrolysis of AB is the preferred option\(^{27}\). There have been extensive studies on this system as seen by the number of review articles on AB\(^{8,28-33}\). Different types of catalyst ranging from noble metals to first row transition elements have been tested for making this system usable for practical application\(^{27,34-40}\) but the system is far from practical usability mainly due to the high cost involved in its synthesis and regeneration cycle. Also it generates meta·borates as byproducts which, if not dissolved, acts as a poison for the catalyst. The irreversibility and the low solubility of the AB/by-product are major hurdles for the implementation of AB hydrolysis-based hydrogen storage system. Moreover, there may be
some NH$_3$ release due to the generation of NH$_4^+$ during the AB hydrolysis (as shown in equation below), which is highly detrimental for fuel cells. The most attractive aspects of AB hydrolysis are its high stability in water (pH>7) without catalysts and its fast kinetics of hydrogen generation over catalysts at room temperature, which is unattainable in most other hydrogen storage material-based systems. Thus, such a hydrogen storage system would likely find a niche in special applications for hydrogen availability where the benefits outweigh the high cost of AB.

\[ \text{H}_3\text{NBH}_3 + \text{H}^+ + 3\text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{B(OH)}_3 + \text{NH}_4^+ \]  
(hydrolysis of ammonia borane)

As an alternative for AB, hydrazine borane (HB) has been proposed as a new hydrogen storage material\textsuperscript{29,41}. HB is of interest only if the hydrogen can be recovered by hydrolysis of the BH$_3$ group and selective decomposition of the N$_2$H$_4$. Thus, the current research devoted to the catalytic decomposition of hydrous hydrazine could be particularly helpful. The complete dehydrogenation of HB–3H$_2$O leads to a high material-based GHSC of 10.0 wt%, which is much higher than that of the AB hydrolysis system. However, HB apparently suffers from the same issues as AB and hydrazine: (1) since HB is prepared by reacting NaBH$_4$ with hydrazine salts, the recycling processes of the spent fuel of HB are cost- and energy-ineffective; (2) the low solubility of HB (6 g HB per 100 g of H$_2$O at 25 °C)\textsuperscript{42} requires a large amount of excess water to realize the liquid-phase hydrogen storage, thus greatly decreasing its material-based excess GHSC; (3) the spontaneous and catalytic hydrolysis of the BH$_3$ group of HB in aqueous solution results in the occurrence of free N$_2$H$_4$, and therefore there are safety issues related to the dehydrogenation of hydrous hydrazine. Consequently, these significant barriers of the HB dehydrogenation severely hinder its application in liquid-phase hydrogen storage. Moreover, owing to its high theoretical GHSC when HB is used as a solid, some special applications could be expected.

\[ \text{N}_2\text{H}_4\text{BH}_3 + 3\text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{B(OH)}_3 + \text{N}_2\text{H}_4 \]  
(hydrolysis of hydrazine borane)

Sodium borohydride (SB) is one the most studied inorganic compounds as a source of hydrogen due to its high theoretical hydrogen capacity of 10.8 wt%\textsuperscript{43}, easy control of the hydrogen generation rate, friendly operation conditions and environmentally benign hydrolysis product (NaB(OH)$_4$ at room temperature and NaBO$_2$ above 120°C)\textsuperscript{43–45}. The hydrogen can be released either by thermolysis\textsuperscript{46,47} or by hydrolysis\textsuperscript{48–52}. However, hydrolysis is more practical approach to generate hydrogen as one half of hydrogen comes from water
resulting in high hydrogen storage capacity. Also the hydrogen produced is free from impurities and humidified and hence be directly used in a fuel cell. NaBH₄ undergoes hydrolysis at room temperature and liberates a theoretical hydrogen content of 10.8 wt% via the following reaction. Ideally, one mole of SB reacts with 4 moles of water to liberate 4 moles of hydrogen.

\[
\text{BH}_4^-(aq) + 4\text{H}_2\text{O (l)} \rightarrow \text{B(OH)}_4^-(aq) + 4\text{H}_2(g) \quad (1a)
\]

Interestingly, H₂ is pure and the by-product, sodium tetrahydroxyborate, can be recycled into SB. However, NaBH₄ provides the harshest conditions faced by any system facilitating hydrolysis. Figure 1.7 illustrates this concept.

So NaBH₄ upon hydrolysis

- generates sodium tetrahydroxyborate which makes the reaction medium highly basic (pH~14),
- is exothermic and the reaction temperature quickly reaches 80°C in certain conditions
- Needs a catalyst such as platinum (Pt) preferentially as nanoparticles distributed on a support to avoid agglomeration and improve the catalytic activity, the support being suitably selected to optimize the Pt activity.

NaBH₄ also suffers from self hydrolysis in the presence of water. This creates a problem in storing it as an aqueous solution.

Step 1: \( \text{NaBH}_4(s) \rightleftharpoons \text{Na}^+\text{(aq)} + \text{BH}_4^-\text{(aq)} \)
Step 2: $\text{BH}_4^-(\text{aq}) + H_3^+ \Leftrightarrow \text{BH}_3(\text{aq}) + H_2(\text{g})$

Step 3: $\text{BH}_3(\text{aq}) + 3\text{H}_2\text{O}(\text{l}) \rightarrow \text{B(OH)}_3(\text{aq}) + 3\text{H}_2(\text{g})$

Step 4: $\text{B(OH)}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \Leftrightarrow \text{B(OH)}_4^-(\text{aq}) + \text{H}_3^+(\text{aq})$

Step 5: $4\text{B(OH)}_4^-(\text{aq}) + 2\text{H}_3^+(\text{aq}) \Leftrightarrow \text{B}_4\text{O}_7^{2-}(\text{aq}) + 9\text{H}_2\text{O}(\text{l})$

To avoid this problem, Step 2 is disfavored by increasing the pH of the system by addition of a base like NaOH. It was observed by Bartkus et al. that the self-hydrolysis rate becomes negligible above pH=13. In addition, to increase the rate of hydrolysis after the addition of a base, a catalyst is needed. This can either be done by homogeneous catalysis, in which an acid is added to the system, or by heterogeneous catalysis, in which a metal/support system catalyzes the reaction by lowering the activation energy. We focus our attention on heterogeneous catalysis as it provides an “on-off” control for catalyzing the reaction.

Most of the currently used and state of the art systems for hydrolysis are oxide based (Al$_2$O$_3$ or SiO$_2$) or carbon based which in our experience undergo massive structural degradation due to harsh conditions like those mentioned above. The oxide based systems start collapsing with increase in pH due to self hydrolysis and the carbon based systems swell due to adsorption of water. The noble metal or transition metal catalyst deposited on these system starts leaching out due to inefficient immobilization and grain growth. As mentioned above NaBH$_4$ offers the harshest conditions upon hydrolysis and any potential system which can withstand these will be able to work with other fuels without degradation. As a consequence we decided to investigate the hydrolysis of NaBH$_4$ and in particular the design of suitable catalytic supports for the hydrolysis of NaBH$_4$. Besides this, we focused on development of electrocatalytic supports and electrode materials for fuel cells and supercapacitors, respectively. Such (electro)catalysts supports including catalysts, electrocatalyst and electrode materials are the topic of the next section.

2.3. (Electro)catalyst supports and electrode materials

2.3.1. Catalyst supports for the hydrolysis of NaBH$_4$

Selection of supports generally depends on the surface area, the pore volume, the arrangement and type of the porosity as well as the Lewis and/or Bronsted acidity of materials. Apart from these few properties which are important but generally overlooked are thermal conductivity, mechanical stability and chemical resistance towards reaction.
medium. Alumina, silica, zeolites and MOFs are generally used as catalyst supports for various catalytic reactions. As an illustration, silica has been used as a support for the catalytic hydrolysis of ammonia borane. However, the application of silica, zeolites, metal oxides or MOFs in catalytic hydrolysis is somehow limited because their hydrothermal stability may turn to be poor in the severe conditions we have imposed in our study, leading in general to the collapse of the porous structure.

Brack et al. compiled a list of all supported heterogeneous catalyst used for hydrolysis of NaBH₄, which are given in Tables 1.2 and 1.3.

**Table 1.2** List of noble metal catalyst on supports

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Form</th>
<th>Activity(mLH₂.min⁻¹(g.catalyst⁻¹))</th>
<th>NaBH₄ conc./wt%</th>
<th>NaOH conc./wt%</th>
<th>Temp/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru</td>
<td>Supported on IRA 400 resin</td>
<td>189</td>
<td>20</td>
<td>10</td>
<td>25</td>
</tr>
<tr>
<td>Pt/Ru-LiCoO₂</td>
<td>Catalyst dispersed on a nickel mesh</td>
<td>2400</td>
<td>5</td>
<td>5</td>
<td>25</td>
</tr>
<tr>
<td>Pt/Pd-CNT</td>
<td>Supported on CNT paper</td>
<td>126</td>
<td>0.1</td>
<td>0.4</td>
<td>29</td>
</tr>
<tr>
<td>Ru₆₀Co₂₀Fe₂₀ alloy</td>
<td>Supported on activated carbon fibers</td>
<td>5030</td>
<td>10</td>
<td>4</td>
<td>25</td>
</tr>
<tr>
<td>Pt/Ru-LiCoO₂</td>
<td>Catalyst bed</td>
<td>3000</td>
<td>10</td>
<td>5</td>
<td>25</td>
</tr>
<tr>
<td>Ru</td>
<td>Supported on ion exchange resin beads</td>
<td>132</td>
<td>5</td>
<td>1</td>
<td>25</td>
</tr>
<tr>
<td>Ru</td>
<td>Supported on polymer beads</td>
<td>216</td>
<td>1</td>
<td>1</td>
<td>Not stated</td>
</tr>
<tr>
<td>Ru on graphite</td>
<td>Supported on graphite</td>
<td>969</td>
<td>10</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>Rh/TiO₂</td>
<td>Immobilized onto titanium dioxide support to form a catalyst bed</td>
<td>210</td>
<td>15</td>
<td>5</td>
<td>23</td>
</tr>
<tr>
<td>Alumina carrier Ru composite</td>
<td>Supported on alumina</td>
<td>68.2</td>
<td>12.5</td>
<td>1</td>
<td>25</td>
</tr>
</tbody>
</table>

**Table 1.3** List of non-noble metal and alloy catalyst on supports
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Form</th>
<th>Activity (mL H₂ min⁻¹ (g catalyst⁻¹))</th>
<th>NaBH₄ conc. (wt%)</th>
<th>NaOH conc. (wt%)</th>
<th>T°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-B/Ni foam</td>
<td>Dip coated</td>
<td>7200</td>
<td>25</td>
<td>3</td>
<td>20</td>
</tr>
<tr>
<td>Co-B</td>
<td>Thin film prepared by pulsed laser deposition</td>
<td>3300</td>
<td>0.1</td>
<td>Not stated</td>
<td>25</td>
</tr>
<tr>
<td>Co-B</td>
<td>Supported on carbon black</td>
<td>2073</td>
<td>0.75</td>
<td>8</td>
<td>25</td>
</tr>
<tr>
<td>Co-P</td>
<td>Electroplated on copper</td>
<td>954</td>
<td>10</td>
<td>1</td>
<td>30</td>
</tr>
<tr>
<td>Co-W-B/Ni foam</td>
<td>Electrolessly plated</td>
<td>15</td>
<td>20</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>Co-B/Ni foam</td>
<td>Electrolessly plated</td>
<td>11</td>
<td>20</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>Co-B</td>
<td>Thin film prepared by pulsed laser deposition</td>
<td>5016</td>
<td>0.1</td>
<td>4</td>
<td>25</td>
</tr>
<tr>
<td>Co/PPX-Cl</td>
<td>Metallized films</td>
<td>4250</td>
<td>2.5</td>
<td>10</td>
<td>25</td>
</tr>
<tr>
<td>Ni(0) nanoclusters</td>
<td>Stabilized on PVP</td>
<td>4250</td>
<td>0.57</td>
<td>0</td>
<td>25</td>
</tr>
<tr>
<td>Co-B/Pd</td>
<td>Dry dip coated</td>
<td>2875</td>
<td>20</td>
<td>4</td>
<td>30</td>
</tr>
<tr>
<td>Co on activated C</td>
<td>Powder</td>
<td>3600</td>
<td>5</td>
<td>1</td>
<td>30</td>
</tr>
<tr>
<td>Co-B</td>
<td>Carbon supported</td>
<td>166</td>
<td>1</td>
<td>5</td>
<td>25</td>
</tr>
<tr>
<td>Co-Ni-P</td>
<td>Electrodeposited</td>
<td>2479</td>
<td>10</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>Co-B</td>
<td>Electrolessly plated</td>
<td>1640</td>
<td>10</td>
<td>5</td>
<td>25</td>
</tr>
<tr>
<td>Ni-Ru</td>
<td>Electrolessly plated</td>
<td>400</td>
<td>10</td>
<td>5</td>
<td>35</td>
</tr>
<tr>
<td>Fe-Co-B/Ni foam</td>
<td>Electrolessly plated</td>
<td>22</td>
<td>15</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>Co-P-B</td>
<td>Thin film prepared by pulsed laser deposition</td>
<td>4320</td>
<td>0.95</td>
<td>1</td>
<td>25</td>
</tr>
<tr>
<td>Material</td>
<td>Method</td>
<td>Temperature</td>
<td>Time</td>
<td>Tension</td>
<td></td>
</tr>
<tr>
<td>--------------------------------</td>
<td>-------------------------</td>
<td>-------------</td>
<td>------</td>
<td>---------</td>
<td></td>
</tr>
<tr>
<td>Co-P/Ni foam</td>
<td>Electrolessly plated</td>
<td>3584</td>
<td>10</td>
<td>1</td>
<td>30</td>
</tr>
<tr>
<td>Co-P on Cu sheet</td>
<td>Electrolessly plated</td>
<td>1846</td>
<td>5</td>
<td>1</td>
<td>25</td>
</tr>
<tr>
<td>Co-B</td>
<td>Supported on attapulgite clay</td>
<td>3350</td>
<td>5</td>
<td>10</td>
<td>25</td>
</tr>
<tr>
<td>Co-alumina on Cu plates</td>
<td>Electrodeposited</td>
<td>383</td>
<td>3</td>
<td>1</td>
<td>80</td>
</tr>
<tr>
<td>Co</td>
<td>CoCl₂ solution added to a solid powder mixture of NaOH and NaBH₄</td>
<td>23,333</td>
<td>50</td>
<td>5</td>
<td>Unregulated</td>
</tr>
<tr>
<td>Co NPs embedded on a B thin film</td>
<td>Pulsed laser deposition</td>
<td>3375</td>
<td>0.095</td>
<td>0</td>
<td>25</td>
</tr>
<tr>
<td>Co-B NPS</td>
<td>Supported on hydrogels</td>
<td>120</td>
<td>0.19</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>Co-Ni-P/Pd-TiO₂</td>
<td>Electrolessly plated</td>
<td>460</td>
<td>1.13</td>
<td>10</td>
<td>25</td>
</tr>
<tr>
<td>Co-B NPs</td>
<td>Supported on TiO₂</td>
<td>12.65</td>
<td>1</td>
<td>3.75</td>
<td>30</td>
</tr>
<tr>
<td>Co-B NPs</td>
<td>Supported on Al₂O₃</td>
<td>11.65</td>
<td>1</td>
<td>3.75</td>
<td>30</td>
</tr>
<tr>
<td>Co-B NPs</td>
<td>Supported on CeO₂</td>
<td>10.39</td>
<td>1</td>
<td>3.75</td>
<td>30</td>
</tr>
<tr>
<td>Co</td>
<td>Supported on colloidal carbon spheres</td>
<td>1911</td>
<td>1</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>Co-B</td>
<td>Impregnation onto carbon supports</td>
<td>1358</td>
<td>1</td>
<td>8</td>
<td>27</td>
</tr>
<tr>
<td>Co-W-P on Cu substrates</td>
<td>Electrolessly plated</td>
<td>5000</td>
<td>10</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>Co-B</td>
<td>Solution plasma process</td>
<td>4380</td>
<td>2</td>
<td>7</td>
<td>25</td>
</tr>
<tr>
<td>Co-ZIF-9</td>
<td>Solvothermal</td>
<td>182</td>
<td>0.5</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>Co-P</td>
<td>Electrodeposition</td>
<td>5965</td>
<td>10</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>Co-Ni-P</td>
<td>Electrolessly plated</td>
<td>3636</td>
<td>10</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>Zr/Co</td>
<td>Impregnation onto carbon supports</td>
<td>1708</td>
<td>5</td>
<td>2</td>
<td>Not stated</td>
</tr>
</tbody>
</table>
Co:B | Supported on carbon black | 8034 | 10 | 5 | 25  
Ni-Co-P | Supported on alumina | 6600 | 2 | 4 | 55  
PAN/CoCl2-CNT nanofibers | Electrospun | 1255 | 1 | 0 | 25  
Co:B/Ni foam | Electrolessly plated | 24,4 | 15 | 5 | 30  
Co/Ni foam | Magnetron sputtered | 2650 | 3.8 | 4.5 | 23  
Co3O4 | Solution combustion synthesized powder | 1240 | 0.6 | 0 | 20  
Co NPs | Supported on a polyacrylamide hydrogel network | 537 | 3.8 | 5 | 30

We looked at Pt support systems which can withstand the harsh conditions mentioned in the previous section without degradation of both the catalyst and the support. B-based non-oxide ceramics such as BN and its nanocomposite as well as Si based ceramic systems like SiC, Si-C:N and Si3N4 warrant attention due to their excellent mechanical properties, good stability in harsh chemical conditions and high thermal conductivity. As a catalyst non-porous (SSA< 60 m².gm⁻¹) Si3N4 has been tested as powdered support for metals like Ag, Pd and Pt58–61. The major problem with powders is the recovery of these systems from the reaction medium, thus making them expensive one time use system. To overcome these difficulties we propose the use of mesoporous BN, SiC, Si-C:N and Si3N4 monoliths and their nanocomposite derivatives through the polymer derived ceramic (PDC) route which will be discussed later in section 3 to 5.

2.3.2. Electrocatalyst supports and electrode materials

Conventional electrode materials can be divided into three different groups depending on the charge storage mechanism. Figure 1.8337 illustrates the taxonomy of the supercapacitor electrode materials.
The electrocatalyst supports and electrode materials play a significant role in the performance of the energy storage and conversion devices. Carbon, metal compounds and conducting polymers are the three main types used as electrode materials for energy storage devices. In particular, carbon based electrodes (activated carbon, carbon nanotubes, graphene, etc.) with high conductivity and stability usually have excellent recycling stability and high power density as supercapacitor electrodes, battery anodes and as support for fuel cells. Furthermore, they are usually cheap and easy to prepare.

In fuel cells, especially in polymer electrolyte membrane (PEM), the carbon black supported platinum (Pt) nanoparticles remains the state-of-the-art electrocatalyst and Vulcan XC-72 carbon black (SSA: 218 m².gm⁻¹ and V_Porosity: 0.41 cm³.gm⁻¹) is the most popular catalyst support currently used in the Pt/C electrocatalysts. However, it has been demonstrated that carbon undergoes corrosion under the oxidizing conditions of a fuel cell, thereby degrading the electrocatalyst and significantly reducing the durability of a PEM fuel cell system. Carbon is known to undergo electrochemical oxidation to form surface oxides and CO/CO₂ under these conditions and potential cycling can further increase the rate of carbon support corrosion. Significant oxidation of carbon support can be expected to decrease the performance of a fuel cell, due to the loss and/or agglomeration of Pt particles caused by the mass loss of carbon supports. Surface C/O groups can also decrease the conductivity of catalysts and weaken its interaction with the support resulting in an accelerated Pt sintering; thus drastically affecting the performance of a PEM fuel cell. These results indicate the vulnerability of carbon support under fuel cell operating conditions.
An ideal catalyst support material should have corrosion resistance properties under strongly oxidizing conditions of PEM fuel cell: high water content, low pH (<1), high temperature (50-90°C), high potentials (> 0.9 V) and high oxygen concentration. Besides this, some basic requirements should be met including good conductivity (at least 0.1 S.cm⁻¹) and high surface area (>500 m².gm⁻¹).

A material which has been extensively investigated as electrode/electrocatalyst support material is titanium nitride (TiN) due to its excellent thermal and chemical stability as well as electrical conductivity. Its performance as an electrocatalyst support for Pt nanoparticles in direct methanol fuel cell is better than that of traditionally used Pt/Vulcan XC-72 catalyst. It has also been tested as supercapacitor electrode material with sufficiently high performance. Sampath and Thotiyil explored the synergetic effect between the Pt and PtRu metallic catalyst deposited on TiN support. They suggested that the TiN scavenges CO during electrochemical oxidation of methanol thereby protecting the Pt nanoparticles from poisoning which is not the case with Pt/vulcan XC-72 system. They also suggested certain electronic synergy between Pt/TiN which leads to enhanced performance and can reduce the amount of Pt required thereby bringing down the cost of the system.

Even with high chemical stability, the TiN support becomes susceptible to corrosion at high current values when the passivating film is broken down this lead to degradation of the support as demonstrated by Avasarala and Haldar. It is also known that the activity of TiN decreases with increasing size of its crystals (aging) which is exactly what happens when it is exposed to high currents in a harsh electrolytic environment. The same can happen when the Pt nanoparticles are not efficiently immobilized on supports thereby decreasing their activity as well. To overcome this problem, we have proposed the use of mesoporous Ti(C)N/SiCN (silicon carbonitride) nanocomposite monoliths through the PDC route as discussed in sections 4-5. The TiN nanoparticles are enclosed within an amorphous SiCN matrix which prevents the nanoparticle growth (ageing) and protects it from corrosion because of the high stability and robustness of the matrix.

In supercapacitor, the high internal resistivity of carbon-based electrodes, due to contact resistance between carbon particles decreases the supercapacitor performance. In addition, the surface area inaccessible to electrolyte ions also impedes the capacitance performance of carbon materials, resulting in limited capacitance values of only 40–160 F.g⁻¹ for both activated carbon and carbon aerogels and 10–35 F.g⁻¹ for CNTs. Furthermore, activated
carbon, the most commonly used carbon based electrode faces a major problem of ageing and corrosion related issues due to harsh operating conditions in terms of a humid oxidative atmosphere. A potential electrode material for supercapacitors should have the following properties:

a. High specific surface areas, in the order of 1000 m².gm⁻¹
b. Good intraparticle and interparticle conductivity in porous matrices
c. Good electrolyte accessibility to intrapore space of carbon materials

Any new material should confer with these properties apart from being low cost, non-toxic, and chemically stable and should have big range of operating temperature. Recently Gogotsi et al. started working with new types of 2D supercapacitor electrode material called MXenes.

MXenes are derived from the family of hexagonal MAX phases (ternary nitrides and carbides), where M represents early transition metals (Ti, V, Cr, Nb), A stands for an A-group element (Al, Si, Sn, In etc) and X represents C and/or N (Figure 1.9).

![Figure 1.9 Structure of MAX phase and MXene formed after selective etching](image-url)
They display the following formula $M_{n+1}AX_n$, where $n = 1$ to 3. MXenes are derived from MAX phases by selective removal of A from the system generally by chemical leaching. Theoretically a lot of MXenes are possible but experimentally only 11 have been synthesized till date\textsuperscript{98,99}. The MXene surface can be modified by surface termination which leads to interesting properties in terms of band gap and conductivity. MXenes are hydrophilic and are majorly hydroxyl terminated. Furthermore, the highly layered 2D structure provides enough surface area for electrolyte to interact and the surface modification provides it with high conductivity. Cation intercalation ($\text{Mg}^{2+}$, $\text{K}^+$, $\text{Na}^+$, $\text{Al}^{3+}$, $\text{NH}_4^+$, $\text{Ba}^{2+}$, $\text{Ca}^{2+}$, $\text{Cs}^+$, $\text{Li}^+$) can lead to high capacitance (over 300 F.cm$^{-3}$). The cation intercalation rates are unusually high in MXene and the process is referred to as intercalation pseudocapacitance\textsuperscript{100}. These reasons have led to recent interest in the use of MXene as electrode material. A binder free $\text{Ti}_3\text{C}_2\text{Tx}$ MXene ($\text{T}^\prime$: Al, Mn) with a surface area of 98 m$^2$.gm$^{-1}$ was obtained by delamination and tested for electrode use. It showed high flexibility and a high volumetric capacitance of 350 F.cm$^{-3}$ with a NaOH electrolyte\textsuperscript{94,96}. Although the shape of the cyclic voltammetry curves slightly differs depending on the cation\textsuperscript{94,101}, there are no pronounced peaks and the cyclic voltammetry profiles look ‘capacitor-like’ (Figure 1.10). However, due to continuous exposure to the electrolyte the MXene electrode undergoes aging (crystal growth).

To avoid MXenes aging, we propose to prepare \textbf{MXene-based ceramic composites} through the \textbf{PDC route} which will be discussed later in section 3. Such composite can provide enhanced electrochemical and mechanical performance while avoiding corrosion of MXenes because of the presence of the ceramic matrix. The later will also protect the MXene structure from

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\textbf{Figure 1.10} a) Ideal ‘capacitor-like’ cyclic voltammetry curve\textsuperscript{102}; b) Electrochemical performance of $\text{Ti}_3\text{C}_2\text{Tx}$-based supercapacitors in various aqueous electrolytes\textsuperscript{94}
effects of leaching and they will provide structural strength without harming its conductive properties. The PDC route is investigated in the following section.
3. The Polymer-Derived Ceramics (PDCs)

Preceramic polymers have been proposed over 50 years ago as precursors for ceramics. More than 10000 research papers have been published regarding precursor ceramics but less than 1% of those use the term precursor/polymer derived ceramics (PDC). The route can be used to prepare Si-based ceramics, which have formed the core of this field, and also B-based and Al-based ceramics in various systems including carbides, carbonitrides, nitrides, borides and silicides.

3.1. Principle of PDC route

In order to produce ceramic components with near net precision and controlled chemical composition, it appeared obvious to chemists that improved control of compositional homogeneity and purity as well as processability in ceramic synthesis should be achieved by use of single-source precursors, preceramic polymers and solution techniques. With this viewpoint focused on, the PDC emerged over the last decades.

The PDC route provides a facile method to synthesize complex shapes of ceramics such as fibers, coating and porous materials, in a way not known with more conventional approaches. In principle, conventional polymer processing techniques like polymer infiltration pyrolysis, injection molding, coating using solvents, extrusion or resin transfer molding can be used to shape the preceramic polymer which can then be converted in to final ceramic component by heating to a temperature high enough to consolidate all the elements in the polymeric structure to the ceramic. Figure 1.11 gives a general overview of the PDC route.

The molecular structure of the monomer unit has a huge influence not only on the chemical/elemental composition of the final ceramic but also on the number of phases present in the ceramic, their distribution and the microstructure. Hence, we not only control the microscopic properties of the final ceramic but also the macroscopic properties just by tweaking the preceramic polymer used. Apart from having the desired elemental composition, we can summarize the properties: the polymer should have sufficiently high molecular mass in order to avoid volatilization of low-molecular components; it should display rheological properties which are suited for processability, and latent reactivity for curing and crosslinking step to provide ceramics with high yield. However, gathering all these requirements in only one molecule is very challenging.
Once the preceramic polymer is selected, the next step in the processing/shaping the polymer to obtain the desired net/green body. Since the preceramic polymers are still polymeric in nature at the temperature at which the shaping/processing is carried out, there are varied and unique ways to shape the polymer as compared to ceramic powders or pastes. One of the main advantages of using preceramic polymers is to avoid problems related to brittle fracture while machining and wear of tool to shape the ceramics since these are shaped before ceramization at significantly lower processing temperatures. Since rheological properties of the preceramic polymer can be easily manipulated, it allows its easy use in plastic forming techniques (resin transfer molding (RTM), extrusion, warm pressing, fiber drawing, injection molding). Table 1.4 compiled by Colombo et al. shows various shaping techniques used in processing of PDC.

As the preceramic polymer needs to transform into a thermoset to retain the shape, a precursor needs to be a cross-linkable compounds. The incorporation of functional group which can take part in with the crosslinking and/or the addition of catalyst, the cross-linking temperature can be brought down, also, the lower cross-linking temperature helps in
reducing the evaporation of oligomers with formation of bubbles and increases the ceramic yield\textsuperscript{109,110}.

\textbf{Table 1.4} Shaping techniques used in PDC processing

<table>
<thead>
<tr>
<th>Shaping technique used</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Casting/freeze casting</td>
<td>Melcher and colleagues\textsuperscript{111–114}</td>
</tr>
<tr>
<td>Impregnation/infiltration</td>
<td>Satoa and colleagues\textsuperscript{115–117}</td>
</tr>
<tr>
<td>Tape casting</td>
<td>Cromme \textit{et al.}\textsuperscript{118}</td>
</tr>
<tr>
<td>Coating (spraying, dip- or spin-coating, chemical vapor deposition)</td>
<td>Goerke and colleagues\textsuperscript{119–121}</td>
</tr>
<tr>
<td>Pressing (cold/warm—uniaxial, cold— isostatic)</td>
<td>Haug and colleagues\textsuperscript{122–124}</td>
</tr>
<tr>
<td>Injection molding</td>
<td>Zhang and colleagues\textsuperscript{125,126}</td>
</tr>
<tr>
<td>Extrusion</td>
<td>Mutsuddy and colleagues\textsuperscript{127–129}</td>
</tr>
<tr>
<td>Fiber drawing</td>
<td>Bunsell and colleagues\textsuperscript{130,131}</td>
</tr>
<tr>
<td>Blowing/foaming</td>
<td>Zeschky and colleagues\textsuperscript{132–134}</td>
</tr>
<tr>
<td>Machining</td>
<td>da Rocha \textit{et al.}\textsuperscript{108}</td>
</tr>
<tr>
<td>Joining</td>
<td>Colombo and colleagues\textsuperscript{135–137}</td>
</tr>
<tr>
<td>Rapid prototyping</td>
<td>Friedel \textit{et al.}\textsuperscript{138}</td>
</tr>
<tr>
<td>Ink jetting</td>
<td>Mott and colleagues\textsuperscript{139,140}</td>
</tr>
<tr>
<td>Electro-hydrodynamic-spraying/spinning</td>
<td>Nangrejo and colleagues\textsuperscript{141–145}</td>
</tr>
<tr>
<td>Aerosol spraying</td>
<td>Xiao and colleagues\textsuperscript{146,147}</td>
</tr>
<tr>
<td>Self-assembly</td>
<td>Garcia and colleagues\textsuperscript{148–150}</td>
</tr>
<tr>
<td>Microcomponent processing (UV/X-ray lithography, nano-/microcasting, replication, microextrusion, embossing/forging)</td>
<td>Hanemann and colleagues\textsuperscript{151–161}</td>
</tr>
<tr>
<td>Microfluidics processing</td>
<td>Ye \textit{et al.}\textsuperscript{162}</td>
</tr>
<tr>
<td>Emulsion processing</td>
<td>Bakumov \textit{et al.}\textsuperscript{163}</td>
</tr>
<tr>
<td>Formation of nanostructures (tubes, fibers, wires, cables, belts, coils), directly by pyrolysis</td>
<td>Otoishi and colleagues\textsuperscript{114,164–171}</td>
</tr>
</tbody>
</table>

The thermal decomposition of the preceramic polymer leads to the formation of the intended ceramic. It is divided broadly into two parts: cross-linking (<500°C) and ceramization (600 -
1400°C). The cross-linking step can involve a lot of reactions depending on the composition of the preceramic polymer. It usually allows thermosetting the polymer. Crosslinking is in general done by thermolysis but for low dimensional components, e-beams and γ radiation can be applied\textsuperscript{172–174}. UV curing can also be used for microcomponents and fibers if photosensitive functional groups are grafted on the backbone of the polymer\textsuperscript{157,175,176}. Cross-linking is followed by ceramization which starts from 600°C and may well exceed to 1400°C in some cases. This step involves the release of all organic groups still attached to the backbone chain and leads to an amorphous ceramic network. Crystallization therefore occurs at higher temperature. The PDC route is an attractive method to prepare 1) crystalline structures, 2) amorphous structures constituted of a combination of elements homogeneously distributed at atomic scale for which the binding energies are derived from predominantly local covalent bonds and 3) composites or nanocomposites composed of 2 or 3 phases. The main family of PDC that has been investigated during the last decades concerns the Si-based non-oxide ceramics. They mainly display an amorphous structure as used. These have been discussed in the following section.

3.2. The PDC route toward Si-based ceramics

Most of the structural and functional ceramics being used are Si-based ceramics including silicon carbide (SiC) and silicon nitride (Si3N4). A third element can be added to these binary systems to form the silicon oxycarbide (Si-O-C) or oxinitrides (Si-O-N) and silicon carbonitride (Si-C-N). These systems are produced from organosilicon polymers as depicted in the Figure 1.12.
Figure 1.12 also shows that metals and metalloids such as titanium (Ti) and boron (B) can be added at molecular scale in these polymers to tune the properties of both the polymers and ceramics. In the next part, we discuss on the preparation of SiC, Si₃N₄ and Si-C-N ceramics which have been investigated in the present PhD thesis.

3.2.1. Silicon carbide (SiC)

As ceramic fibers of silicon carbide (SiC) was done in the middle of the seventies¹⁷⁷,¹⁷⁸,¹⁷⁹. There are two types of commercially available organosilicon polymers to prepare SiC. They display the structural configuration [-Si-C-]ₙ. Yajima et al. reported in 1975 the preparation of β-SiC through pyrolysis of methyl-substituted polysilanes, namely PCS. PCS, a solid, fusible and soluble preceramic polymer, has been investigated as a precursor for SiC fibers for over 30 years. The first synthesis was reported by Kumada et. al. via thermal reorganisation of polymethyilsilane (Figure 1.13)¹⁸⁰. This reaction is better known as the Kumada rearrangement.
Figure 1.13 a) Synthesis of SiC from dichlorosilane involving Kumada rearrangement- Yajima process; b) Basic structural formula for SiC precursors

Apart from Yajima’s process, other route like polycondensation of chlorosilanes, hydrosilylation reactions or polymerization by ring-opening mechanism can lead to designing of new polymers which form SiC\textsuperscript{181}. Pyrolysis of PCS under argon lead to formation of SiC but with considerable amount of free carbon while that of polymethylsilane leads to excess Si as discussed before\textsuperscript{182}. The presence of excess Si and C degrades the thermomechanical properties of this ceramic at high temperature by making it more prone to thermal oxidation. Furthermore, the preparation of geometries other than fibers is procedurally difficult because of the low ceramic yield of PCS and the dimensional changes which occur during the pyrolytic conversion into SiC.

To avoid this, Interrante et al. developed hyperbranched polycarbosilanes, hydridopolycarbosilanes (HPCS) (Figure 1.14) which produced a stoichiometric ceramic Si:C as 1:1\textsuperscript{183}. Interrante et al.\textsuperscript{183} observed a highly branched structure with a chemical formula corresponding to [SiH\textsubscript{x}CH\textsubscript{2}]\textsubscript{n} (where x= 0-3). By using IR spectroscopy, they observed peaks for SiH, SiH\textsubscript{2} and SiH\textsubscript{3}. The \textsuperscript{13}C NMR spectra confirmed the presence of SiCH\textsubscript{2}CH\textsubscript{3}, SiCH\textsubscript{2}Si and Si(CH\textsubscript{2})\textsubscript{3} type groups. So the overall structure of HPCS was highly branched.

Figure 1.14 Structure of HPCS as described by Interrante et al.\textsuperscript{184}
HPCS was later modified to allylhydridopolysilane (AHPCS)\textsuperscript{185}, in which 10% H on Si is replaced by allyl group in order to provide better processability, in particular to produce ceramic matrix composites\textsuperscript{184}. AHPCS has a nominal structure of 

\[ \text{[Si(\text{CH}_2\text{CH}=\text{CH}_2)\text{CH}_2]_{0.1}[\text{SiH}_2\text{CH}_2]_{0.9}} \]

(manufactured by Starfire Systems, Inc., 877 25th St., Watervliet, NY, 12189)\textsuperscript{186}. The presence of allyl groups in its structure results in a precursor with improved thermal cure characteristics, as well as enhanced ceramic yield after pyrolysis.

At an intermediate stage of HPCS preparation the chloropolycarbosilane is substituted with a small amount of olefinic functionality like allyl leading to formation of allylhydridopolycarbosilane. This is done to modify the viscosity vs temperature and cross-linking characteristics. Upon pyrolysis under argon Interrante et al.\textsuperscript{187} observed that the polymer thermoset via thermally induced hydrosilation process between 150-400°C which is a hard clear glass with no weight loss. This crosslinked polymer converted to SiC with a yield of nearly 80-90% upon pyrolysis to 1000°C with a little amount of excess carbon. They further explored the use of AHPCS as liquid polymer for preparation of SiC/SiC\textsubscript{f} composite using vacuum polymer impregnation and pyrolysis process (PIP). AHPCS is used in different shaping process to generate dense pieces as Ionescu et al.\textsuperscript{186} demonstrated, membranes as our group did recently and as macroporous supports\textsuperscript{188}. AHPCS can also be mixed with other elements like titanium to form nanocomposites as our group recently investigated. To avoid formation of cracks they prepared the green body by pressing at room temperature and then cross-linking the pellet at 300°C with a mass loss of 6 wt%. This green body was then pyrolyzed at 1050°C under an argon atmosphere. The prepared pellet was crack free but still had high porosities. To tackle this, PIP process was employed and the pyrolyzed pellet was immersed in AHPCS for 24 hours and then pyrolyzed again. This process was repeated multiple times and a dense piece with <0.5% porosity was obtained after 6 cycles. Although the pellets contained excess free carbon and oxygen, they were removed upon annealing till 1700°C. This lead to increase in porosity but the pellet was still crack-free. They concluded that the PIP process could be employed a multiple number of times to generate a dense piece with a density of 2.5 to 2.6 gm.cm\textsuperscript{-3}. However, this is still lower than SiC made from conventional routes.

In the present work, we have investigated the conversion of AHPCS into SiC (chapter 5).
3.2.2. Silicon nitride (Si₃N₄) and silicon carbonitride (Si-C-N)

Polysilazanes are well known as Si₃N₄ and Si-C-N ceramic precursors. There exists a large variety of compounds that allows to tailor the chemistry and structure of final materials. Polysilazanes composed of only Si, N and H such as hydridopolysilazane (HPZ) later called perhydropolysilazane PHPS ([H₃SiNH]ₙ) or those composed of Si, N, C and H and pyrolyzed under ammonia can lead to formation of Si₃N₄ or amorphous SiNₓ ceramics with low or no carbon contamination as shown in the Table 1.5. A lot of work has been done on the synthesis of Si₃N₄ from the beginning of this century.

Table 1.5 Synthesis of silicon nitride from different precursors and the effect of pyrolysis atmosphere and temperature

<table>
<thead>
<tr>
<th>Silazanes/Pyrolysis atmosphere/Temperature</th>
<th>Ceramics</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H₃SiNH)ₙ/Nₙ/1150°C ¹⁹²</td>
<td>Si₃N₄ powders (free Si)</td>
</tr>
<tr>
<td>(H₃SiN(CH₃)ₙ/Nₙ/850–1600°C</td>
<td>Si₃N₄ powders</td>
</tr>
<tr>
<td>(H₂SiNH)ₙ/Nₙ or NH₃/1100–1300°C</td>
<td>Si₃N₄ powders &amp; fibres (free Si)</td>
</tr>
<tr>
<td>(RSi(NH)₂)ₓ/NH₃/400–1200°C</td>
<td>α-Si₃N₄ powders</td>
</tr>
<tr>
<td>(H₂SiNH)ₙ/NH₃/400–1000°C</td>
<td>α-Si₃N₄ powders</td>
</tr>
<tr>
<td>((CH₃)₂HSiNH)ₙ/NH₃/600–800°C</td>
<td>α-Si/N/(H) films (CVD)</td>
</tr>
<tr>
<td>(CH₃CH₂SiNH)ₙ/NH₃ or H₂/600–800°C</td>
<td>α-Si/(C)/N/H films (CVD)</td>
</tr>
<tr>
<td>((CH₃)₂SiNH)ₙ/NH₃/900–1500°C</td>
<td>Si₂N₄(NH) &amp; Si₃N₄ powders</td>
</tr>
</tbody>
</table>

Silicon diimide [Si(NH)₂]ₙ has been used for synthesis of pure Si₃N₄ (alpha form) at 1250°C. However, the high viscosity and insoluble nature of the precursor restricted its widespread use for processability in solution. By ammonolysis of various carbon containing polysilazanes, monolithic Si₃N₄ was synthesized. SiC and C free α-Si₃N₄ was formed by pyrolysis of polymethylsilazane (PMSZ), -(SiH₂NMe)ₓ-, under NH₃ although the ceramic yield was considerably low, 38 wt%¹⁹⁶. A vinyl-containing silazane was also pyrolyzed under ammonia and crystalline Si₃N₄ with 2 wt.% of carbon was obtained. In this case, the nitridation temperatures were much lower, they were found to be between 300°C and 650°C. In addition, Si₃N₄ was also synthesized using a carbon-containing ethylsilazane precursor and ammonia in CVD processes. Pyrolysis of perhydropolysilazane (H₂SiNH)ₙ at 1150°C under Ar and N₂ leads to the formation of Si₃N₄ (along with free silicon) with a ceramic yield
of 70-85 wt% whereas the polymer under ammonia leads to formation of pure near stoichiometric Si₃N₄ with a ceramic yield of 60-75 wt% ¹⁹²,¹⁹⁸–²⁰⁰.

PHPS is a highly reactive preceramic polymer containing two Si-H and N-H functions in its structure²⁰²⁻²⁰⁵. Through pyrolysis under nitrogen, PHPS leads to a composite material composed of a majority of Si₃N₄ and around 13 wt% of silicium (Si)²⁰². As PHPS is commercially available in solution (to avoid its further polymerization) and is highly reactive even at room temperature, the precise measurement of its ceramic yield is difficult because cross-linking inherently occurs at low temperature. As an illustration, the measured weight loss at 1000°C varies from 16.0 %²⁰² to 24.7%²⁰³ in the literature; therefore the ceramic yield is calculated to vary from 75.3 % to 84 %. Such values, even though they are different, are sufficiently high to keep the maximum of product in the porosity of templates through the nanocasting process meaning that PHPS seems to be an ideal precursor for preparing materials with tailored mesoporosity. Within this context, we have investigated the ceramic conversion of PHPS into Si₃N₄ in chapter 4 and we focused in chapter 5 on the designing of mesoporous Si₃N₄ monoliths from PHPS.

Polysilazanes consisting of Si, N and C backbone elements are ideal precursors for formation of ternary Si-C-N ceramics. A lot of work was devoted to the fabrication of ternary Si-C-N systems by using different kinds of polysilazane precursors. Chemistry of the backbone structure, functionality and degree of cross-linking are factors that control the ceramic yield of polysilazanes. It was observed that with cross-linked polysilazanes like ((RSiHNH)ₙ and (R₂SiNH)ₘ R= -H, -CH₃, -CH=CH₂, phenyl etc) gave high ceramic yield of 80-85% upon pyrolysis at 1400°C under argon²⁰⁴,²⁰⁵. Besides the pyrolysis temperature and precursor chemistry, ceramic yield is affected by heating rate and pyrolysis atmosphere. It was observed by Bahloul et al.²⁰⁶ that ceramic residue of vinylsilazane increased from 15 to 30% with increase in heating rate from 1 to 60°C/min. Table 1.6 shows different precursors that can be used for preparing Si-C-N system with their ceramic yield under different atmospheres. Cross-linking of various polysilazanes was studied by Vioux et al.²⁰⁷. They cross-linked various models containing vinyl, NCH₃, SiCH₃ groups Si-H and/or N-H bonds and identified the mechanisms that governed the crosslinking as well as the kinetic rate. They observed that by efficient cross-linking they avoided the early distillation of oligomers during pyrolysis thereby increasing the ceramic yield. They identified that the occurrence of hydrosilylation reaction at around 120°C allows more cross-linking. This led to formation of
Si-C-Si and Si-C-C-Si bonds which are immune to depolymerization reaction (transamination and exchange of Si-N bonds) hence leading to higher yields. These carbosilane bridges led to higher carbon content in the final ceramics. Hence the use of co-organosilazanes with a balance between vinyl and Si-H will lead to ceramics with higher yields and lower carbon content in the final ceramics. Such polymers display the highest ceramic yield to produce Si-C-N ceramics. HTT1800® called later Durazane is a co-organosilazane which has been explored in this thesis.

Another study by Vioux et al. explored the mechanism of the polymer-to-ceramic conversion for various cross-linked polysilazanes under atmospheres of argon and ammonia using TGA-MS. They observed that under inert atmosphere, mineralization involves various free radical reaction and large amounts of excess carbon were obtained when the precursor had unsaturated carbon groups like vinyl or benzene rings. While for ammonia, the mechanism was heavily dependent on the nature of group attached to Si atoms. But generally, amination was complete in the range of 300°C to 750°C by nucleophilic substitution in case of Si-H bonds and hemolytic cleavage of Si-C incase of carbon based substituent groups. Amination and carbon removal coincide in the same temperature range for polysilazanes containing methyl and phenyl groups as they are removed by hydrogen abstraction from ammonia as methane and benzene while for vinyl groups the carbon is removed only after decomposition of ammonia at 750°C as HCN.

### Table 1.6 Ceramic yield of preceramic polymers under various atmospheres

<table>
<thead>
<tr>
<th>Silazanes</th>
<th>Ceramic yield (wt.%)</th>
<th>Pyrolysis conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHMS (Poly(hydridomethylsilazane))</td>
<td>80–85</td>
<td>1000°C, Ar, 10°C/min</td>
</tr>
<tr>
<td>PHMS (NCP 200)</td>
<td>60–70</td>
<td>1000°C, Ar</td>
</tr>
<tr>
<td>PUMVS (Ceraset)</td>
<td>70–80</td>
<td>1000–1100°C, Ar</td>
</tr>
<tr>
<td>PVS (Poly(vinylsilazane))</td>
<td>85</td>
<td>1150°C, Ar, 10°C/min</td>
</tr>
<tr>
<td>PVS (VT 50)</td>
<td>70–80</td>
<td>1000°C, Ar</td>
</tr>
<tr>
<td>Poly(carbosilazane) (PCS)</td>
<td>50–80</td>
<td>1000°C, Ar</td>
</tr>
<tr>
<td>Poly(phenylsilazane) (PPS)</td>
<td>50–70</td>
<td>800°C, N₂, 0.5°C/min</td>
</tr>
<tr>
<td>Poly(hexylsilazane) (PHS)</td>
<td>25–40</td>
<td>800°C, N₂, 0.5°C/min</td>
</tr>
<tr>
<td>Poly(silacyclobutasilazane)</td>
<td>66–73</td>
<td>1200°C, Ar</td>
</tr>
<tr>
<td>Poly(ureidosilazanes)</td>
<td>61–73</td>
<td>1000–1400°C (Ar, NH₃)</td>
</tr>
</tbody>
</table>
Pyrolysis of polysilazane under an inert atmosphere in the temperature of 800°C to 1200°C generally yields an amorphous Si-C-N ceramic. Table 1.7 shows the chemical composition of Si-C-N ceramics derived from various polysilazanes under inert gas.

<table>
<thead>
<tr>
<th>Polysilazane</th>
<th>Chemical composition of the derived ceramics</th>
<th>Pyrolysis conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyhydridomethylsilazane, PHMSZ (NCP 200)</td>
<td>SiC$<em>{0.58}$N$</em>{0.90}$</td>
<td>1000°C, Ar</td>
</tr>
<tr>
<td>Polyvinylsilazane (PVSZ)</td>
<td>SiC$<em>{1.47}$N$</em>{0.98}$O$<em>{0.06}$H$</em>{0.06}$</td>
<td>1400°C, N$_2$</td>
</tr>
<tr>
<td>Polyureavinylmethylsilazane, FUMVSZ (Ceraset)</td>
<td>SiC$<em>{0.86}$N$</em>{0.82}$O$_{0.02}$</td>
<td>1000°C, Ar</td>
</tr>
<tr>
<td>Polymethylvinylsilazane (PMVSZ)</td>
<td>SiC$<em>{1.08}$N$</em>{0.78}$O$<em>{0.16}$H$</em>{0.66}$</td>
<td>850°C, N$_2$</td>
</tr>
<tr>
<td>Polymethylvinylsilazane (PMVSZ)</td>
<td>SiC$<em>{0.06}$N$</em>{0.01}$O$<em>{0.08}$H$</em>{0.18}$</td>
<td>800°C, O$_2$</td>
</tr>
<tr>
<td>Polycarbosilazane (PCSZ)</td>
<td>SiC$<em>{0.78}$N$</em>{0.48}$O$<em>{0.03}$H$</em>{0.18}$</td>
<td>1100°C, Ar</td>
</tr>
</tbody>
</table>

Si-C-N phase diagram can be used to determine the composition and phases of polysilazane derived ceramics. Above 1440°C (without presence of any additives), amorphous Si-C-N will transform into Si$_3$N$_4$ and SiC and probably above 1600°C will likely convert completely into SiC with loss of N$_2$ due to reaction between free carbon and Si$_3$N$_4$. The final crystalline phases are mainly determined by the composition of the amorphous Si-C-N materials obtained at lower temperatures. Analysis of the ternary Si-C-N phase diagrams provides a very useful way to evaluate the composition of an amorphous Si-C-N ceramics or to predict the final crystalline phases.

In the present study, we used commercially available HTT1800 polysilazane to investigate its conversion into Si$_3$N$_4$ and Si-C-N to prepare mesoporous monoliths.

As an alternative to Si-based non-oxide ceramics, B-based non-oxide ceramics such as boron nitride (BN) display interesting chemical and thermal stability for the applications we targeted. The preparation of precursor-derived BN is discussed below.

### 3.2. The PDC route toward Boron Nitride (BN)

In contrast to Si-based ceramics, precursor-derived BN are not stable as amorphous structure. Therefore, BN should be prepared in its thermodynamic stable phase, i.e.,
hexagonal. With a preformed ring like structure, the correct boron to nitrogen ratio and only hydrogen as the extra element, borazine $\text{H}_3\text{B}_3\text{N}_3\text{H}_3$ appears to be an ideal molecular precursor of boron nitride. It is easy and economical to produce by a simple reaction between ammonium sulfate and sodium borohydride in tetruglyme at a low temperature of 120-140°C. Molecular hydrogen and ammonia are only by-products of conversion of borazine to BN by pyrolysis till 1450°C. But borazine is a highly volatile compound and is therefore first self-condensed at low temperature in an autoclave to generate polyborazylene, a preceramic polymer, with a controlled molecular weight, physical state and composition. A large number of studies were focused on the self-condensation of borazine to polyborazylene, most of which suggested the generation of naphtalenic (a) and biphenylic (b) type structures as shown in Figure 1.15.

Sneddon et al.\textsuperscript{221–223} were the first authors to isolate a solid polyborazylene through the self-condensation of borazine under vacuum at 70°C for approximately 48 hours. Even though it had a highly branched or partially crosslinked structure it was soluble and hence proved to be an excellent precursor to prepare fiber coatings.\textsuperscript{221} Polyborazylene delivered BN by pyrolysis under argon or ammonia in the temperature range 900–1450°C in excellent chemical (89%–99%) and ceramic yield (84%–93%). Through the study of the self-condensation of borazine at low temperature (45–60°C) under argon in an autoclave, the possibility to control the physical state of polyborazylene from liquid (45–55°C) state (with viscosity increasing with the increase of the synthesis temperature) to solid state (≥60°C) by adjusting the temperature of thermolysis was demonstrated. Since polyborazylenes varied in their physical state from liquids to solids, they appeared suitable for various processing and shaping techniques. Table 1.8 shows the physical state, chemical composition and ceramic yield of polyborazylenes isolated at different temperatures.
Moreover polyborazylene is complex to prepare and not commercially available. Alternatively, we focus on the use of ammonia borane NH$_3$BH$_3$ (AB) as a preceramic precursor which is commercially available. Suib et al studied the polymer to ceramic conversion of AB to h-BN under nitrogen. They found the conversion to be divided into 3 different steps. The first weight loss occurred around 120°C suggesting the formation of polyaminoborane. It was immediately converted to polyimminobrane in some cases leading to formation of borazine ring structure at 210°C, the second weight loss regime. The next and final weight loss occurred around 1150°C due to loss of H$_2$ and indicating the completion of ceramization of process. These precursors have been utilized in chapter 3, and then used to prepare mesoporous monoliths in chapter 5.

In the following section we discuss on the preparation of nanocomposites from the precursors we discussed previously. In particular we focus on nanocomposites with SiC, Si$_3$N$_4$, Si-C-N and BN matrix.

### 4. The PDC route towards the design of nanocomposites

#### 4.1. Definition of nanocomposites

“A nanocomposite may be defined as a material system containing at least two Gibbsian phases one of which is nanoscaled.”

Or
“Nanocomposite is a multiphase solid material where one of the phases has one, two or three dimensions less than 100 nanometers or structures having nano-scale repeat distances between the different phases that make up the material.”

The term “nanocomposites” was first used in the 1980’s to describe heterogeneity in systems prepared by sol-gel synthesis by Roy and Komarneni\textsuperscript{230}. The term was extended by Niihara in the 1990’s to cover the domain of ceramic composite nanostructures\textsuperscript{231}. Nanocomposites are essentially different from conventional composites materials in the sense that there is an exceptionally high surface to volume ratio for the reinforcing phase and/or a very high aspect ratio. The secondary phase (Figure 1.16) can be made up of nanoparticles (e.g. minerals), nanosheets (e.g. exfoliated clay stacks) or nanofibers (e.g. carbon nanotubes or electrospun fibers). The area of interface between matrix and secondary phase is greater than conventional composite materials by an order of magnitude.

Depending on the composition of the secondary phase the nanomaterials can be classified into three types (Figure 1.17):

1. **Metal Matrix Nanocomposite**: A nanoscale composite with at least one part as metal (matrix) and other may be a metal, ceramic or organic compound.
2. **Polymer Matrix Nanocomposite**: Polymer nanocomposites (PNC) consist of a polymer or copolymer having nanoparticles or nanofillers dispersed in the polymer matrix.
3. **Ceramic Matrix Nanocomposite**: Type of nanocomposite with matrix as a chemical compound from the group of oxides, nitrides, borides, silicides etc. and second phase, metal or a ceramic, generally being dispersed homogeneously.
The ceramic matrix nanocomposite can be further divided into five different types depending on the dispersion of second phase, crystallinity of the matrix and size of the secondary phase particles. Based on the previously mentioned parameters Niihara further divided the ceramic matrix nanocomposite into the first four following parts as shown in Figure 1.18.

The fifth part was added by Veprek and Reiprick when then developed super hard coatings using precipitated nanocrystalline TiN in an amorphous Si₃N₄ matrix, which is the type of nanocomposite of particular interest to us. This type of ceramic matrix nanocomposite shows extremely high values of strength which is a requisite for catalyst supports working in harsh environments, as those we target. The mechanical strength of brittle and ductile materials depends on the formation and propagation of dislocations and cracks. Elastic modulus of the material controls the stress needed to form and propagate both the dislocations and cracks. Although there are other factors like the type and shape of dislocations and cracks which also influence the stress required, in general we can say that the strength of material increases with increasing modulus. The Hall-Petch model gives a mathematical formulation of the strength of materials. It suggests that smaller grain sizes are preferred for higher...
strengths. Strength of a material also increases due to precipitation hardening where a dislocation is pinned when it encounters a hard precipitates. A simple analysis yields the Hall-Petch relationship between the strength in terms of the critical stress $\sigma_C$ and grain size $d$.

$$\sigma_C = \sigma_0 + kl^{1/2}$$

The hall petch relationship is valid only for sufficiently large grains ($>100$ nm) which can accommodate dislocation source hence it can be used to explain the exceptionally large strength values for these nanocomposites with nanocrystalline precipitates in amorphous matrix. Koehler suggested that two epitaxial heterostructures, one with high elastic modulus and other with lower elastic modulus, can lead to enhancement in strength. This was based on the argument that frank-read source multiplication of dislocation cannot operate in thin layers and the dislocation formed in the layer with lower elastic modulus will stay trapped in the same layer as it will be opposed by its mirror image when it tries to cross the interface between the two layers. Koehler extended his argument and that this mechanism will work even if one of the layers is amorphous. The amorphous material has further advantage that it can easily accommodate any strain due to lattice mismatch due to randomly oriented crystalline material in an isotropic composite.

### 4.2. PDC-based strategies to design ceramic nanocomposites

PDC nanocomposites can be made from different route. Interrante et al. suggested two routes, firstly from direct reaction between two preceramic polymers and secondly from a single source preceramic precursor. Paine et al. in their review extended this by adding a work of Seyferth et.al, regarding synthesis of nanocomposites by adding various active or passive fillers to preceramic polymers. In this section we discuss these various synthesis techniques briefly.

#### 4.2.1. Addition of fillers to preceramic polymers

The polymer-to-ceramic conversion is inevitably accompanied by the release of gaseous by-products, which causes a more or less important weight loss (generally not lower than 15%) and an overall volume shrinkage of the component (can reach $70\%$). The addition of filler as a secondary phase within the polymer can offset this shrinkage and thereby prevent a catastrophic failure of the component. There are two types of fillers. Passive fillers remain
totally inert during the whole polymer-to-ceramic conversion. They do not undergo any transformation or evolution during the heat treatment and do not react with the ceramic residue of the preceramic polymer, or with the gaseous by-products released during pyrolysis or the treatment atmosphere. Their only function is to diminish the percentage of the whole volume that evolves during the pyrolysis step, thus reducing the total weight loss, shrinkage and generation of cracks, as well as to favor the escape of gaseous species by the creation of an easier means of escape. Figure 1.19 shows a schematic representation of the passive filler in a preceramic polymer.

![Figure 1.19 Schematic representation of controlling shrinkage using passive filler](image)

Typical examples of passive fillers for preceramic polymers can be micro or nanopowders of SiC or Si₃N₄. Katsuda et al. suggested use of nano-sized fillers like multi-walled carbon nanotubes for increasing the fracture toughness of polymer derived ceramics. The CTE (coefficient of thermal expansion) of the filler phase is also of fundamental importance, since it determines the global CTE of the final composite. A tailorable CTE could be useful in applications such as coatings (e.g. on metals), but it should be noted that a high CTE mismatch between the ceramic residue and the filler(s) could cause the formation of micro-cracks that could have detrimental effects on the final mechanical properties.
The concept of active or reactive fillers was introduced in the early 90’s by the work of Greil et al. and Seyferth et al. It was carried on further by Paine et al. These fillers permit the obtainment of a near-net-shape conversion of preceramic polymers into bulk components with extremely limited (or even absent) global shrinkage. Active fillers can increase their volume during pyrolysis by reacting with gaseous species released from the polymer decomposition, or by reacting with the atmosphere of the furnace, thus effectively compensate the polymer shrinkage. In some cases as shown by Seyferth et al., the choice of temperature and atmosphere along with reactive filler can lead to formation of different phases. As in case of tungsten (W) powder in a polysilazane (W:Si = 5:3) leads to formation of WC and W₅Si₃ at 1500°C under Ar but the same system under NH₃ till 800°C and then under Ar till 1500°C resulted in the formation of only W₅Si₃. Another important aspect of this study was complete absence of Si₃N₄ in the presence of W which is otherwise the primary reaction product from the used polysilazane under NH₃. Even in Si rich ratios formation of Si₃N₄ was completely suppressed by presence of W. Thus it was shown that presence of various metallic active fillers can lead to various effects on the phases formed. Apart from these nanosized filler can also be used as active fillers in oxynitrides and silicates as shown by Bernardo et al.

4.2.2. Mixed precursors and polymers

This method involves mixing precursors of two different ceramics homogeneously as a neat liquid as suggested by Interrante et al. followed by pyrolysis. They suggested a “hot drop” approach which involves a rapid pyrolysis of the mixture of preceramic polymers by dropping it onto a preheated surface. For mixture compositions where the phase separation may not an issue lower heating rates could be employed. Interrante et al. used this procedure for synthesis of AlN/SiC composite using [Et₂AlNH₂]₃ and SiC forming precursors like vinylic polysilane (VPS), methylhydridopolysilane (MPCS) or hydridopolysilane (HPCS). Nanocrystalline composites of 2H AlN and 6H-SiC and 2H solid solutions of SiC/AlN can be obtained as products of the pyrolysis, depending on the specific pyrolysis procedure (hot drop vs. direct pyrolysis) and precursor combination employed. In any case, following annealing of the ceramic powders at 1600 °C, the crystallite sizes were less than 500 nm and typically on the order of 10-50 nm. They have also blended VPS with [Et₂AlNH₂]₃ and pyrolyzed the mixture under NH₃. This results in formation of Si₃N₄/AlN composites with grain sizes of 40-80 nm. The crystallinity and phase of the grains varied greatly with processing and annealing conditions. Similarly, mixtures of VPS with
polyborazylamine (PBZA)\textsuperscript{250} gave a precursor that, upon pyrolysis, gave Si\textsubscript{3}N\textsubscript{4}/BN composites\textsuperscript{251}. Sneddon \textit{et al.} blended liquid borazine with hydridopolysilazane (HPZ), and pyrolysis of the resulting polymer gave boron containing β-Si\textsubscript{3}N\textsubscript{4}/β-SiC composites in which the crystallization is again suppressed by BN\textsuperscript{252}.

The main issue using this method is separation of phases if the pyrolysis rates are not high enough, which generally is the case of component/ shaped ceramic processing. Ceramic composites prepared using this method require conventional powder processing routes for component production which can cause grain growth during high temperature processing leading to inferior properties.

\textbf{4.2.3. Single-source precursors}

Due to the need to avoid phase separation and easy processability, Interrante \textit{et al.} suggested to form single source molecular compounds that contain all the necessary elements of the desired composite in requisite proportions. This process involves deliberate construction of very distinct molecular moieties which contain the compositional elements in specific stoichiometric combination or reactions of preformed polymers or molecular species. By controlling the pyrolysis temperature, atmosphere and heating rate we can control the phase distribution and crystallite size of the composite formed. Apart from providing a homogeneous distribution of elements this process allows us to obtain an easily processable precursor which could be used for developing coatings, fibers or monolithic structures.

Using the single-source precursor route, Interrante \textit{et al.}\textsuperscript{241} synthesized SiC/AlN composite in effort to have improved homogeneity over mixed precursor route. They reacted cyclotrisilazane with triethylaluminium and formed a polyaluminosilazane (PAS). These single-source precursors are generally formed by condensation reactions between the most reactive groups of the reactants. In this case N-H of the polysilazane reacts with the organoaluminum compound forming a new Al·N bond which forms a part of the backbone of the single source precursor as well as the ceramic. Different properties like rheology of the polymer and yield of the ceramic can be controlled by adjusting the ratio between the two reactants. Heating PAS-derived composites to 1600-1800°C produced 2H-SiC/AlN following pyrolysis in N\textsubscript{2} or α-, β-Si\textsubscript{3}N\textsubscript{4}/AlN if pyrolysis was done in NH\textsubscript{3}. Nanocrystallites (5-500 nm) were typically observed in samples that were poorly crystalline by XRD powder patterns. They also prepared other nanocomposite systems like AlN/BN, TiN/BN, TiN/AlN and
Si₃N₄/BN and investigated the effects of various parameters. Hence this method offers great control over the synthesis of the final ceramic and allows tailoring properties at the molecular level. The focus of this thesis is using the single source precursor strategy to develop silicon and boron-based nanocomposites through modification of the Si₃N₄, Si-C·N and BN precursors described previously with transition metals such as titanium (Ti), zirconium (Zr) and hafnium (Hf).

4.3. Transition metal-containing PDC nanocomposites

4.3.1. Si-based nanocomposites through modification of organosilicon precursors with transition metals

Three systems are considered here: the Si·M·C, Si·M·C·N and Si·M·N systems.

- The Si·M·C system

The term polymetallo(carbo)silane²⁵³ refers to a class of polymers composed of Si, C, H and sometimes O as well as a metal M (Ti, Zr, Hf). They can be synthesized by reacting transition metal-based molecular precursors like metallocenes (dichlorometallocenes) and/or metal tetrachlorides with SiC precursors like polycarbosilane (HPCS, AHPCS, etc.). Table 1.9 shows an overview.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Precursor</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polycarbosilanes</td>
<td>(C₅H₅)₂MCl₂ MCl₄ / MOCl₂</td>
<td>MC/SiC</td>
</tr>
<tr>
<td></td>
<td>M(CH₂C₅H₅)₄</td>
<td>Si₄CyM₂</td>
</tr>
<tr>
<td></td>
<td>M(X)₄ X=OCH₂CH₂CH₂CH₃/CH₃COCHCOCH₃</td>
<td>SiC/MC/C/MSi</td>
</tr>
</tbody>
</table>

The reaction mechanism depends on the nature of the metal precursor. In the first case there is a direct reaction between the two precursors, the metallic precursor reacts directly with polycarbosilane via the chlorinated groups of the metal precursor and the Si·H bonds of the polycarbosilane thereby by removing the chloride with hydrogen. This reaction was evidenced by Amoros et al.²⁵⁹ when they showed the reaction via three dichlorides of metallocene and
polycarbosilane according to the following reaction. The heat treatment under an argon atmosphere resulted in the formation of nanocomposite MC/SiC.

\[
\begin{array}{c}
\text{Si} \quad \text{H} \quad \text{Cl} \quad \text{Zr} \quad \text{Cl} \quad \text{Cp} \quad \text{Cp} \\
\text{Si} \quad \text{Zr} \quad \text{HCl}
\end{array}
\]

**Figure 1.20** Removal of excess chlorine to synthesize non-oxide polymers

Zhaoju *et al.*\(^{260,261}\) used the same reaction with dichloride of titanocene to generate a TiC/SiC type nanocomposite from the AHPCS (Figure 1.21). However, some chlorinated residues can be found in the polymer thereby altering the properties of the final ceramic nanocomposites. Recent studies have allowed the synthesis of precursor non-oxide polymers containing zirconium and silicon by using organolithiols by metathesis, in order to eliminate the residual chlorine, reaction represented by Figure 1.20.

\[
\begin{array}{c}
\text{Cp}_2\text{TiCl}_2 + 2.1 \text{ equiv MeLi} \\
\rightarrow 0^\circ \text{C} \\
\text{Et}_2\text{O}
\end{array}
\]

**Figure 1.21** Synthesis of Cp₂TiMe₂

The Cp₂TiMe₂ was synthesized for the first time in 1956 by Clauss and Bestian, starting from a titanocene and 2.1 equivalents of methyllithium in diethyl ether. This reaction represents the synthesis of Petasis reagent by metathesis of a methyllithium and a titanocene dichloride. Grignard reagents are also used for the synthesis of Petasis reagents\(^{265}\). Here the primary use of Petasis reagents based on Ti or Zr and the use of the Grignard reagents of type RMgCl or RMgBr, the objective is twofold: substitute the chlorinated groups of the metallocene dichlorides by the groups of reagents like alkene, vinyl, allyl type, etc. in order to react them with the functional groups of the polycarbosilane and eliminate the residual chlorine by forming solid by-products of type MgCl₂ or MgBr₂ easily separable from the final product. Other parameters are important in the development of such nanocomposites like the ratio molar ratio between the precursor and the preceramic polymer as well as the temperature and the pyrolysis atmosphere. The crystalline phases obtained will therefore be influenced
by the molar ratio chosen; an example is given in Figure 1.22. In the case of Ti-Si-C ternary system which has different phase compositions at two temperatures of 1100 and 1300°C.

The characteristic features of the Si-based non-oxide ceramics include their resistance to crystallization and the high thermal and chemical stabilities. Wide ranging applications are observed for these materials including high performance coatings, sensors, nanocomposites and fibers. The potential of these materials, for instance in energy technologies, can be extended by the incorporation of metallic or intermetallic nanoparticles/phases. Late transition metals form metallic particles or phases during pyrolysis due to the reductive conditions in combination with their noble character, and they are highly relevant for
catalytic applications. This system includes both MCN/SiC type nanocomposite and npM/SiCN (metal nanoparticle in SiCN matrix) nanocomposite. In the first type we have a SiC matrix with metal carbonitride nanoparticles inside it, like the works of Ionescu et al.\textsuperscript{267} on high temperature ceramic nanocomposites HfC\textsubscript{x}N\textsubscript{1-x}/SiC, while second type includes systems which have a SiCN matrix with metal nanoparticles embedded in the matrix like Pt/SiCN\textsuperscript{268} system studied by Zaheer et al. and Fe/SiCN\textsuperscript{269,270} system studied by Francis et al. and Li et al.

For the first type, Wen et al.\textsuperscript{267} designed a one pot synthesis technique to generate HfC\textsubscript{x}N\textsubscript{1-x}/SiC nanocomposites as ultra high temperature ceramic. The purpose of preparing this nanocomposite was to exploit its high hardness, high elastic modulus, chemical stability, and electrical conductivity and relatively high thermal conductivity even under extremely harsh environments\textsuperscript{271–274}. It is known that the preparation of HfC using conventional route faces problems in densification due to low self diffusion, grain growth at high temperature and low stability in oxidative environments\textsuperscript{275–283}. Encapsulation of this in an amorphous matrix of SiC overcomes these problems but such a system can only be prepared using precursor routes. The nanocomposite was prepared by reaction between AHPCS and tetrakis(dimethylamino)Hafnium(IV) (TDMAH) precursor. The polymer to ceramic conversion was carried out under argon atmosphere at 1100°C. The ceramic nanocomposite powder was then further converted into a monolith using Spark Plasma Sintering. Based on solid state \textsuperscript{13}C and \textsuperscript{29}Si NMR studies, Wen et al. established that the reaction pathway between AHPCS and TDMAH involved two types of reactions: the allyl and Si–H groups of SMP10 are involved in hydrosilylation, which leads to an increased crosslinking degree of the precursor; additionally, TDMAH reacts with the Si–H groups of AHPCS to form Si–N–Hf linkages and gaseous CH\textsubscript{4}. This is depicted in the Figure 1.23\textsuperscript{267}.

\[ \text{Figure 1.23 Two possible reaction pathways for reaction b/w AHPCS and TDMAHf} \]
The high temperature behavior of these samples was found to be very interesting. At 1400°C the HfC\(_{x}\)N\(_{1-x}\) was found encapsulated in a 2-4 nm thick layer of turbostratic carbon. These second phase nanoparticles were uniformly distributed throughout the matrix with a particle size of 8 nm at 1400°C to 37 nm at 1700°C. The very low increase in grain size was attributed to the surrounding carbon layer which is known to act as a diffusion barrier\(^{284,285}\). The SPS sintered nanocomposite monolith was found to have a higher electrical conductivity of 136 S cm\(^{-1}\) over a Hf free SiC monolith due to the presence of nano HfC\(_{x}\)N\(_{1-x}\) and carbon which provide it metallic properties.

Additionally further work was done to increase the high temperature oxidation behavior of this nanocomposite system by addition of B to the system. The work done by Yuan et al. involved use of commercially available HTT1800 polymer to produce the matrix instead of AHPCS and the dimethyl boron sulfide was added to the reaction mixture as the boron source\(^{286}\). Figure 1.24 shows the reaction pathways that could have occurred.

![Figure 1.24 Reaction pathway for reaction b/w HTT1800 and TDMAHf\(^{286}\)](image_url)

Different ratios were synthesized and the polymer to ceramic conversion was carried out under two different gases, Ar and N\(_2\), to compare the prepared ceramics. It was observed that at 1700°C there was an amorphous matrix of SiBCN with HfC(N) nanoparticles distributed across the matrix. In both argon and nitrogen atmospheres, high temperature annealing of SiHfBCN leads to ceramic nanocomposites with interesting phase compositions (i.e., HfC(N)/HfB\(_2\)/SiC in argon and HfNC/Si\(_3\)N\(_4\)/SiBCN in nitrogen), which are expected to be promising candidates for applications at (ultra)high temperatures and under extreme environmental conditions.
The second system npM/SiCN (metal nanoparticle in a SiCN matrix), were prepared by reacting a coordination compound (metal complex) of late transition metals with a polymeric preceramic precursor. The metal transfer from the complex to the polymer chain leads to formation of a metal modified precursor which upon pyrolysis converts to metal containing PDCs. For this purpose polysilazanes containing vinyl and Si-H bonds were chosen so that the presence of all these reactive sites allows better incorporation of metal atom in the polymer chain. The formation of a covalent bond between the metal atom and polymer chain is important to avoid loss of metal atom via sublimation during pyrolysis. This technique also allows broad dispersion of metal atom, wide applicability (easy availability of various metal coordination complexes) and use of commercially available polymers. One of the earliest nanocomposite prepared using this was Fe@SiCN system by reaction of FeCl₃ and polysilazane followed by pyrolysis under ammonia, nitrogen and argon. Along with low ceramic yields, contamination from left over FeCl₃ posed a problem. Francis et al. milled Fe powder along with Ceraset™ cross-linked at 280°C and the milled mixture was warm pressed before being pyrolyzed to a ceramic. XRD of the samples showed formation of crystalline phases are Fe₃Si, Fe₅Si₃, and SiC. The crystallization of SiC was assumed to occur from the liquid Fe–Si–C alloy being formed during the molten state of silicides at 1300°C. Further work was carried out by Riedel et al. when then used HTT1800 as the polysilazane and modified it using a Ni(II) complex. This resulted in formation of nanoporous silicon oxycarbonitride ceramic modified by Ni nanoparticle. Furthermore Kempe et al. developed a aminopyridinato metal complex using metals from late transition series like Pt, Ir, Ru, Pd, Cu, Pd etc. The copper aminopyridinato complex [Cu₂Ap₂TMS] coordination compound undergoes a metal transfer reaction with the PSZ, here HTT1800, with the release of ApTMSH. After cross-linking with dicumylperoxide (DCP) at 120°C the preceramic green body is formed (Figure 1.25). Pyrolysis results in an amorphous SiCN ceramic enhanced by Cu nanoparticles (Cu@SiCN).
Sachu et al.\textsuperscript{268} prepared a hierarchically mesoporous Pt@SiCN system using a similar technique but also added a sacrificial filler in the synthesis which would generate mesoporosity. It was observed that the size of metal nanoparticle increases with increase in the content of the metal aminopyridinato complex. Wiesner et al.\textsuperscript{293} developed a highly innovative bottom-up approach to fabricate porous SiCN ceramics with integrated platinum nanoparticles. The material was structured through a combination of micromolding and multicomponent colloidal self-assembly. The coordination compound [(cod)PtMe\textsubscript{2}] (COD = 1,5 cyclooctadiene) was used as a platinum precursor. Heat treatment (1000°C under inert atmosphere) resulted in hierarchically structured porous ceramic material functionalized with Pt nanoparticles. The nanostructuration of these metals in the metal enhanced SiCN nanocomposite leads to development of properties like superparamagnetism and ferromagnetism in these materials. Kempe et al. extensively used these nanocomposites in heterogeneous catalysis application. As a proof of concept we did performed a preliminary investigation on Pt/SiCN nanocomposites as catalyst in the hydrolysis of NaBH\textsubscript{4} to generate H\textsubscript{2}. This will be discussed in perspectives.
The Si-M-N system:

Most of the early work done on ternary systems like Si-M-N system was mainly focused on these systems developed by techniques like CVD and rarely used single source precursor route. Ternary Si-M-N materials exhibit outstanding high-temperature stability as well as good mechanical and interesting electrical properties\(^{294,295}\). Thus, Si-M-N ceramics such as Si-Ta-N, Si-Mo-N, Si-Ti-N and Si-Hf-N exhibit effective work function values in the range of 4.16 to 4.8 eV\(^{296}\) and high dielectric constants \((\varepsilon = 5–15, \text{dielectric constant values changed with the variation of metal and silicon content})^{297,298}\) making them attractive candidates for e.g. nano/micro electro mechanical systems (NEMS/MEMS). The single source precursor route leading to MN/Si\(_3\)N\(_4\) nanocomposites was first investigated by Iwamoto et al.\(^{299}\). This was offered a much better homogeneity in composition and properties over the work of Wang et al.\(^{299}\) where they used Si\(_3\)N\(_4\) powder and Ti(OBu)\(_4\) as in situ source of Ti. Ziegler et al.\(^{300}\) explored the use of polytitanosilazanes for synthesis of a hybrid nanoscale composite system of SiC/Si\(_3\)N\(_4\)-TiC/TiN. The polymer to ceramic conversion was carried out under N\(_2\) at 1000°C. They used 3 different types of polysilazanes to study their effect on the state (liquid or solid) of the polymer. They observed that for all three polysilazanes the polymer was liquid for smaller (<4) Si/Ti ratio, solid for intermediate ratios (4<Si/Ti<15) and again liquid for all higher ratios. They extensively studied the reaction occurring between the TDMAT and the polysilazanes. They concluded that below the Si/Ti atomic ratio of 2 the reaction would not be complete as the high number of adjacent [Ti(N(CH\(_3\))\(_2\))] attached to the polysilazane backbone result in steric hindrance. While as they increased the Si/Ti atomic ratio above 13 the reaction mixture was less and less polytitanosilazane and primarily unreacted polysilazane. Thus they concluded that only between 3 to 8 Si/Ti atomic ratios was it possible to obtain the hybrid nanoscale composite system.

Using PHPS as matrix precursor and tetrakisdimethylaminotitanium (TDMAT) as nanophase precursor, Iwamoto and Sato both proposed a highly cross-linked structure for polytitanosilazane with N-Ti-N bridges as shown in Figure 1.26.
The ratio between Ti/Si in these systems has a lot of effect on the microstructural composition of the ceramic. Iwamoto et al.\textsuperscript{301} observed that for Ti/Si ratios greater than 0.1 lead to a stable amorphous Si₃N₄ matrix till 1400°C which is not the case with ratios smaller than this and in absence of Ti from the system. The same was observed by Sato et al.\textsuperscript{302} when they studied the low temperature crystallization of this system. Ionescu\textsuperscript{303} changed the metal in the ternary system from Ti to Hf and performed pyrolysis of these polymers with different ratios to generate Si₃N₄-HfN system. Figure 1.27 gives the illustration with reaction between PHPS and (tetrakis(dimethyl)amino)Hafnium. The reaction can occur at the either the N-H bond or the Si-H bond. Although the spectroscopy study by Ionescu et al.\textsuperscript{303} suggests that the reaction is generally faster at the N-H bond (a) given its more reactive nature.

The crystallization of Si₃N₄ matrix was pushed from 1300°C to 1600°C as the content of Hf in the system increases. Figure 1.28 shows the effect of increasing Hf content in the Si-Hf-N system on the microstructural composition. The mass ratio of Hf:Si ratio was increased from 2:98 (SiHfN-1), 30:70 (SiHfN-3).
Another interesting observation made by Ionescu et al., Sato et al., and Iwamoto et al. was the crystallization of only α-Si₃N₄ when using PHPS as the matrix forming polymer.

Since the PhD thesis of Mirna Chaker Bechelany, our group has explored these materials for different applications. We firstly demonstrated the high potential of preceramic polymers to generate dense structures made of TiN nanocrystals homogeneously dispersed in an amorphous structure of Si₃N₄ to propose very high hardness and Young’s modulus. Here, we have investigated the chemistry behind the preparation of Si-M-N ceramics (with M as Ti, Zr, Hf) (Chapter 4) as well as their use as supports for platinum nanoparticles to be used in the hydrolysis of NaBH₄ (Chapter 5).

### 4.3.2. B-based nanocomposites through modification of borazine, polyborazylene and ammonia borane with transition metals:

Polymer derived nanocomposite ceramics based on boron nitride and transition metal nitrides have not been discussed much in the literature although a lot of work has been done on nanocomposite systems like BN/Si₃N₄, BN/ SiC, BN/Carbon based 2D materials etc. These have been extensive used as structural materials due to the high strength and high temperature stability provided by BN to the matrix or has been used to remove organic/inorganic pollutants in the case of BN/Carbon based 2D materials.

Very recently some attention has been focused on preparing a nanocomposite with BN and transition metal nitride, more specifically Tantalum Nitride (Ta₅N₅). Tantalum nitride (Ta₅N₅), with Ta⁵⁺ in the preferable d0 electronic configuration, has attracted tremendous
attentions due to its suitable band gap position for overall water splitting and visible light absorption\textsuperscript{306–308}. However, Ta\textsubscript{3}N\textsubscript{5} photo-catalyst usually suffers from recombination of photo-generated electron-hole pairs and poor stability due to self-oxidation by photo-generated holes\textsuperscript{305,309}. Liu \textit{et al.}\textsuperscript{310} noted that the presence of a low light responsive and optically inert support like SiO\textsubscript{2} lead to suppressed aggregation of Ta\textsubscript{3}N\textsubscript{5} nanoparticles during high temperature nitridation process, improved photocatalytic activity and improved dispersion of photo-catalyst in the solution. In the same way, hexagonal BN (hBN) with its optical inertness and chemical durability and more importantly its negatively charged surface lead to efficient charge carrier separation in other nanocomposite photo-catalysts systems like BN powders/TiO\textsubscript{2}\textsuperscript{311}, BN fibers/TiO\textsubscript{2}-xN\textsubscript{x}\textsuperscript{312}, BN nanosheets/\textit{BiOBr}\textsuperscript{313} and BN nanosheets/\textit{In\textsubscript{2}S\textsubscript{3}}\textsuperscript{314} etc. These systems have also shown superior photocatalytic activity on dye degradation. Wang \textit{et al.} predicted that porous hBN fibers are assumed to be an efficient support of the adsorption-enhanced heterocatalysts, which cannot only promote the transfer of holes and subsequently suppress the oxidative deactivation of Ta\textsubscript{3}N\textsubscript{5}, but can also adsorb the reactants in the liquid phase to the surface of photocatalysts. It is predictable that the heterostructure photocatalysts based on porous BN fibers labeled BN\textsubscript{f} should exhibit good photocatalytic performance. They were able to prepare Ta\textsubscript{3}N\textsubscript{5}/BN\textsubscript{f} nanocomposite with Ta\textsubscript{3}N\textsubscript{5} having spherical morphology and a diameter of 10 nm. The specific surface area of Ta\textsubscript{3}N\textsubscript{5}/BN\textsubscript{f} composites was much higher than that of pure Ta\textsubscript{3}N\textsubscript{5} nanoparticles. The absorbance of Ta\textsubscript{3}N\textsubscript{5}/BN\textsubscript{f} composites to visible light gradually decreased with increasing the content of BN\textsubscript{f} in the composites. By comparison with pure Ta\textsubscript{3}N\textsubscript{5} powders, both the photocatalytic activity and stability of Ta\textsubscript{3}N\textsubscript{5}/BN\textsubscript{f} composite were significantly enhanced. The negatively charged BN\textsubscript{f} support can not only effectively enhance the separation of photogenerated electrons and holes, but also acts as the efficient adsorbent to dye molecules. Even with such good performance these materials face the economic challenge of being too costly due to the use of Ta. We propose the use of early transition element based nitrides like TiN\textsuperscript{315}, which has both electronic and photocatalytic activities similar to Ta\textsubscript{3}N\textsubscript{5} while ZrN\textsuperscript{315} has electronic properties similar to Ta\textsubscript{3}N\textsubscript{5} and can be easily synthesized in a nanocomposite with BN matrix using single source precursors.

We have investigated the chemistry behind the preparation of B-M-N (M: Ti, Zr, Hf) ceramics in chapter 3 before their preparation as mesoporous monoliths in chapter 5. Because a large
part of the thesis has been focused on the design of mesoporous components, the next section describes the strategy to design mesoporosity in PDCs.

5. The PDC route towards the design of mesoporous components

In general, the specific surface area, the pore volume, the arrangement and type of the porosity as well as the Lewis and/or Brønsted acidity of materials are primarily considered when selecting a support for catalysts or electrocatalysts as well as an electrode material. The mechanical strength and especially the chemical resistance towards the reaction medium are not always viewed as the most important properties.

A lot of work has been done with regard to developing polymer-derived porous ceramics. The applications of porous ceramics are not only dependent on the chemical composition of porous scaffold but also on the pore size distribution (PSD), tortuosity, specific surface area (SSA), closed/open (3D interconnectivity), etc., which all are determined by the selected manufacturing process. For example, while high surface area (provided by micro- (<2 nm) and meso- (2–50 nm) pores) gives the functionality to the component, macroporosity (50 nm to several mm) improves heat and mass transfer. For the envisioned applications, we targeted mesoporous materials. There are three methods to develop the mesoporosity of polymer-derived ceramics.

5.1. Sacrificial fillers

Highly porous ceramics can be obtained by homogeneous dispersion of a solid sacrificial filler (in form of a micro or nanosized beads/particles generally made of organics or natural salts) throughout the preceramic polymer by stirring or ball milling. Upon heat treatment these fillers are generally decomposed and leave behind microstructure with pores. Depending on the filler loading the porosity can vary anywhere from 20 to 90% and can also be percolating network of interconnected porosities. Template removal always produces dense and thick struts, resulting in, generally speaking, enhanced mechanical properties with respect to those of components obtained via the replica technique, in some cases compressive strengths of up to 30 MPa were reported depending on the amount of porosity. Figure 1.29 shows a schematic of the process.
5.2. Soft templating

A lot of pioneering work has been done with respect to using soft templating approach to generate porous ceramics with PDC route by use of wood, coral, polymeric foams, etc. This route is suitable with preceramic polymers to generate macroporous cellular solids due to enhanced wetting and partial melting of cross-linked polymer during heat treatment. The final formed macroporous ceramic has a homogeneous crack free structure. As defined by Greil et al., his approach is identified by the fact that the template is removed in the same step as the conversion of preceramic polymer to ceramic. Figure 1.30 shows the schematic of the process.
Polyurethane (PU) template has been used to generate SiOC foam with hierarchical macro pore size ranging from 300 micrometer for infiltrating foam to 2500 micrometer for matrix foam. Similar SiOC foams with SiC nanowires were produced using PU template. Infiltration of the foam with a silicone resin and pyrolysis at 1400°C led to the formation of SiC NWs inside the pores, due to carbothermal reactions. The resulting foams had porosity and cell size in the 77–85 vol% and 400–600 mm range, respectively. The shape and size of these porosities and the porous structure depend completely on the shape and surface structure of the template and the extent of infiltration of preceramic polymer in the template. Polysilazane was infiltrated into a porous polyethylene (PE) monolith, prepared from a polymeric bicontinuous microemulsion. The PSZ/PE composite was crosslinked and pyrolyzed (1000°C) to obtain nanoporous SiCN, with a pore diameter in the range of 60–100 nm and SSA of 24 m².g⁻¹. Soft template can also be considered as the mixture of preceramic polymer and block copolymers as proposed by Wiesner in 2004. The idea behind the process is that a part of the block is soluble into the preceramic polymer and the other is not. Therefore, micelles are formed and this leads to mesoporous materials (usually ordered) after pyrolysis.

5.3. Hard templating

Hard templating approach is different from the previous method by the fact that an extra step is required to remove the template after the polymer to ceramic conversion to generate a porous structure. This step is either a pyrolysis under reactive atmosphere or leaching using an acid. This method is generally used to prepare highly ordered or disordered mesoporous ceramic. It is also known as nanocasting. Templates like SBA-15 and CMK-3 have been used to synthesize ordered mesoporous (OM) SiOC using polysiloxane, OM-SiC using polycarbosilane with SSA (PSD) of 616 m².g⁻¹ (3.3 nm) and 460-720 m².g⁻¹ (2 - 3.7 nm) respectively. In the first case the silica template of SBA-15 is removed by HF etching after conversion to ceramic and in the second case the CMK-3 is removed by using a reactive atmosphere of NH₃ at 400°C. Two or more templates can be used to form ceramics with extremely high SSA and very narrow pore size distribution. OM-SiC with SSA of 942 m².g⁻¹ was synthesized by addition of triblock copolymer as binder to preceramic polymer with hard template of silica like KIT-6. Mesoporous SiBCN was prepared by direct nanocasting of a boron-modified PCSZ into OM-silica, followed by crosslinking, pyrolysis (1000°C / 2h / N₂) and HF etching. An open, continuous and highly ordered 2D hexagonal
SiBCN framework was produced. The SSA, pore volume and pore diameter were reported as 337 m².gm⁻¹, 0.55 cm³.gm⁻¹, and 4.6 nm, respectively. Our group used an integrated chemical route to synthesize micro/mesoporous BN monoliths. We initially prepared silica foams using sol–gel process, lyotropic mesophases and biliquid foams as dual soft templates. These foams served as hard template to synthesize carbonaceous templates by impregnating them a carbon precursor followed by carbonization under an inert atmosphere. The silica template was then removed using HF and the carbonaceous template was then impregnated with BN precursor like polyborazylene and then converted in to ceramic under N₂. The template was then removed under NH₃ in the subsequent step at high temperature. Bernard and co-workers used a similar process to generate micro/mesoporous BN, but instead of silica template they used fau type zeolite. This zeolite was impregnated and fixed with carbon at high temperature using a CVD process. The zeolite was then removed with HF and the carbonaceous template impregnated with polyborazylene. This was then converted to BN under N₂ followed by carbon template removal under NH₃. Figure 1.31 shows a schematic representation of hard templating process.

![Figure 1.31 Schematic of Hard Templating approach](image)

This approach has been majorly used to generate ordered or disordered mesoporous ceramics with interconnected porosities from preceramic polymers. We employed this approach using activated carbon monoliths to prepare 3D mesoporous BN, SiC, Si₃N₄ and Si·C·N ceramic monoliths and their nanocomposite to be used as supports in catalytic hydrolysis of NaBH₄ and as proof of concept, as electrocatalyst supports and electrode materials.
6. Conclusion

This chapter dealt with providing a literature survey of the electrochemical power sources and in particular are the two major issues that still limit their commercialization as fuel cells and supercapacitors, i.e., the hydrogen source, electrocatalyst support and electrode materials. With this context, we prepared non-oxide ceramics with high potential as supports for Pt for the hydrolysis of sodium borohydride to generate hydrogen on demand to fuel cells and as electrocatalyst supports and electrode materials in fuel cells and supercapacitors respectively. We provided a state of the art on synthesis of Si and B based carbide, carbonitride, nitride and their nanocomposites using the polymer derived ceramic (PDC) route. We focused our attention on the PDC route in this thesis due to its advantages to control the ceramic composition precisely, its ability to synthesize complex shapes and the relatively low processing temperature. The approach involves use of “single source” precursors to generate BN, SiC, Si-C-N, Si₃N₄ ceramics and their derived nanocomposite ceramics with in-situ growth of MN (M= Ti, Zr, Hf) nanocrystals in the matrix of before mentioned ceramics. This approach involves reacting two precursors, one being the precursor of the nanophase and the other that of the matrix. The synthesis is directed so that there is phase separation during crystallization where the nanophase emerges out of the amorphous or crystallized matrix. These materials are prepared as mesoporous components. Template impregnation has been discussed as the preferred process to design the mesoporosity in PDCs. These systems have potential applications technologies like fuel and supercapacitors and are discussed in thesis under the same purview.
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CHAPTER 2
MATERIALS AND METHODS
1. Introduction
The various ceramic systems were synthesized keeping in mind the properties required in their intended final application. This chapter represents the experimental part of this manuscript. We firstly discuss on the use of commercial polymers and synthesis of the home-made preceramic polymers for preparing non-oxide ceramics like Silicon Carbide (SiC), Silicon Nitride (Si₃N₄), Silicon Carbonitride (Si-C-N) and BN, as well as (nano)composite systems like Metal Nitride (Ti, Zr, Hf)/Silicon (Carbo) Nitride and Metal Nitride (Ti, Zr, Hf)/Boron Nitride as presented in chapters 3 and 4. Secondly, we describe the process to prepare mesoporous monoliths made from the above mentioned compositions to be used in various applications like hydrogen generation from chemical hydrides from aqueous media as discussed in chapter 5. Thirdly, the synthesis of MXene/SiCN composites is detailed. They are prepared for electrocatalysis tests as reported in chapter 5. Finally the chapter ends with the detail of the various tools used for the characterization of the materials at each step of their preparation.

2. Molecular precursors and preceramic polymers
All chemical products are handled in an argon-filled glove box (MBraun MB200B; O₂ and H₂O concentrations kept at < 0.1 ppm). The preceramic polymers were synthesized under argon atmosphere due to their sensitivity to air and moisture. Argon (> 99.995 %) is purified by passing through successive columns of phosphorus pentoxide, siccapent™, and BTS catalysts. Schlenk flasks are dried at 120°C overnight before pumping under vacuum and filling them with argon for synthesis.

2.1 Presentation of the commercially-available organosilicon polymers
The following organosilicon polymers were briefly discussed in the first chapter. Here we detail the physical properties and the nature of these polymers. Table 2.1 details the list of commercial polymers and solvents used.
Table 2.1 List of various chemicals used along with their manufacturer details and commercial name

<table>
<thead>
<tr>
<th>Product</th>
<th>Manufacturer</th>
<th>Commercial Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>AHPCS (allyhydridopolycarbosilane)</td>
<td>Starfire Systems</td>
<td>AHPCS SMP10</td>
</tr>
<tr>
<td>HTT1800 (polycarbosilazane)</td>
<td>Clariant Advanced Chemicals</td>
<td>HTT1800</td>
</tr>
<tr>
<td>PHPS (perhydropolysilazane)</td>
<td>Mitsuya Boeki Ltd.</td>
<td>Aquamica NN-120</td>
</tr>
<tr>
<td>Ammonia Borane</td>
<td>Sigma·Aldrich</td>
<td>Borane·ammonia complex 97%</td>
</tr>
<tr>
<td>Toluene</td>
<td>Acros Organics</td>
<td>99.85 %, Extra Dry over Molecular Sieve, AcroSeal(R)</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>Sigma·Aldrich</td>
<td>Tetrahydrofuran anhydrous, ≥99.9%, inhibitor-free</td>
</tr>
</tbody>
</table>

1) Perhydropolysilazane (PHPS)

This is polysilazane free of any carbon atom. It has Si, N and H as its constituent elements and is the precursor used to prepare Si₃N₄ (figure 2.1). It can be synthesized by different route like ammonolysis of dichlorosilane (H₂SiCl₂) in benzene as solvent¹.

\[
\begin{align*}
\text{H} & \quad \text{Cl} \quad \text{Si} \quad \text{Cl} \\
\text{H} & \quad \text{H} + \text{NH}_3 \\
\text{H} & \quad -\text{NH}_4\text{Cl} \quad \rightarrow
\end{align*}
\]

Figure 2.1 Synthesis of perhydropolysilazane from dichlorosilane

Due to the highly reactive nature of dichlorosilane to air and moisture and its hazardous nature, it is complex to synthesize it in academic laboratory.

As a consequence, we obtain PHPS from Aquamica (Japan) under brand name NN110-20. It is 20 vol% solutions in xylene. It is a transparent liquid with a density of 1-1.1 g.cm⁻³ (0.92 g.cm⁻³ with solvent) and viscosity of 30-50 mPa.s at 25°C. It can have a ceramic yield up to 80% depending on the pyrolysis atmosphere. It is heavily used in the electronic industry to synthesize SiO₂ films and make dielectrics. Now Merek manufactures PHPS through a subsidiary DurXtreme®. The polymer is investigated in chapter 4 and chapter 5.

2) Poly(methylvinyl)-co-(methyl)silazane HTT1800®:

HTT1800 is a polycarbosilazane commercially known as KiON-HTT1800® and sold by Clariant Technologies (Germany). It is a co-polymer composed of various reactive
sites such as vinly, Si·H and N·H groups (Figure 2.2). Upon pyrolysis at 1000°C under N\(_2\) it gives Si·C·N ceramic while under NH\(_3\) it gives Si\(_3\)N\(_4\), although the yield is lower. Due to the presence of methyl and vinyl groups it can have free carbon in the ceramics.

\[
\begin{align*}
\text{Si} & \quad \text{N} \\
\text{CH}_3 & \quad \text{H} & \quad 0.2 \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{Si} & \quad \text{N} \\
\text{CH}_3 & \quad \text{H} & \quad 0.8 \\
\end{align*}
\]

**Figure 2.2 Chemical formula HTT1800**

<table>
<thead>
<tr>
<th>Properties</th>
<th>HTT 1800</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity</td>
<td>20–50 mPa.s</td>
</tr>
<tr>
<td>Density</td>
<td>1.0 g.cm(^{-3})</td>
</tr>
<tr>
<td>Fire point</td>
<td>16.25°C</td>
</tr>
<tr>
<td>Shelf Life</td>
<td>24 months from date of manufacture at 20°C</td>
</tr>
<tr>
<td>Solubility</td>
<td>Hexane/Toluene/Insoluble in water</td>
</tr>
<tr>
<td>Crosslinking</td>
<td>175–200°C</td>
</tr>
<tr>
<td>Appearance</td>
<td>Pale yellow liquid</td>
</tr>
</tbody>
</table>

This liquid polycarboxilazane is most often used in infiltration processes and as a coating due to its low viscosity and good adhesion. It is now sold by Merck with the commercial name Durazane. The polymer is investigated in chapter 4 and 5.

3) **Allyldihydridopolycarboxilane (AHPCS):**

AHPCS is commercially sold as SMP-10 by Starfire Systems®, USA. It is a preceramic polymer to synthesize Silicon Carbide (SiC). It is a yellow colored viscous liquid.

<table>
<thead>
<tr>
<th>Properties</th>
<th>AHPCS SMP-10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity</td>
<td>0.1 Pa.s</td>
</tr>
<tr>
<td>Property</td>
<td>Value</td>
</tr>
<tr>
<td>--------------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>Density</td>
<td>0.998 g.cm(^{-3})</td>
</tr>
<tr>
<td>Fire Point</td>
<td>89°C</td>
</tr>
<tr>
<td>Surface Tension</td>
<td>30 dynes.cm(^{-2})</td>
</tr>
<tr>
<td>Solubility</td>
<td>Hexane/Toluene/Insoluble in water</td>
</tr>
<tr>
<td>Cross-linking Temperature</td>
<td>121-124°C</td>
</tr>
</tbody>
</table>

It is a hyper-branched polycarbosilane (figure 2.3). Whitmarsh and Interrante\(^2\) were the first to synthesize hydridopolycarbosilane (HPCS), a predecessor of AHPCS, by reaction between a Grignard reagent and (chloromethyl)trichlorosilane followed by reduction with lithium tetrahydroaluminate (LiAlH\(_4\)). It is a precursor comprising silicon-bonded hydrogen atoms and leading to the stoichiometric SiC 1:1, i.e., free of any free carbon. Substitution of 5-10% of the Si-X groups (X = H, Cl) in HPCS with Si-allyl groups before reduction with LiAlH\(_4\) lead to the formation of AHPCS which had better cross-linking properties and a higher ceramic yield as compared to HPCS.

\[
\begin{align*}
\text{H}_3\text{C} & \equiv \text{CH}_2 \\
\begin{array}{c}
\text{Si} \\
\text{H}
\end{array} & \text{CH}_2 \quad 0.1 \\
\begin{array}{c}
\text{H} \\
\text{Si} \quad \text{CH}_2
\end{array} & \quad 0.9
\end{align*}
\]

*Figure 2.3 Chemical formula AHPCS*

### 2.2 BN precursors

1) Ammonia Borane: Ammonia borane (>98%) is supplied by Sigma Aldrich as a part of their hydrogen generation kit. It is a white crystalline solid first synthesized by Shore and Parry in 1955. It is also used as one of the monomeric BN generators. Upon pyrolysis it undergoes crosslinking to first form diborane which further converts to borazine and polyborazine at high temperature and finally gets converted to boron nitride as shown in the following figure 2.4\(^3\). Ammonia borane is investigated in chapter 3.
2) Borazine and polyborazylene: Any potential polymeric precursor for BN should have good ratio of B:N and should (Figure 2.5) have H as the only other element apart from B and N. Borazine (BZ) \((\text{H}_3\text{B}_3\text{N}_3\text{H}_3)\), a preformed six-membered hexagonal planar ring, has the correct elemental composition for forming BN. It was first discovered by Stock in 1926 but it was only in 1995 that Sneddon *et al.* synthesized it economically by reaction between \((\text{NH}_4)_2\text{SO}_4\) and \(\text{NaBH}_4\) in tetraglyme in a low temperature range \((120^\circ\text{C} \text{ to } 140^\circ\text{C})\).}

We used the same reaction to synthesize borazine and the initial reactants were supplied by Sigma Aldrich. Due to its high volatility sometimes it is used as its polymeric form polyborazylene (PBZ) (Figure 2.6). BZ is polymerized to PBZ by dehydrocoupling between B-H and N-H during thermolysis in an autoclave. The autoclave is sealed with BZ at 0°C under an argon atmosphere and heated to 45°C to 60°C temperature range to produce different types of PBZ. These change viscosity and state as we move from 45°C to 60°C. The PBZ obtained at 60°C labelled as \(\text{PB60}\), is
solid and used for further experiments. Figure shows the general structure of PBZ, it is either a biphenylic or naphtalenic type structure.

Figure 2.6 Biphenylic and naphtalenic stuctures of polyborazylene

3. Li modified BN precursor: The presence of first group light elements like Li, Na is known to improve the crystallization of BN produced by powder metallurgy. For this purpose we synthesized a Li modified BNH precursor which will give BN upon pyrolysis. The reaction was carried in two ways: solution synthesis and reactive ball milling. Solution synthesis is carried out in an inert atmosphere in an ice bath at 0°C as the reactivity of LiNH$_2$ is very high. LiNH$_2$ is added to a solution of ammonia borane in THF drop by drop using an addition ampule with B:Li molar ratio of 1:1. Once the entire Li precursor was added the reaction temperature was increased to 40°C and allowed to continue for 24 hours. After this solvent was removed under reduced pressure using a recovery Schlenk Distillation Bridge and a liquid nitrogen trap. A white insoluble powder was obtained after drying which was named ABLi1. While for reactive ball milling, the powders were added to the reactor in a glove box in 1:1 ratio by mole (1:5 weight ratio of powder and balls) and then ball milled at 200 rpm for 4 hours with 10 min intervals. The retrieved powder was labelled ABLi1·BM.

2.3 Synthesis of metal-modified organosilicon polymers and BN precursors
The modification of organosilicon polymers including PHPS and HTT1800 and BNH precursors including AB, BZ and PBZ occurs by their reaction with tetrakisdialkylaminometallics. The characterization and behavior of metal modified organosilicon polymers and BNH precursors are discussed in chapter 3 and 4. In chapter 5 these are used to prepare mesoporous monoliths.
2.3.1 Tetrakis(dialkylamido)metallics:
Tetrakis(dialkylamido)metallics of Titanium (Ti), Zirconium (Zr) and Hafnium (Hf) were used as sources for metal nitrides in this study. These are commercially available at Sigma Aldrich with a purity of 99.999%. These amines are pungent smelling corrosive liquids in case of Ti and Zr and solid in case of Hf at room temperature. They are highly volatile precursors, sensitive to air and moisture and hence were always handled under inert atmosphere. Table 2.4 below shows the structure of the precursors and some basic properties.

<table>
<thead>
<tr>
<th>Metal Precursor</th>
<th>Molecular weight (g mol⁻¹)</th>
<th>Density at 25°C (g cm⁻³)</th>
<th>Boiling point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrakis(dimethylamido)titanium(IV) (TDMATI)</td>
<td>224.17</td>
<td>0.947 (orange liquid)</td>
<td>50</td>
</tr>
<tr>
<td>Tetrakis(diethylamido)zirconium(IV) (TDEAZr)</td>
<td>379.74</td>
<td>1.026 (yellow liquid)</td>
<td>128</td>
</tr>
<tr>
<td>Tetrakis(dimethylamido)hafnium(IV) (TDMAHf)</td>
<td>354.79</td>
<td>1.098 (white solid)</td>
<td>26-29 (melting point)</td>
</tr>
</tbody>
</table>

2.3.2 Synthesis of metal-modified organosilicon polymers
The synthesis of polymetallosilazane and poly(metallo)carbosilazane is done by a simple reaction between the silazane like PHPS or HTT1800 and the metallic precursors TDMAT, TDEAZr or TDMAHf with a fixed ratio. To illustrate the process, we explain synthesis of NCPTi2.5-RT, made from reacting PHPS and TDMAT with a Si/Ti molar ratio of 2.5. Other polymers can be synthesized in the same manner just by changing the polysilazane, metal precursor and the Si/M ratio.

The Si/Ti molar ratio is set to be 2.5. To achieve this, the following equation is followed:

\[
\frac{n(\text{PHPS})}{n(\text{TDMATI})} = 2.5
\]
A specific quantity of TDMAT (17.84 mmol) is added dropwise to a 10 g solution of PHPS in xylene (20 vol%) dissolved in 150 ml of toluene at ambient temperature under an inert atmosphere. The system is prepared as shown in Figure 2.7 and the reaction is connected to a bubbler for the gaseous byproduct to escape the system. The mixture is stirred for 3 hours and the solution changes color from yellow or orange to black or dark. At the end of three hours the system is heated to 115°C (reflux temperature of toluene) for three days to allow the reaction to approach completion.

After three days the reaction mixture is cooled down to ambient temperature and the solvent is removed under reduced pressure at room temperature using a distillation bridge, recovery Schlenk and a liquid nitrogen trap as shown in the Figure 2.8.
A dried black metallic looking powder was obtained in the Schlenk. It was heated till 60°C for 1 hour under reduce pressure to remove any traces of solvent.

Depending on the metal precursor, polysilazane and the Si/M molar ratio, the final product can range from a dark black liquid to a bright yellow powder. Various polynetallosilazanes were synthesized namely, $\text{NCPMX} (X=\text{Si/Ti} = 1, 2.5, 5) \ (M=\text{Ti, Zr, Hf}) \ (\text{PHPS-M precursor})$ and $\text{NCHMX} (X=\text{Si/Ti} = 1, 2.5) \ (M=\text{Ti, Zr, Hf}) \ (\text{HTT1800-M precursor})$. The physical state of these polymer ranges from viscous liquids to solid powders.

2.3.3 Synthesis of metal-modified BNH precursors

The synthesis of transition metal modified BNH precursors is very similar to the previously described process of polynetallosilazane. A reaction between BNH precursors and metallic precursors leads to formation of polynetalloborane. The following equation is used to fix the molar ratio between B/M.

$$\frac{n(\text{Ammonia borane})}{n(\text{TDMATi})} = 3$$

To illustrate the process, we describe the synthesis of $\text{ABTi3}$ sample from ammonia borane and TDMAT with a B/Ti molar ratio of 3. Other polymers can be synthesized in the same
manner but we should take care that the B content in ammonia borane, PZ and PBZ are different. A fixed quantity of TDMAT (17.84 mmol) is added dropwise to a 1.65 g of Ammonia borane solution in 120 ml of THF at ambient temperature under inert atmosphere using a setup similar to shown in Figure 2.9. The system is prepared as shown in the figure and the reaction is connected to a bubbler for the gaseous byproduct to escape the system. The mixture is stirred for 3 hours and the solution changes color from yellow or orange to black or dark. At the end of three hours the system is heated to 75°C (reflux temperature of THF) for three days to allow the reaction to approach completion. After three days the reaction mixture is cooled down to ambient temperature and the solvent is removed under reduced pressure at room temperature using a distillation bridge, recovery Schlenk and a liquid nitrogen trap as shown in Figure 2.8. A dried black metallic looking powder was obtained in the Schlenk. It was heated till 60°C for 1 hour under reduce pressure to remove any traces of solvent. The black powder obtained is a polytitanoborane.

Depending on the B precursor used we can obtain different precursors like polymetalloborazine, borazine or polyborazylene is used. The powder changes color (light to dark) as the B/M ratio decreases. The following table shows all the polymetalloboranes and polymetalloborazines synthesized. The ammonia borane based nanocomposites were denoted by \( \text{ABMX} \) (X=B/M=1, 3, 5) (M=Ti, Zr, Hf).
Table 2.3 Different types of polymetalloboranes/borazines synthesized

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>BN precursor</th>
<th>Metal precursor</th>
<th>B/M ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABTi3</td>
<td>Ammonia borane</td>
<td>TDMAT</td>
<td>3</td>
</tr>
<tr>
<td>ABTi1</td>
<td>Ammonia borane</td>
<td>TDMAT</td>
<td>1</td>
</tr>
<tr>
<td>ABTi5</td>
<td>Ammonia borane</td>
<td>TDMAT</td>
<td>5</td>
</tr>
<tr>
<td>ABZr3</td>
<td>Ammonia borane</td>
<td>TDEAZr</td>
<td>3</td>
</tr>
<tr>
<td>ABHf3</td>
<td>Ammonia borane</td>
<td>TDMAHf</td>
<td>3</td>
</tr>
<tr>
<td>PB60Ti3</td>
<td>Polyborazylene</td>
<td>TDMAT</td>
<td>3</td>
</tr>
</tbody>
</table>

3. Pyrolysis of preceramic polymers as powders

The powder was transferred into a silica tube inserted in a horizontal tube furnace (Thermoconcept® OS50/450/12) under an argon flow. The tube was pumped under vacuum for 30 min and then refilled with argon, nitrogen or ammonia depending on the chemistry of polymers. For AHPCS, pyrolysis was done under Argon. For PHPS and PHPS derived polymetallosilazane it was done under ammonia and for HTT1800 and its derived polymetallosilazane the pyrolysis was performed both under nitrogen and ammonia. For BNH precursors and their derived polymetalloboranes pyrolysis was performed under ammonia. The powder was heated till 1000°C for 2 hours under ammonia with a heating and cooling rate of 5°C/min. These samples underwent heat treatment at higher temperature using a graphitic furnace (Gero Model HTK 8). The furnace is pumped out for 30 min then refilled with nitrogen (200 mL/min) before undergoing a cycle consisting of ramping at 5°C/min to the final temperature, remaining there for 2 hours and then cooling down to RT at 2°C/min.

4. Preparation of mesoporous monoliths via nanocasting using template

Preceramic polymers were used to prepare 3-D mesoporous monoliths by nano-casting technique in chapter 5.

4.1 Nanocasting using template

Nanocasting refers to replicating the structure of template material on to an intended material by impregnating the template with the precursor and then removing the template while converting the precursor into a solid using either heat or light (figure 2.10)
Activated carbon monolith has been used as a template. It is labelled as ACM. Before using as template it is passivated, i.e., removal of any residual oxygen, moisture or dangling groups (-OH, -COOH), under vacuum ($5 \times 10^{-1}$ mbar) at 600°C for 10 hours in a tubular furnace without any structural modifications. The activated carbon used for templating has the following structural and textural properties: monolith/rod type; specific surface area of 953 m$^2$ g$^{-1}$ and 5.2 nm of pore size. The treated monoliths were transferred in to the glove box to be stored under inert atmosphere. A specific amount of ACMs are weighed and taken in a Schlenk flask. The Schlenk is put under dynamic vacuum for 30 mins to remove any inert gas from the porosities.

![Figure 2.10 Schematic of nanocasting route](Image)

### 4.2 Mesoporous SiC and Si-C-N monoliths

The preceramic polymers, stored in Schlenks, are infiltrated into the ACM under reduced pressure conditions to allow better impregnation in to the porosities of the template. The amount of preceramic polymer infiltrated is calculated using an optimum mass ratio between the polymer and the monolith. The system was sonicated for 24 hours while the being under static vacuum. This was followed by washing off excess polymer from the monoliths by toluene under inert gas flow. The system was again put under dynamic vacuum for one hour to allow the monoliths to dry. This generated the impregnated monoliths labelled APCS/ACM and HT1800/ACM.

The Schlenk was taken to the glove box to store the monoliths in an inert atmosphere before being transferred into a tubular furnace for pyrolysis. The samples are transferred into a silica tube inserted in a horizontal tube furnace (Thermoconcept® OS50/450/12) under an argon flow. The tube is pumped under vacuum for 30 min and refilled with argon (APCS/ACM) and nitrogen (HT1800/ACM) (120 mL min$^{-1}$) to be subjected to a cycle of ramping at 1°C min$^{-1}$ to 1000°C, dwelling there for 2 h. Then cooling to RT is carried out at 2°C min$^{-1}$ to produce samples Si/ACM (obtained from APCS/ACM) and Si-C-N/ACM.
We apply higher temperatures using a graphitic furnace (Gero Model HTK 8) to follow the evolution of their porosity as a function of the pyrolysis temperature. The furnace is pumped out for 30 min then refilled with argon (Si/ACM) or nitrogen (Si-C·N/ACM) (200 mL min⁻¹) before undergoing a cycle consisting of ramping at 5°C min⁻¹ to the final temperature, remaining there for 2 h and then cooling down to RT at 2°C min⁻¹. Then, as-received samples undergo heat-treatment under air (to remove the ACM) in a muffle furnace (Thermoconcept® KLS03/10) through a cycle of ramping of 1°C min⁻¹ to 600°C, dwelling there for 5 h, and then cooling to RT at 1°C min⁻¹. Samples are labelled mSiCX and mSi·C·NX (X being the two first numbers of the final temperature, e.g., 12 for 1200).

4.3 Mesoporous Si₃N₄, Si-M-N and B-M-N monoliths

The synthesis of mesoporous silicon nitride, Si-based metal nitride nanocomposite and B-based metal nitride nanocomposite are done using the same nanocasting technique as mentioned above. It differs from SiC and Si·C·N in its pyrolysis procedure. The pyrolysis procedure applied to all nitride based systems is similar. Although the pyrolysis procedure is same for both simple nitride and nanocomposite nitride, we explain them separately so as to avoid confusion in naming the systems.

4.3.1 Mesoporous PHPS derived Si₃N₄ monolith

The infiltration of preceramic polymer was done following the same protocols as before and the infiltrated monolith was named as PHPS/ACM. For pyrolysis 3 different strategies are applied. In a first strategy, the tube is filled with nitrogen to be subjected to a cycle of ramping at 1°C min⁻¹ to 1000°C; dwelling there for 2 h. Cooling to RT is carried out at 2°C min⁻¹ generating samples Si₃N₄·Si/ACM. After the polymer-to-ceramic conversion process, the samples Si₃N₄·Si/ACM undergo a further heat-treatment under ammonia (to remove the ACM) at 5°C min⁻¹ to 1000°C, dwelling there for 5 h. Cooling produces the mesoporous Si₃N₄ monoliths labelled mSi₃N₄1010. In a second strategy, the tube is filled with ammonia to be subjected to a cycle of ramping at 1°C min⁻¹ to 1000°C, dwelling there for 5 h. Cooling directly produces the mesoporous Si₃N₄ monoliths labelled mSi₃N₄10. In a third strategy, the tube is filled with nitrogen to be subjected to a cycle of ramping at 1°C min⁻¹ to 400°C, dwelling there for 1 h then under ammonia at 1°C min⁻¹ to 1000°C, dwelling there for 5 h. Cooling directly produces the mesoporous Si₃N₄ monoliths labelled mSi₃N₄410. The sample mSi₃N₄410 undergoes heat-treatment at higher temperature using a graphitic furnace (Gero Model HTK
8) to follow the evolution of its porosity as a function of the pyrolysis temperature. The furnace is pumped out for 30 min then refilled with nitrogen (200 mL min⁻¹) before undergoing a cycle consisting of ramping at 5°C min⁻¹ to the final temperature, remaining there for 2 h and then cooling down to RT at 2°C min⁻¹ to generate the samples mSisN₄X (X being the second number of the temperature, e.g., 2 for 1200°C).

4.3.2 Polymetallosilazane/borane derived mesoporous monoliths

The polymetallosilazane/borane (before extraction from solvent ~ 5wt%), are infiltrated into the ACM under reduced pressure conditions to allow better impregnation in to the porosities of the template. The amount of preceramic polymer infiltrated is calculated using an optimum mass ratio between the polymer and the monolith. The system was sonicated for 24 hours while the being under static vacuum. This was followed by washing off excess polymer from the monoliths by toluene under inert gas flow. The system was again put under dynamic vacuum for one hour to allow the monoliths to dry. The generated monoliths are labelled NCPMX/ACM (polymetallosilazane prepared from PHPS), NCHMX/ACM (polymetallosilazane prepared from HTT1800) and NCABMX/ACM (polymetalloborane prepared from ammonia borane). The infiltrated monoliths were stored in the glove box being transferred into silica tube inserted in a horizontal tube furnace (Thermoconcept® OS50/450/12) under Argon flow. The polymer to ceramic conversion and removal of template was done under a single pyrolysis. The samples were treated under different conditions to find the optimum settings to achieve maximum SSA and mechanical stability. In a first strategy, the tube is filled with nitrogen to be subjected to a cycle of ramping at 1°C min⁻¹ to 1000°C; dwelling there for 2 h. cooling to RT is carried out at 2°C min⁻¹. After the polymer-to-ceramic conversion process, the samples undergo a further heat-treatment under ammonia (to remove the ACM) at 5°C min⁻¹ to 1000°C, dwelling there for 5 h. Cooling produces the mesoporous Si·M·N or B·M·N monoliths. In a second strategy, the tube is filled with ammonia to be subjected to a cycle of ramping at 1°C min⁻¹ to 1000°C, dwelling there for 5 h. Cooling directly produces the mesoporous Si·M·N or B·M·N monoliths. In a third strategy, the tube is filled with nitrogen to be subjected to a cycle of ramping at 1°C min⁻¹ to 400°C, dwelling there for 1 h then under ammonia at 1°C min⁻¹ to 1000°C, dwelling there for 5 h. Cooling directly produces the mesoporous Si·M·N or B·M·N monoliths labelled mNCPMX₁₀, mNCHMX₁₀ and mNCABMX₁₀. The samples mNCPMX₁₀, mNCHMX₁₀ and mABMX₁₀₀₀ undergo heat-treatment at higher temperature using a graphitic furnace (Gero Model HTK
8) to follow the evolution of its porosity as a function of the pyrolysis temperature. The furnace is pumped out for 30 min then refilled with nitrogen (200 mL/min) before undergoing a cycle consisting of ramping at 5°C/min to the final temperature, remaining there for 2 hours and then cooling down to RT at 2°C/min to generate the samples $m_{NCPMX-Y}$, $m_{NCHMX-Y}$ and $m_{ABMX-Y}$ (M is Ti, Zr, Hf; X is the molar ratio between Si/M and Y is the first two numbers of crystallization temperature of the sample, for eg $m_{NCPTi2.5-14}$ stands for Si-Ti-N nanocomposite with a Si/Ti ratio of 2.5 and annealed till 1400°C).

4.4 Deposition of Platinum Nanoparticles (np-Pt) on the ceramic monoliths

The platinum nanoparticles (Pt NPs) synthesized from the precursor $H_2PtCl_6.6H_2O$ were supported over the mesoporous Si-based non-oxide ceramic/nanocomposite monoliths with the highest SSA in each system by wet impregnation followed by heat-treatment under a hydrogen/argon flow. A low platinum loading was targeted (1 wt. %). The platinate was dissolved in 1 ml filtered water (obtained from Millipore systems $\Omega < 18 S m^{-2}$) and ultrasonicated for 30 min generating a yellowish solution. The mesoporous Si-based non-oxide ceramic/nanocomposite monoliths were suspended in 2.5 ml of filtered water and the platinate solution was added to this. The mixtures were allowed to age under sonication for 24 hours. The mixtures were then dried at 80°C overnight and then heat treated under diluted $H_2$ flow (5 % $H_2$ and 95 % Ar) at 450°C for 4 h to reduce the platinate to platinum and generate the materials labelled $Pt_{-mSi_3N_4X}$, $Pt_{-mSiCX}$, $Pt_{-mSi-C-NX}$ where X is the first two numbers of the crystallization temperature of sample with highest specific surface area in case of binary systems and $Pt_{-mNCPMX-Y}$ and $Pt_{/mNCHMX-Y}$, where M is Ti, Zr, Hf; X is the molar ratio between Si/M and Y is the first two numbers of crystallization temperature of the sample, for eg. $Pt_{-mNCPTi2.5-14}$ stands for Si-Ti-N nanocomposite with a Si/Ti ratio of 2.5 and annealed till 1400°C before Pt deposition. For comparison, $Pt/ACM$ was prepared following the same experimental procedure.

5. Preparation of MXene/SiCN composite

2D MAX phase known as MXene is prepared by the following route. Ti$_3$AlC$_2$ MAX phases were synthesized using a conventional powder metallurgy technique. Titanium (~200 mesh, 99,95%, Alfa Aesar Karlsruhe Germany), titanium carbide TiC (4µm, 99,5%, Alfa Aesar) and aluminum (60-100 mesh 99,8%, Alfa Aesar) were used as starting materials. The powders
were weighted according to the desired composition (Ti₃AlC₂) except for Al which was introduced with a 10 wt% excess in order to compensate its loss by evaporation during the sintering process. After mixing for 30 min (Turbula Shaker Mixer), a homogeneous mixture without agglomerates is obtained. This mixture was then packed into a glass tube sealed under vacuum. The sintering has been performed in a Nabertherm furnace under argon atmosphere for 2 h at 1450°C. Finally, the powders were sieved in order to select MAX phases with grain sizes lower than 25 µm. The as obtained powder was sonicated for 2 hours in filtered water to open up the structure and form a layered structure. The solution was dried in a hot air oven at 80°C for 24 hours. The powder was then transferred into a 25 mL long Schlenk closed using a septum. The system was put under dynamic vacuum (5·10⁻¹ mbar) for 2 hours. HTT1800 (polycarbosilsilazane) was injected into the Schlenk under this reduced pressure to allow proper impregnation of the polymer into the spaces between the MXene layers. Various mass ratios between HTT1800 and MXene were synthesized ranging from excess MXene to excess HTT1800. The system was sonicated for 24 hours before being transferred into silica tube inserted in a horizontal tube furnace (Thermoconcept® OS50/450/12) under argon flow. The tube was put under dynamic vacuum for 30 mins before being refilled by argon. The polymer to ceramic conversion was carried out at 800°C under 200 ml/min flow of argon. The temperature was ramped upto 800°C at a rate of 1°C/min. It was held at 800°C for 2 hours before being cooled down to room temperature at a rate of 2°C/min. The prepared sample was labelled as X-SiCN/MXene (X is the mass ratio between HTT1800 and MXene).

6. Synthesis of Pt/Si-C-N nanocatalysts
The preparation of Pt/Si-C-N nanocatalysts involved two separate steps: firstly, preparation of Pt complex and secondly preparation of single source polymer. The method is same as described in our paper.⁵

The platinum complex was synthesized adding exchanging existing ligands from a platinum salt with reactive ones. An 8 millimolar solution of ApTMSH ligand was prepared in diethylether. To this solution we added 8 mmol of n-butyllithium at 0°C. This solution was named L1. The reaction was allowed to continue for two hours with continuous stirring. Another 4 millimolar suspension of [PtCl₂(cod)] was prepared in diethylether. To this suspension we added the previously prepared L1 solution at 0°C. The mixture was allowed
to warm to room temperature slowly along with continuous stirring for 24 hours. After filtration and crystallization we obtained yellow crystals of the platinum complex ([Pt(Ap\text{TMS})_2]) with a yield of 85%.

The single source polymer was prepared under inert atmosphere of Ar using a Schlenk line. PEOH was dissolved in toluene at 110°C in round bottom three-necked Schlenk under flow of Argon. HTT1800 was added to this in weight ratio of 30:70 to PEOH. The mixture was held for one hour under static conditions at 110°C. The previously prepared Pt complex was dissolved in toluene and added to the HTT1800-PEOH solution in fixed Pt/Si ratio under Argon flow along with DCP. The mixture was allowed to cross-link at 110°C for 12 hours before being cooled down to room temperature. The solvent was removed under reduced pressure and the single source polymer obtained was named as NCHPtX, where X is the ratio between Pt and Si and varies from 1/10 to 1/60.

The samples are transferred into a silica tube inserted in a horizontal tube furnace (Thermoconcept® OS50/450/12) under an argon flow. The tube is pumped under vacuum for 30 min and refilled with argon. The samples were pyrolyzed under a flow of N\textsubscript{2} till 1000°C with a heating ramp of 1°C.min\textsuperscript{-1} with 2 hour steps each at 200°C, 300°C, 400°C and 500°C. At 1000°C the sample was held only for 30 mins before being cooled down to room temperature at 4°C.min\textsuperscript{-1}. The obtained sample was labelled as mPt@SiCNX, where X is the initial Pt:Si ratio in the polymer.

7. Characterization Techniques

7.1 Physico-Chemical Characterizations

a) Elemental Analysis

Elemental analysis was performed on all synthesized pre-ceramic polymers and in some cases intermediate samples at Mikroanalytisches Labor Pascher in Germany. A double determination was performed for all elements present and the samples were handled under inert gas to avoid oxidation.

b) Fourier-transformed Infrared Spectroscopy (FT-IR)
Infrared spectroscopy was performed on all polymer samples at room temperature and samples isolated at intermediate temperatures during pyrolysis. This was done to study the polymer to ceramic conversion mechanism for each polymer.

A ThermoFischer Nicolet Nexus FT-IR machine was used to collect the data. Collected data was analyzed using OMNIC32. For samples sensitive to air, the polymer was mixed with KBr and made into pellets to protect it from oxidation, while for ceramic samples the acquisition was done using ATR (Attenuated Total Reflectance) accessory.

c) Raman Spectroscopy

Raman spectroscopy was performed on all ceramic samples treated from 1000°C to 1800°C to study the chemical evolution of ceramic at high temperature and check the presence of free carbon.

It was performed using a M.F.O. microscope from Horiba Scientific. A red laser of wavelength 647.1 nm was used and the reflected signals were collected using a HCX PL FLUOTAR 50x0.55 O/C 8 detector from Leica Microsystems. The data was analyzed using LabSpec software.

d) Nuclear Magnetic Resonance (NMR) Spectroscopy

Liquid-phase NMR analyzes were carried out on Bruker Avance 300 MHz machine using deuterated chloroform as solvent since it is the only solvent in which the polymers dissolve even partially. The data was collected using the software TopSpin and analyzed using Spinwork.

Solid-state NMR is carried out at LCMCP (Université Paris 6) by Dr. Christel Gervais using a Bruker Avance 300MHz. It was used to analyze the nuclei of $^{11}$B, $^{29}$Si, $^{13}$C and $^{15}$N.

e) Thermogravimetric analysis (TGA)

TGA was performed on all pre-ceramic polymers to study the polymer to ceramic conversion behavior and to access the yield of the polymer. The experiments were carried out in a SETARAM TGA 92-16-18 apparatus till 1000°C. For TGA analysis between 1000°C and 1800°C a SETRAM Setsys Evolution TGA apparatus was used.

f) Inductively-coupled plasma mass spectrometry
ICP-MS was performed on ceramic samples to know the composition of the ceramics. ICP-MS for Si, Ti, Hf, Zr, B and Pt was carried out by Dr. Johan Alauzun at Institut Charles Gerhardt Montpellier.

g) X-ray diffraction analysis
X-ray diffraction analysis for the ceramic samples was carried out on an X'pert Pro apparatus from Pan Analytical (Philips), using the copper Kα line (= 1.5405 Å). Identification of the phases was done using EVA and pdf4+ database provided by ICDD, the diagrams were otherwise processed using LabSpec software.

h) X-ray photoelectron spectroscopy
XPS was carried out on ceramic samples with/without metal nanoparticles to study the interaction between the support and nanoparticles and also to determine the precise amount of nanoparticle loading. It was carried out at Science et Surface Company based in Ecully, France using a PHI Quantera SXM equipment with sputtering upto 20 nm and by Dr. Valérie Flaud at Institut Charles Gerhardt Montpellier using a Thermo Electron ESCLAB 250 and a Al Kα line as a monochromatic source of excitation.

i) Brunauer-Emmett-Teller (BET)
Specific surface area for the mesoporous monoliths was determined using the Brunauer–Emmett–Teller (BET) method. The data was collected using a Micromeritics ASAP 2020 apparatus. The pore size distribution was calculated using Barrett–Joyner–Halenda (BJH) method. The total pore volume ($V_p$) is estimated from the amount of N$_2$ adsorbed at a relative pressure of ($P/P_0$) 0.97.

For samples having Macroporosities a MicroMeritics Autopore IV 9500 was used to perform Hg porosimetry.

### 7.2 Electron Microscopy

a) Scanning Electron Microscopy
The specimens are observed on a high resolution S4800-FEG SEM from Hitachi. A lower resolution SEM EVO HD 15 from Zeiss was also used to perform Energy dispersive X-ray spectroscopy (EDX) not only for point areas but also for surface mapping of all the elements present.

b) Transmission Electron Microscopy
To analyse the nanocomposite samples with an amorphous matrix and a crystallized second phase TEM was performed at Indian Institute of Technology Madras, Chennai using TECHNAI 20G², FEI instruments, USA using an accelerating voltage of 200 kV & JEOL 3010 (Japan) instrument at an accelerating voltage of 300 kV. It was also used to determine the exact size and agglomeration in the loaded nanoparticles on the support.
References:


CHAPTER 3
BORON-BASED NON-OXIDE CERAMICS
1. Introduction:

In the category of III-V nitrides, boron nitride (BN) is an important compound which is currently considered as a wide band gap semiconductor with a band gap energy corresponding to the UV region. BN is isoelectronic to carbon and thus, in the same way that carbon exists as diamond and graphite, boron nitride can be synthesized in the tetrahedral structure (cubic BN, c-BN) and in a layered structure (hexagonal: h-BN). In h-BN, the in-plane B and N atoms are bounded by strong covalent bonds while the out-of-plane layers are held together by Van der Waals forces. In comparison to graphite, the layered BN hexagons are arranged vertically and each nitrogen atom is surrounded by two boron atoms of the adjacent layers. Hexagonal BN (h-BN but expressed in the following discussions as BN) is the most widely studied polymorph. It is the focus of the present chapter.

BN is a synthetic binary compound discovered in the early 19th century and developed as a commercial material at the latter half of the 20th century. This form shows similar physical properties analogous to graphite and like graphite the different bonding cause high anisotropy of the properties of the layered BN. It displays good lubricating properties according to its layered structure (weakly held layers can slide over each other). It displays a very high thermal conductivity (in the direction of hexagons), a high thermal stability, a high resistance to corrosion and oxidation as well as a strong UV emission. It is not wetted by most molten metals such as aluminium, iron and copper as well as hot silicon, glasses and salts and hence has a high resistance to chemical attack. It is nontoxic and it has good environmental compatibility. Unlike graphite, it offers high dielectric breakdown strength and high volume resistivity. As a consequence, the layered BN displays unique combination of properties that distinguish it from graphite and allow it to be potentially applied in a wide range of application.

Because transition metal nitrides in general exhibit extremely high melting points, high hardness and wear resistance, one can anticipate that a B·M·N (M = Ti, Zr, Hf) composite phase may adapt the combined advantages of the two phases and exhibit a better performance that either of the single phases made by metal nitride or boron nitride alone. Furthermore, because of the layered, graphite-like, BN structure, the BN matrix in the B·M·N ceramics is expected to act as solid lubricant in a similar way as the “diamond-like carbon”, DLC, does in the TiC/C coatings. However, the B·M·N ceramics may have some potential
disadvantage in dry machining due to the low oxidation resistance of BN, especially if it is not prepared in its purely hexagonal phase.

In this chapter we discuss the synthesis and characterization of boron nitride (BN) -based nanocomposites. These nanocomposites are made of MN nanocrystals (M = Ti, Zr, Hf) dispersed in a BN matrix. They are prepared by chemical modification of BN precursors like ammonia borane (AB) and polyborazylene (PB) with organometallic precursors. In particular, we will investigate the synthesis pathway to produce these nanocomposites. By the combination of infrared spectroscopy and solid state NMR, we will give a detailed view on the polymer structural characteristics in order to confirm the reproducibility of the synthesis pathway. We will investigate the influence of the amount of metals on the synthesis of polymers with a particular attention on the effect on their ceramic yield to form the B·M·N (M = Ti, Zr, Hf) ceramics and the high temperature thermal behavior of the latter. To better understand the role of the chemistry behind the preparation of these precursors, the part focused on nanocomposites is preceded by a small part which describes the preparation of BN from AB and PB. A last part of the present chapter is focused on the main disadvantage of precursor-derived BN and B·M·N ceramics we highlight in the present chapter: the relatively low degree of crystallinity of the BN phase which can induce high sensitivity to oxidation. We therefore propose a way to improve the BN crystallinity and prepare the hexagonal phase by chemical modification of BN precursors such as AB and PB. The materials are characterized at each step of their process. This chapter is purely fundamental. In particular, by reporting the synthesis, processing and pyrolysis behavior of a series of chemically modified BN precursors, we contribute to build new knowledge toward a more rational approach to the preparation of BN and B·M·N (M = Ti, Zr, Hf) ceramics.
2. Results and Discussion:
2.1. Preparation and characterization of BN from AB and PB:

Conventionally BN is prepared by reaction of B₂O₃ or H₃BO₃ with ammonia or urea¹,³ in a nitrogen atmosphere by the following reactions:

\[
\begin{align*}
B₂O₃ + 2 NH₃ & \rightarrow 2BN + 3H₂O \quad (T=900°C) \\
B(OH)₃ + NH₃ & \rightarrow BN + 3H₂O \quad (T=900°C) \\
B₂O₃ + CO(NH₂)₂ & \rightarrow 2BN + 2H₂O + CO₂ \quad (T>1000°C) \\
B₂O₃ + 3CaB₆ + 10N₂ & \rightarrow 20BN + 3CaO \quad (T>1500°C)
\end{align*}
\]

The resulting BN formed is amorphous and has up to 10% B₂O₃ impurity. To remove the impurity, it needs to be treated above 1500°C. These high temperatures result in crystallization of BN along with grain growth. To allow low temperature synthesis of BN and easier shaping as fibers and nanosheets, its preparation from preceramic polymers has been reported⁴–⁷. In this first part, we discuss the preparation of BN from two single-source precursors: Ammonia Borane (AB) and Polyborazylene (PB).

2.1.1 BN from ammonia borane:

Ammonia borane (AB, H₃N-BH₃) is a molecular solid generally used as hydrogen storage material due to its high hydrogen content (19.6 wt%) as discussed in chapter 1. Here we look at its use as molecular precursor for synthesis of BN (Figure 3.1⁴⁶).

![Resonance structure of ammonia borane (AB)](image)

AB is a promising precursor for BN due to the fact that it has all the elements required to form stoichiometric BN and the only extra element to be removed is hydrogen. Suib et al⁸ investigated the thermal conversion of AB to BN under nitrogen (N₂) atmosphere as described
in Chapter 1. They reported the formation of a semi-crystalline BN at 1500°C after 24 hours under an N\textsubscript{2} atmosphere. However, loss of nitrogen can occur at high temperature when using N\textsubscript{2} as atmosphere. Furthermore, the B-M-N ceramics prepared in the second part of this chapter are prepared using ammonia (NH\textsubscript{3}) as an atmosphere because of the objective to generate purely nitride compounds. Here, we therefore explore the conversion of AB to BN under NH\textsubscript{3} atmosphere to understand the pyrolysis conversion under NH\textsubscript{3} of metal-modified AB compounds that are synthesized to prepare the B-M-N ceramics in the second part of the present chapter.

2.1.1.1 Characterization of Ammonia borane:
Figure 3.1 showed the resonance structure of AB.

Figure 3.2 shows the FTIR spectrum of AB. The FTIR spectrum is similar to that given in the literature\textsuperscript{8}. Between 3200 and 3400 cm\textsuperscript{-1} we have the bands due to stretching of N-H bonds. The broad band centered around 2300 cm\textsuperscript{-1} corresponds to stretching of B-H bonds. Two sharp bands corresponding to deformation of N-H bonds appear at 1625 and 1375 cm\textsuperscript{-1}. Similarly, bands due to the deformation of B-H bonds come up at 1170 and 1060 cm\textsuperscript{-1}. Finally, there are two intense peaks corresponding to stretching and rocking of B-N bond at 780 cm\textsuperscript{-1} and 740 cm\textsuperscript{-1} respectively. However, we should mention that in the literature B-N stretching has been also attributed to peaks at 1440 cm\textsuperscript{-1}, 1380 cm\textsuperscript{-1} and 850 cm\textsuperscript{-1}\textsuperscript{9–12}.

![Figure 3.2 FTIR spectrum of AB](image-url)
2.1.1.2 Conversion of AB into BN:
The pyrolysis of AB under NH\textsubscript{3} flow at 1000°C for 2 hours leads to a poorly crystallized sample we labeled **ABBN-1000** as shown in Fig. 3.3. Unfortunately, it was not possible to measure the weight loss of AB under NH\textsubscript{3} by TGA because of a lot of gaseous by-products are escaped at 120 °C which deposited on the cold part of the suspensions significantly altering the measurement.

![Figure 3.3 XRD of BN produced by pyrolysis of AB at 1000°C and 1450°C](image)

Based on the scheme depicted in Fig. 3.4, it seems that borazine (that polymerizes into polyborazylene in the cold part probably) and polyaminoborane are formed during the pyrolysis of AB into BN.
2.1.1.3 Structural evolution at high temperature:

Structural evolution of BN derived from ammonia borane was investigated using XRD as shown in Figure 3.3. The samples were named as **ABBN-1000** (sample pyrolyzed at 1000°C under NH₃) and **ABBN-1450** (ammonia-treated sample annealed at 1450°C under N₂). The annealing was stopped at 1450°C because higher temperatures did not allow obtaining higher degree of crystallinity. The XRD pattern of the **ABBN-1450** sample has broad and weak peaks emerging at 25.3°, 42.4° and 76.7°. These coincide in position and intensity with the reflections from a P63/mmc hexagonal phase of BN. This has a graphitic structure where N atoms are stacked in-line between the B atoms of adjacent sheets and vice versa. The XRD pattern for **ABBN-1450** is similar to turbostratic BN (t-BN). The crystallite size calculated using Scherrer equation at the dominant (002) peak was found to be 2.73 nm which clearly indicates a very low degree of crystallization. It should be mentioned that two disordered BN phases, *i.e.*, turbostratic-BN (t-BN) and amorphous-BN (a-BN), are usually found in addition to the hexagonal phase. The turbostratic BN phase is characterized by a random stacking sequence of the (002) layers and a disorientation of these layers around the c-axis, whereas the amorphous BN phase represents a structure disordered at atomic level. XRD patterns of such phases are significantly distinct from that of h-BN.

The poor crystallinity of BN prepared from AB is clearly an advantage to prepare the nanocomposites with the structural organization we targeted (nanocrystalline phase dispersed in an amorphous matrix). However, to prepare pure BN, it appears that the use of
AB as a BN precursor does not allow generating a material with the intrinsic properties of the hexagonal phase of BN.

2.1.2 BN from polyborazylene:
Polyborazylene (PB) as a BN precursor has been also explored. Such a polymer is synthesized with controlled cross-linking degrees by thermolysis of borazine at low temperature inside an autoclave. A large number of studies have been focused on the thermolysis of borazine and the identification of polymerization mechanisms\textsuperscript{20-22}. In the fifties and sixties, several authors studied the self-condensation of borazine forming biphenylic and naphtalenic-type structures given the ideal polyborazylene structure proposed in Fig. 3.5\textsuperscript{16,17,22,23}.

In our group, we prepared PB by thermolysis of borazine at 60°C in an autoclave (\textit{See the experimental part in Chapter 2}) we labeled \textbf{PB60}.

2.1.2.1 Characterization of Polyborazylene:
Figure 3.6 shows the FTIR comparison of borazine and the \textbf{PB60} sample derived from it. Borazine showed absorption bands at 3475 cm\textsuperscript{-1}, 2525 cm\textsuperscript{-1}, 1464 cm\textsuperscript{-1}, 916 cm\textsuperscript{-1}, and 718 cm\textsuperscript{-1}. The absorption bands at 3475 cm\textsuperscript{-1} and 916 cm\textsuperscript{-1} are attributed to N-H stretching and B-N bending respectively. The absorption bands at 2525 cm\textsuperscript{-1} and 718 cm\textsuperscript{-1} are assigned to B-H stretching and bending, respectively. The absorption band at 1464 cm\textsuperscript{-1} is attributed to B-N stretching in cyclic B-N ring. In comparison \textbf{PB60}, the sharp B-N absorption band at 1464 cm\textsuperscript{-1} changes to a broad absorption band at 1435 cm\textsuperscript{-1} in the \textbf{PB60} sample, confirming that thermolysis of borazine proceeded through ring condensation forming naphthalene-like derivatives and hydrogen release.
The $^{11}$B solid-state NMR spectrum of PB60 (Fig. 3.7) recorded at 7 T shows a large signal in the region of tricoordinated boron atoms that was tentatively simulated with two sites at 27 ppm ($C_Q = 2.7$ MHz, $\eta = 0.1$) and 31 ppm ($C_Q = 2.9$ MHz, $\eta = 0.1$) assigned to $BN_3$ and $BN_2H$ environments respectively. This confirms the naphtalenic-type structure of PB60.

\[ Figure 3. 7 \ ^{11}\text{B SS NMR spectrum for PB60} \]

\(BN_2H\) \(BN_3\) Exp Sim

\(ppm\)

2.1.2.2 Conversion of polyborazylene to boron nitride:
The polymer to ceramic conversion of PB60 to BN was carried out under ammonia up to 1000°C. Figure 3.8 shows the TGA curve for conversion of PB60 to BN. A ceramic yield of 90.9% was obtained with PB60 which is very high compared to that obtained from AB.
Whereas AB is a molecule, PB60 is a polymer and therefore, this high ceramic yield is attributed to the highly cross-linked structure of PB60.

The polymer to ceramic conversion can be divided into three steps. The three-step weight loss starts with an initial weight loss occurring from 70 to 290 °C (4.5 wt%), a second one from 290 to 750 °C (3.5 wt%) and a third one from 750 to 1000 °C (1.1 wt%) which is the maximum temperature of the TG apparatus. The low weight loss of PB60 is related to its highly cross-linked structure as mentioned previously but also to its ability to further cross-link by dehydrocoupling upon heating according to the presence of reactive B-H and N-H units. Both avoided depolymerization of the PB60 during the polymer-to-ceramic conversion. However, it is clear that the polymer-to-ceramic conversion is not fully achieved at 1000 °C most probably due to the fact that the polyborazylene-derived material produced at 1000 °C contains residual hydrogen. Hydrogen is completely removed during the further heat-treatment to 1200 °C\textsuperscript{24}.

Figure 3.8 a) TGA curve and b) DTG curve of the PB60 sample

2.1.2.3 High temperature structural evolution of PB60 derived BN:
The samples are named PB60BN-X (where X is the annealing temperature). The PB60BN-1000 is poorly crystallized with a XRD pattern (Fig. 3.9) similar to that one obtained from
AB at the same temperature as shown on Fig.3.10 although the crystallite size is slightly higher for the PB60BN-1000 sample.

After annealing to 1450 °C leading to the PB60BN-1450 sample, the presence of the broad (002) peak \(2\theta = 25.35^\circ\); FWHM = 3.5°) and diffuse (10)/(100) and (004) peaks which are shifted from the Bragg angles of h-BN in the XRD pattern (Fig. 3.11) is representative of a disordered structure. In particular, the asymmetric shape of the (002) peak and the absence of the (102) and (112) peaks suggests in a coherent way the presence of t-BN.
Again, a comparison of the XRD patterns of the ABBN-1450 and PB60BN-1450 samples shows that the FWHM of the (002) peaks is sharper in the PB60BN-1450 sample which indicates a slightly higher crystallite size for the PB60BN-1450 sample (Fig. 3.12). However, both samples still display the turbostratic phase of BN.

In this section, we have seen that the formation of the hexagonal phase of BN is not possible using AB and PB as BN precursors. The following section will investigate the effect of the addition of a second metal nitride (MN, M = Ti, Zr, Hf) phase to AB and PB-derived BN. We will investigate the addition of Ti, Zr, Hf to AB and PB at molecular scale and their effect on the polymer synthesis, polymer thermal behaviour and ceramic microstructural evolution at high temperature.
2.2. Preparation and characterization of B-M-N ceramics (M = Ti, Zr, Hf)

Here, we investigated the synthesis of a series of metal-modified compounds from AB and PB precursors which have been described previously. Because AB is commercially available, a large part of this section is focused on the use of AB as a BN precursor. In our experiments, we focused on the reaction between AB and PB with three liquid molecular entities each containing one transition metal respectively as precursors of the MN nanophase:

1) TiN precursor: tetrakis(dimethylamino)titanium (TDMAT, Ti[N(CH₃)₂]₄),
2) ZrN precursor: tetrakis(diethylamino)zirconium (TDEAZr, Zr[N(CH₂CH₃)₂]₄),
3) HfN precursor: tetrakis(methylethylamino)hafnium (TMEAHf, Hf[N(CH₂CH₃)(CH₃)]₄).

The metal-modified BN precursors are labeled ABMX (synthesized from AB) and PB60MX (synthesized from PB₆₀) with M the metal (Ti, Zr or Hf) and X the B:M ratio.

It is particularly shown by complementary techniques involving solid-state NMR and FTIR spectroscopies that we can modulate/tailor the metal-modified BN precursors characteristics (composition and degree of crosslinking) via selection of the BN precursors and control of the B:Ti ratio at molecular scale during the polymer synthesis. This has an effect on the pyrolysis behavior and the nano-/microstructural features of the B·M·N ceramics.

2.2.1 Preparation and characterization of B-Ti-N ceramics

In the present part, we investigate the modification of AB and PB₆₀ with TDMAT at a same intermediate B:Ti ratio (= 3) to identify the mechanisms that govern the polymer synthesis. Then, using a same BN precursor, we investigated the effect of the B:Ti ratio on the polymer thermal behavior and on the high temperature behavior of the resulting B·Ti·N ceramics.

2.2.1.1 Synthesis of titanium-modified BN precursors

Firstly, we compared the effect of the BN precursors on the structure of the derived metal-modified BN precursors keeping a B:Ti ratio constant by FTIR and solid-state NMR spectroscopies. It should be mentioned that amount of B in one mole of AB is 1 which is different from that present in one mole of PB₆₀ (3).

Figure 3.13 shows the FTIR spectra for AB₃Ti and PB₆₀Ti₃ compared with their native precursors AB and PB₆₀.
As expected, FTIR spectroscopy suggests an introduction of \( \cdot \text{N(CH}_3\text{)}_2 \) groups present in TDMAT in the \textbf{ABTi3} and \textbf{PB60Ti3} samples by comparing their infrared spectra with those of \textbf{AB} and \textbf{PB60}. It is found that the intensity of the C-H stretching bands significantly increases while the intensity of the bands assigned to N-H stretching and B-H stretching mode decreases. This clearly suggests that there are reactions involving N-H and B-H bonds in BN precursors and \( \cdot \text{N(CH}_3\text{)}_2 \) groups in TDMAT according to equations (1) and (2). Such equations represent an amine displacement reaction from TDMAT to \textbf{AB} or \textbf{PB60} samples with evolution of dimethylamine or methane, respectively.

\[
B_2N - H + (\text{CH}_3)_2N - Ti \equiv \rightarrow B_2N - Ti \equiv + (\text{CH}_3)_2NH \quad (1)
\]

\[
N_2B - H + (\text{CH}_3)_2N - Ti \equiv \rightarrow N_2B - N(\text{CH}_3) - Ti \equiv + \text{CH}_4 \quad (2)
\]

In addition, the broadening of the bands attributed to B-N stretching in the \textbf{ABTi3} sample is indicative of the polymerization of AB into polyamminoborane (PAB). Therefore, in addition to reactions depicted in equations (1) and (2) that occur during synthesis of the \textbf{ABTi3} and \textbf{PB60Ti3} samples, other reactions, independently of the addition of TDMAT such dehydrocoupling between B-H and N-H units according to equation (3) probably occur to build the molecular weight and degree of cross-linking of BN precursors. This reaction leads to B-N bond formation.

\[
B_2N - H + H - BN_2 \rightarrow B_2N - BN_2 + H_2 \quad (3)
\]
In order to obtain a complete view of the structure of the compounds, solid-state NMR spectroscopy was carried out on the ABTi3 and PB60Ti3 samples to probe the local B and C environments. The cross-polarization (CP) technique was used for 13C NMR experiments to obtain spectra with reasonable acquisition times and signal-to-noise ratios. Figure 3.14 shows the 11B MAS NMR spectra of the ABTi3 and PB60Ti3 samples. Signals are broaden partially due to the heterogeneity in the local chemical environment of the boron nuclei and line shapes are moreover distorted by quadrupolar interactions since 11B is at spin 3/2. It appears therefore useful to record spectra at different magnetic fields since the intensity of the quadrupolar interaction is inversely proportional to the magnetic field. Therefore, spectra have been recorded at 7 T (for PB60Ti3) and 15 T (for ABTi3).

![11B MAS NMR spectrum of a) ABTi3 and b) PB60Ti3](image)

11B MAS NMR spectra of both polymers exhibit a broad signal centered in the region of tri-coordinated boron atoms (B[3]) that can be tentatively simulated with two sites as done on the ABTi3 sample (Figure 3.14). The two signals which can be assigned to BN3 and BN2H environments as already identified for PB60 at δiso = 31 ppm (BN3) and 27 ppm (BN2H). The signal is shifted with the ABTi3 sample because it is recorded at a different magnetic field:...
the small signal emerging at 18 ppm can be attributed to $\text{BN}_2\text{H}$ units while the signal at 31 ppm attributed to $\text{BN}_3$ formed by dehydrocoupling process of AB $^{25-27}$.

Figure 3.15 shows the $^{13}$C CP MAS spectra for the two samples being discussed.

![Figure 3.15 $^{13}$C CP MAS NMR spectra of a) ABTi3 and b) PB60Ti3](image)

The spectra exhibit a main signal at 39 ppm which is broad suggesting the presence of overlapping components. The signal can be assigned to Ti·N·CH$_3$ groups regarding their position in good agreement with the position of the signal found in the $^{13}$C NMR of Ti[N(CH$_3$)$_3$]$_4$ (Fig. 3.16).
However, the presence of a broad signal suggests, especially in $\text{ABT}_3$, more than a single environment. Based on equations (1) and (2) we mentioned previously, N(CH$_3$)$_x$ groups appear as ending group ($x = 2$, eq. (1)) or as a bridge ($x = 1$, eq. (2)) which can involve the presence of two signals. Interesting, the shape of this signal evolves by changing the B:Ti ratio in PB$_{60}$Ti$_X$ ($X = \text{B:Ti} = 1\rightarrow 5$) (Fig. 3.17). In particular a high-field signal as a broadened shoulder emerges around 50 ppm and its intensity increased from PB$_{60}$Ti$_5$ to PB$_{60}$Ti$_1$ (Fig. 3.17a). As a consequence, the main signal is clearly attributed to =Ti-N-CH$_3$ groups regarding their position in good agreement with the position of the signal found in the $^{13}$C NMR of Ti[N(CH$_3$)$_2$)$_4$ as mentioned previously whereas the signal at around 50 ppm is attributed to =B-N(CH$_3$)-Ti=.

The $^{15}$N CP MAS NMR spectra (Fig. 3.17b) show a composite signal made of overlapping peaks ranging from -250 to -330 ppm which is inherently difficult to interpret. In addition, we can see that the samples exhibit a more resolved signal at -347 ppm. The intensity of this signal decreases in line with the increase of the B:Ti ratio; thereby with the decreased amount of used Ti[N(CH$_3$)$_2$]$_4$ during the synthesis. Therefore, we suggests that it corresponds either to Ti-$\text{N}$CH$_3$)$_2$ or B$_2$N$^-$Ti[N(CH$_3$)$_2$]$_3$ environments. The signal with the higher chemical shift value (-268 ppm) can be assigned to a $\text{MB}_3$ environment because a $^{15}$N signal with a similar chemical shift ($\delta_{iso}$ ($^{15}$N) = -268 ppm) has been already observed in PB$_{28}$. Another signal at -285 ppm can be assigned to B$_2$NH units of borazine rings based on previous observations in PB$_{28}$. A broad component centered at -307 ppm can be simulated with two signals at -302 and -313 ppm which are most probably attributed to Ti-based nitrogen environment according to
the change in their intensity with the evolution of the B:Ti ratio. Regarding the reactions we have suggested based on IR spectroscopy (Eq. (1) and (2)), they can be assigned to either \( \text{B}_2\text{N}^=\text{Ti}= \) or \( \text{N}_2\text{B}^=\text{N}(\text{CH}_3)^=\text{Ti}= \) sites. The signal at \( \approx 313 \text{ ppm} \) could be ascribed to a \( \text{B}^=\text{N}(\text{CH}_3)^=\text{Ti}^= \) bridge based on an assignment performed in a previous study in which \( \text{N}(\text{CH}_3)^= \) bridges connecting boron atoms have been observed at \( \approx 317 \text{ ppm} \) in a borylborazine molecule\(^{29}\). The signal at \( \approx 302 \text{ ppm} \) has been therefore attributed to \( \text{B}_2\text{N}^=\text{Ti}= \) sites. As a consequence of the reaction process, it turns out that Ti-modified BN precursors are composed of at least five structural nitrogen sites that are consistent with FTIR, \(^{11}\text{B} \) and \(^{13}\text{C} \) NMR data.
Figure 3.17 $^{11}$B (a), $^{15}$N (b) and $^{13}$C CP (c) MAS NMR spectra of PB60TiX (X = B:Ti = 1→5)
It appears therefore that the change of the B:Ti ratio has no effect on the nature of the mechanisms that govern the polymer synthesis. As an illustration, the boron, environment in PB60TiX (X = B:Ti = 1→5) does not evolve in the $^{11}$B MAS, spectra (Fig. 3.17c). However, it changes the extent of the reactions and probably modifies the degree of crosslinking of the polymer as we observed by investigating the polymer-to-ceramic conversion in the following part.

2.2.1.2 Polymer-to-ceramic conversion:
The direct pyrolysis of titanium-modified BN precursors leads to colored powders depending on both the B:Ti ratio and temperature. Such materials propose a range of different colors which makes these compounds ideal candidates for decorative applications. Such variations of color can be explained by the growth of the titanium nitride nanocrystals and the change in the crystalline plane orientation with increasing annealing temperature. The chemistry involved during the polymer-to-ceramic conversion includes a complex sequence of structural and chemical changes based on molecular rearrangements and the release of gaseous by-products which are inherently related to the molecular structure and chemistry of preceramic polymers. Therefore, it is particularly essential to control as much as possible thermally induced molecular rearrangements by carefully adjusting the molecular structure of preceramic polymers.

Here, we have investigated the pyrolytic decomposition of titanium-modified BN precursors under NH$_3$ by thermogravimetric analyses (TGA). This part is shared into two studies. Firstly, we followed the thermal behavior of the ABTi3 sample under NH$_3$ from room temperature (RT) to 1000 °C. We compared this sample with the analogs with a B:Ti ratio of 1 (ABTi1) and 5 (ABTi5). As pyrolysis atmosphere, NH$_3$ is well known to remove carbon-based groups, N(CH$_3$)$_x$ ($1 \leq x \leq 2$) groups, linked to the basal polymer network and also to involve rearrangements of the structure. Furthermore, NH$_3$ is used to adjust the nitrogen content in our sample by nitridation and generate PDCs free of carbon and even enriched with nitrogen.
Figure 3.18 shows the TGA curves of ABTiX samples with $X = 1 \rightarrow 5$ during decomposition up to 1000 $\degree$C under NH$_3$.

The ceramic yield of the ABTiX samples with $X = 1 \rightarrow 5$ increases with increasing the B:Ti ratio in the polymer from 53.5 % for ABTi1 to 61 % for ABTi5. The ceramic yield of the ABTi3 sample is 53.5 %. This tends to demonstrate that the crosslinking degree of the ABTiX samples with $X = 1 \rightarrow 5$ increased from 1 to 5. To further confirm this tendency, a similar study was performed for PB60Ti1$\rightarrow$5 under NH$_3$. Figure 3.19 shows the TGA for PB60TiX samples with $X = 1 \rightarrow 5$ under NH$_3$. 
Figure 3.17 TGA for PB60TiX samples with X = 1→5 under NH₃ up to 1000°C

It is also obvious that the weight loss of the PB60TiX samples with X = 1→5 depends on the B:Ti ratio fixed during synthesis: the weight loss of PB60TiX samples with X = 1→5 increases with the decrease of the B:Ti ratio, from 16.7% (PB60Ti5) to 34.4% (PB60Ti1). The highest ceramic yield of PB60TiX samples with X = 1→5 than ABTiX samples with X = 1→5 is clearly attributed to the fact that PB60TiX samples with X = 1→5 are prepared from a relatively highly cross-linked polymer, i.e., PB60, whereas ABTiX samples with X = 1→5 are prepared from a “monomer” i.e., AB, although AB most probably polymerizes into a polyaminoborane during the synthesis.

The TGA behavior can be understood as follows: with the decrease of the B:Ti ratio, the quantity Ti increases; thereby the amount of -N(CH₃)x (1 ≤ x ≤ 2) groups introduced in the structure of BN precursors increases. Such groups are evolved during the polymer-to-ceramic conversion under NH₃ to form dimethylamine ((CH₃)₂NH). This explains why the strongest presence of these groups involves the highest weight loss.

As a consequence, the behavior of titanium-modified BN precursors is relatively simple to understand through equations shown below. Initially, -N(CH₃)x (1 ≤ x ≤ 2) groups are displaced by amido group (-NH₂) by reaction with NH₃, whereby -Ti-NH₂ units form and (CH₃)₂NH is released involving mass loss: the higher quantity of -N(CH₃)₂ group is, the higher the weight loss will be. With the increase of the pyrolysis temperature, as-formed moieties
subsequently condense with elimination of NH$_3$ and/or ((CH$_3$)$_2$NH leading to secondary units, then N(B)$_{3-x}$(Ti)$_x$ units (0 < x ≤ 3).

$$\text{TiN(CH}_3)_x + \text{NH}_2\cdot\text{H} \rightarrow \text{TiNH}_2 + \text{HN(CH}_3)_x \quad (4)$$

$$\text{TiNH}_2 + \text{TiNH}_2 \rightarrow \text{Ti\cdotNH\cdotTi} + \text{NH}_3 \quad (5)$$

$$\text{TiNH\cdotH} + \text{TiN(CH}_3)_x \rightarrow \text{Ti\cdotNH\cdotTi} + \text{HN(CH}_3)_x \quad (6)$$

$$\text{Ti\cdotNH\cdotTi} + \text{TiNH}_2 \rightarrow N(Ti)_3 + \text{NH}_3 \quad (7)$$

$$\text{TiNH}_2 + \text{BNHB} \rightarrow \text{B\cdotNH\cdotTi} + \text{BNH}_2 \quad (8)$$

$$\text{B\cdotNH\cdotTi} + \text{TiNH}_2 \rightarrow \text{BNTi}_2 + \text{NH}_3 \quad (9)$$

Beside these reactions, there are reactions involving only the groups present in the BN precursors such as BH and NH units that can condense to form BN$_3$ groups. A poorly crystallized ceramic network is thus produced at 1000 °C according to the extremely diffuse peaks in the corresponding XRD pattern which is reported in the following section.

2.2.1.3 Microstructural evolution and high temperature crystallization behavior of B-Ti-N ceramics

Ammonia-treated B-Ti-N ceramics derived from ABTiX samples with X = 1 → 5 have been annealed under N$_2$ flow at high temperature to investigate their microstructural evolution and their crystallization behavior. After pyrolysis at 1000°C under NH$_3$, ABTiX-1000 samples with X = 1 → 5 are poorly crystallized according to the extremely diffuse peaks identified in the corresponding XRD pattern (Fig. 3.20a, b and c). These peaks correspond to the face-centered cubic (fcc) TiN phase (JCPDS file 00-038-1420) which appear at $2\theta = 36.7^\circ$ (111), 42.72° (200), 62.11° (220), 74.42° (311) and 77.97° (222) in the XRD pattern of the ABTi1-1000 sample. Phase identification is achieved by locating the characteristic diffraction peaks of the respective phases in the XRD spectra. With the increase of the B:Ti ratio, the peak become more and more diffuse and those corresponding to (220), (311) and even (111) (in the ABTi5-1000 sample) planes gradually disappear. This clearly indicates a decrease of the crystallinity and the degree of crystallization of the samples with the increased B:Ti ratio. Through annealing at 1450°C leading to the ABTi1-1450, ABTi3-1450 and ABTi5-1450 samples, crystallization of the nanophase occurred. As an illustration, the XRD pattern of
the **ABTi3-1450** sample (Fig. 3.20b) shows sharp intense peaks at the position described previously, *i.e.*, \( 2\theta = 36.7^\circ, 42.6^\circ, 61.8^\circ, 74.12^\circ \) and \( 77.98^\circ \). The crystallite size, calculated at the dominant (200) peak, increased from 3.8 nm (**ABTi3-1000**) to 27 nm (**ABTi3-1450**) (Table 3.1). The small peak belonging at \( 26.5^\circ \) is attributed to the (002) plane of the BN matrix. Interesting this peak is not present in the **ABTi1-1450** sample (Fig. 3.20a) whereas it is relatively intense in the **ABTi5-1450** sample (Fig. 3.20c). A further annealing at 1600 °C confirms the observations made for the XRD pattern of the **ABTi1-1450**, **ABTi3-1450** and **ABTi5-1450** samples: the crystallite size continues to increase as shown in the Table 3.1, a slight shift towards right of the TiN peaks occurs and the (002) peak corresponding to BN becomes more intense in samples. Interestingly, the TiN peaks at \( 61.8^\circ, 74.12^\circ \) and \( 77.98^\circ \) identified in all samples reveal the presence of a shoulder peak which could be attributed to TiB\(_x\) phase. Further confirmation of this was done with the **ABTi3-1600** sample which could not be spun during solid-state NMR experiments most probably due to the presence of a metallic phase (TiB\(_x\)).

![Figure 3.20 XRD patterns](image)

**Figure 3.20** XRD patterns of a) **ABTi1**, b) **ABTi3**, c) **ABTi5**-derived ceramics with temperature and d) comparison of XRD patterns of **ABTiX-1600** with \( X = 1\rightarrow5 \) samples.
In Fig. 3.20d, it can be clearly seen that the intensity of peak belonging to BN (26.5°) decreases with the decreased B:Ti ratio from ABTi5:1600 to ABTi1:1600. Furthermore, in the insets of the figures 3.20d, it can be seen that the separation of shoulder peaks at 61.8°, 74.12° and 77.98° from the TiN peaks increases with the decreased B:Ti ratio from 5 to 1, i.e., increase of the TiN content in the system. It therefore seems that the increase of the Ti content in the precursor increases the TiN content in the final material which is expected but it tends also to stabilize the amorphous structure of BN and shift its crystallization to higher temperatures.

Table 3.1 Crystallite size calculated in the ABTiX-Y samples with X = 1→5 and Y = 1000, 1450 and 1600

<table>
<thead>
<tr>
<th>System (B:Ti) ratio in nanocomposite (ABTiX)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1000°C</td>
</tr>
<tr>
<td>ABTi5</td>
<td>3.71</td>
</tr>
<tr>
<td>ABTi3</td>
<td>3.8</td>
</tr>
<tr>
<td>ABTi1</td>
<td>10.39</td>
</tr>
</tbody>
</table>

A same behavior was observed using PB60 as a BN precursor. Figure 3.21 investigates the Raman spectra of ABTi1→5 samples pyrolyzed at 1000 °C under NH3 then annealed at 1450 and 1600 °C in flowing N2. Raman spectroscopy confirms the observations made by X-ray diffraction for the samples: the signal appearing around 1360 cm⁻¹ corresponds to the typical vibration frequency observed in h-BN materials. It is due to the E₂g symmetric vibration mode in h-BN (B-N in plane atomic displacements). This signal is the most intense and the sharpest in the Raman spectrum of the ABTi5:1600 sample which means that the BN matrix displays the highest degree of crystallization among all samples. Beside this, we confirmed the growth of the TiN nanophase in the samples. As illustrated in Fig. 3.21, the Raman spectra of the samples are characteristic of the face-centered cubic (fcc) TiN phase. The low frequency peaks below 400 cm⁻¹ can be attributed to acoustical phonons, whereas the high frequency mode around 540 cm⁻¹ is due to optical phonons. Both Raman peaks at 209 and
300 cm\(^{-1}\) are representative of the transverse acoustic (TA) and longitudinal acoustic (LA) modes of TiN, respectively\(^{32}\). The Raman peak at 410 cm\(^{-1}\) can be attributed to the 2A mode and the Raman peak centered at 539 cm\(^{-1}\) completed by the shoulder at 600 cm\(^{-1}\) correspond to the transverse optic/longitudinal optic (TO)/LO modes\(^{32}\). The phonon bands in the acoustic and optic range are due to vibrations of the heavy Ti\(^{4+}\) ions and the lighter N\(^{3-}\) ions, respectively. In the 817-1075 cm\(^{-1}\) wavenumber range, we can assign the Raman peaks to the A+O and 2O modes.

This study showed the strong effect on the B:Ti ratio fixed at the polymer synthesis level on the extent of the reactions occurring during the polymer synthesis. This changes the degree of crosslinking of polymers which influences the weight loss measured during the subsequent pyrolysis under NH\(_3\). Ammonia-treated samples are X-ray amorphous and evolve toward a nanocomposite structure with the annealing under N\(_2\) up to 1600°C. The nanocomposite
structural organization changes with the B:Ti ratio fixed at molecular scale. Below, we investigate the effect of the nature of the metal introduced at molecular scale in the metal-modified BN precursors.
2.2.2 Preparation and characterization of B-Zr-N and B-Hf-N ceramics

2.2.2.1 Polymer synthesis and pyrolysis

The mechanisms that govern the polymer synthesis and the polymer to ceramic conversion for Zr- and Hf-modified BN precursors are similar to those identified for Ti-modified BN precursors. The unknown is the extent of the reactions which take place and the only difference is the nature of the dialkylamino groups linked to Zr (diethylamino) and Hf (methyl/ethylamino) which are different of those linked to Ti (dimethylamino): diethylamine/ethane (for Zr, Eqs. (10 and (11)), methylvamine/ethylamine/methane/ethane (for Hf) are evolved as gaseous by-products during the polymers synthesis. We have also such reactions during the polymer-to-ceramic conversion.

\[
B_2N - H + (CH_3CH_2)_2N - Zr \equiv \rightarrow B_2N - Zr \equiv + (CH_3CH_2)_2NH \quad (10)
\]

\[
N_2B - H + (CH_3CH_2)_2N - Ti \equiv \rightarrow N_2B - N(CH_3) - Ti \equiv + C_2H_6 \quad (11)
\]

The thermal conversion of the polymers into ceramic materials is accompanied by the formation of gaseous byproducts and therefore weight loss during the polymer-to-ceramic conversion as shown previously. Because of the difference in the nature of the gaseous by-products, the weight change upon pyrolysis must be different. The ceramic yields for Zr and Hf-modified BN precursors were determined using TGA and the results compared with the TGA of the Ti-modified BN precursors. The data in Figure 3.22 suggest that the substitution of Ti in polymers with Zr does not change the pyrolysis behavior: the ceramic yield of the \( \text{ABZr}3 \) under \( \text{NH}_3 \) up to 1000°C is found to be 56 %, a value close to the ceramic yield calculated for the \( \text{ABTi}3 \) sample (56.5 %) although the lower weight substituents \( \text{N(CH}_3\text{)}_2 \) in \( \text{ABTi}3 \) that split off as gaseous by-products are expected to cause a lower weight loss than bulk groups \( \text{N(CH}_2\text{CH}_3\text{)}_2 \) in \( \text{ABZr}3 \). The ceramic yield calculated for the \( \text{ABHf}3 \) sample is unexpectedly high (82 %) as shown in Figure 3.22.
A number of factors, such as polymer structure, molecular weight, the degree of cross-linking, \textit{i.e.} the structure of the polymer backbone and the nature of the functional groups that are attached to boron and/or nitrogen strongly influence the ceramic yields. An additional important issue in this regard is the decomposition chemistry of the precursors, including the ability to cross-link further during the heat treatment. Taking these factors into account and considering that the reaction occurring during the polymer synthesis lead to the same polymer degree of crosslinking, the ceramic yields should increase in the expected sequence ABZr₃, ABHf₃, ABTi₃. ABHf₃ does not fit in this sequence. This is most probably a consequence of the extent of the reactions which occur between TDMAHf and BN precursors. Reactions between NH and BH groups in BN precursors and N(CH₃)(CH₂CH₃) probably occur with more efficiency to generate a more highly cross-linked polymer. Such a behavior is documented in case of Si-based polymers modified with TDMAHf as reported by Ionescu et al\textsuperscript{33}. The evaluation of structural intermediates that arise during the various stages of thermolysis will be performed by using multinuclear solid-state NMR and FT-IR spectroscopy and will be available soon. This will help us to confirm such observations.
2.2.2.2 Microstructural evolution and high temperature crystallization behavior of B-Zr-N and B-Hf-N ceramics

Ammonia-treated B-Zr-N and B-Hf-N ceramics derived from the ABZr3 and ABHf3 samples have been annealed under N2 flow at high temperature to investigate their microstructural evolution and their crystallization behavior. After pyrolysis at 1000°C under NH3, samples labeled ABZr3-1000 and ABHf3-1000 are poorly crystallized according to the extremely diffuse peaks identified in the corresponding XRD pattern (Fig. 3.23). Upon further annealing to 1450°C, the XRD pattern of the ABZr3-1450 sample (Fig. 3.23a) has number of sharp peaks corresponding to monoclinic ZrO2 appear (marked in green) along with (002) peak attributed to h-BN. The ZrO2 peaks, usually observed in such system because of the high sensitivity of the polymers, are due to the extremely high sensitivity of the polymer toward oxidation. Final annealing at 1600°C (ABZr3-1600) leads to further crystallization of ZrO2 but along with that sharp and intense peaks corresponding to ZrN (JCPDS file: 04-004-2860) at 33.3°, 38.6°, 55.94°, 66.8°, 70.1° and 83.3° (Fig. 3.23a). The crystallite size calculated using Scherrer equation at the dominant (111) peak is found to be 32.82 nm.

Figure 3.23b shows the phase evolution for of the ABHf3-1000 sample at 1450 and 1600°C. Further annealing at 1450°C leads to the ABHf3-1450 Sample. The XRD pattern has a number of sharp peaks at 30.76°, 33.82°, 35.64°, 39.34°, 51.22°, 56.89°, 61.1°, 67.85°, 71.4° and 84.6°. These belong to two different cubic structures of HfN, rock salt (JCPDS file: 00-033-0592) and zinc blende (JCPDS file: 01-079-5779). The two HfN phases differ from each other in terms of their space groups. The crystallite size calculated at the dominant peaks (111) peak in both cases was found to be 10.71 nm for (Zinc blende)HfN and 8.1 nm for (Rock salt)HfN. At 1600°C, the crystallite size of the ABHf3-1600 sample increases to 16.13 nm (zinc blende structure) and to 11.95 nm (rock salt structure). There are no peaks corresponding to BN suggesting that the matrix is still amorphous at this temperature which demonstrated the very high stability of the B-Hf-N ceramics, i.e., HfN/BN nanocomposites, as we observed with the B-Ti-N ceramics with a B:Ti ratio of 1. This clearly shows that, at a same B:M ratio, the B-Hf-N ceramics are more stable at high temperature than B-Ti-N ceramics. We attributed this phenomenon to the high efficient reactions which occur between AB and TDMAHf allowing introducing more Hf in the polymer structure than the reaction between AB and TDMAT at a same B:M ratio. This increases the HfN content in the final materials which stabilize the amorphous phase of BN. Elemental analyses of the polymers and final
ceramics and HRTEM investigations should help us to confirm our observations. This will be performed soon.

Figure 3.23 Evolution of the XRD patterns of the a) ABZr3 and b) ABHf3 samples with temperature from 1000°C to 1600°C
Raman spectroscopy allowed us to confirm the presence of BN. Figure 3.24 shows the Raman spectra of ceramics derived from $\text{ABZr}_3$ and $\text{ABHf}_3$. The presence of the $E_{2g}$ peak of the B-N bond vibration in the $\text{ABZr/Hf}_3$-1200 and $\text{ABZr/Hf}_3$-1600 is visible in both cases at around 1360 cm$^{-1}$ which confirms the presence of BN in the systems even though it may not be crystallized.

Figure 3.24 Raman spectra with temperature for a) $\text{ABZr}_3$ and b) $\text{ABHf}_3$

In this section, we showed that the presence of metal nitride nanocrystals in a BN matrix can suppress the crystallization of the latter if the B:M ratio is sufficiently low. However, the nc-MN/a-BN (nc for nanocrystalline and a for amorphous) nanocomposites especially with M = Ti and Hf may have some potential disadvantage in some application due to the low BN crystallinity which can involve a low oxidation resistance. To overcome this problem, we focused the last part of the present chapter on the investigation of the improvement of the BN crystallinity using AB and PB as BN precursors and then, we changed the nature of the matrix toward $\text{Si}_3\text{N}_4$ in chapter 4 which is well know as a ceramic highly resistant to oxidation.

2.3. Preparation and characterization of highly crystallized BN

In the previous section we discussed synthesis of boron nitride from ammonia borane (AB) and polyborazylene (PB60). Under standard conditions, both the precursors give a semi-crystalline and turbostratic BN at 1450 °C and it is almost impossible to generate the hexagonal phase even at higher temperatures. The use of such high temperatures defeats
one of the major reasons of using the PDC route, *i.e.*, processability at low temperatures. However, we can take advantage of the PDC route by modifying the BN precursors with further elements that improve the BN crystallinity in contrast to Ti and Hf that hinder BN crystallisation.

The crystallization of h-BN at low temperature has been reported in metal fluxes, such as in sodium at 700–800 °C\(^{34,35}\) and in molten hydrogen saturated nickel below 1000 °C\(^{36}\). The synthesis and growth of h-BN crystallites at low temperature have been investigated by carrying out in a lithium bromide (LiBr) melt in 600–700 °C\(^{37}\). The molten salt was found to have a strong effect on the crystal growth.

Li\(_3\)N is traditionally known to be an additive which lowers the conversion temperature of h-BN to cubic (c-)BN\(^{38–42}\). Yuan *et al.* explored its use as an additive to polymer in order to lower the crystallization temperature of BN obtained from precursor route. Li\(_3\)N was mixed as a powder with the precursor thus leading to a physical mixing, *i.e.*, precursor blend, not a *single-source* precursor. This inherently led to a poor reactivity between both compounds and certain inefficiency.

Use of Li based compounds which can react with the polymer and modify the polymer at a molecular level to lead to a homogeneous distribution of the crystallization promoter in the system is the focus on the present chapter part. For this purpose, we have explored the reaction between BN precursors and lithium amide (LiNH\(_2\)) in solution and by reactive ball-milling. We showed that this reaction can occur also with lithium hydride (LiH).

### 2.3.1 Synthesis in solution

The synthesis in solution consists of adding LiNH\(_2\) to a solution of AB in THF drop by drop with a molar B:Li ratio of 1:1. A white powder labelled **ABLi1** was obtained after drying. Figure 3.25 compares the FTIR spectra of AB and the **ABLi1** sample.
Modification of AB with LiNH₂ leads to a lot changes in its structure. The two bands at 780 cm⁻¹ and 740 cm⁻¹ representing the stretching and rocking of BN bond drastically reduces in intensity and appears as one broad band. As mentioned before, B-N stretching/elongation bonds have been reported at different wavenumbers also. The bands relating to deformation of B·H bonds at 1125 and 1070 cm⁻¹ completely reduce in intensity and are nearly lost behind the broad band for B-N bond stretching. The broad band of B·H bond stretching is slightly shifted to the right and the N·H bond stretching bands become into one broad band. There is appearance of two new bands in the range of 2800 to 300 cm⁻¹. These are attributed to stretching of ammonium bonds of $NH_2^+$ and $NH_3^+$ which are formed after reaction with LiNH₂. The presence of broad bands suggests the formation of a polymer as it occurs when AB is transformed into a PAB. By the way, a branched or cyclized PAB displays a very similar IR spectrum without significant shifts in stretching frequencies from the purely linear case.

To have a better idea of the reaction between AB and LiNH₂ in solution we performed $^{11}$B MAS solid-state NMR of the ABLi1 sample (Figure 3.26).
Similar to the FTIR spectrum, the $^{11}$B MAS NMR spectrum of the $\text{ABLi}_1$ sample significantly changes in comparison to the spectrum of $\text{AB}$ (Fig. 3.27). In particular, the signals observed in the $^{11}$B spectrum of $\text{AB}$ between -20 and -30 ppm is significantly reduced which means that BH$_3$ units are mostly absent. In contrast, it shows the presence of three different B environments namely BN$_2$H, BN$_3$ and BNH$_2$ which tends to demonstrate that the sample is in an oligomeric or polymeric state.

To complement the data, we investigated $^{15}$N CP MAS NMR (Figure 3.28).
The $^{15}\text{N}$ CP MAS NMR spectrum of the ABLi1 sample displays three major peaks centered at -310 ppm, -350 ppm and -380 ppm. The peak at -310 ppm is very broad and most probably represents a composite signal made of overlapping signals. In this chemical shift, non-protonated $\text{N}_3$ sites (-294 ppm) and $\text{N}_2\text{H}$ groups (-311, -326 ppm) can be identified. The signal at -350 ppm is usually attributed to $-\text{N(H)CH}_3$ groups but we do not have such groups in our system. In the chemical shift range around -364 ppm, AB displays a signal. In addition, the signals relative to $-\text{NH}_2\text{BH}_2$ in PAB are in this chemical shift range. We may therefore suggest the identification of tetracoordinated nitrogen for both signals.

2.3.1.1 Precursor-to-ceramic conversion:

The polymer to ceramic conversion of the ABLi1 sample has been achieved at 1000°C under $\text{NH}_3$ for 2 hours. In contrast to AB, we could measure the weight loss that occurs during the pyrolysis up to 1000 °C under $\text{NH}_3$. The ceramic yield has been calculated to be around 69 % at 1000 °C but, as seen in Fig. 3.29, the weight loss continues above 1000 °C.
Figure 3.29 TGA curve recorded for the ABLi1 sample under NH3 up to 1000°C

The weight loss profile is very complex: the precursor displays a first weight loss up to 125 °C which is similar to the weight loss recorded under nitrogen for AB50: it is attributed to loss of H2 due to formation of PAB. Here, it probably forms a Li-containing PAB. This first weight loss is followed by a second weight loss up to 225 °C which may again be due to loss H2 and formation of a lithium-containing polyiminoborane (PIB) up to 450 °C. Then, a weight gain is recorded between 450 and 675 °C. The weight is then stable over around 300 °C before a third weight loss that most probably continues above 1000 °C. The weight loss above 900°C has been reported to be due to evaporation of Li3BN2 liquid phase formed during the pyrolysis as reported for Li3N mixed with PB.46

To learn more about the mechanisms involved in the precursor-to-ceramic conversion, ex situ analyses of intermediates isolated during pyrolysis up to 1000 °C under NH3 have been carried out by solid-state NMR. The 11B MAS NMR on the intermediate pyrolysis product isolated at 450 °C (end of the second weight loss, ABLi-450) shows the complete vanishing of the signal attributed to BNH2 environments, most probably because of their self-condensation (=BNH2 + =BNH2 → =BN2H + BH3). As-formed = BN2H units can react with =BNH2 groups to form BN3 units. Because 15N NMR has identified NBzH groups, ammonia is also probably removed. This is in good agreement with the increase of the intensity of the signals attributed to =BN2H and BN3 environments which tends to demonstrate the formation of borazine-type rings in the product. The continuous increase of the intensity of the signal attributed to BN3 units up to 1000°C (ABLi-1000) confirms condensation reactions.
The solid-state NMR highlights the TG results that showed a weight loss occurring above 1000 °C: it identifies the presence of the BHN₂ environments in the ABLi₁₀₀₀ sample which are expected to be released at higher temperatures.

2.3.1.2 High temperature behavior of Li modified AB based BN
The phase evolution of the ABLi₁₀₀₀ sample has been studied using XRD and Raman spectroscopy. Figure 3.31 depicts the XRD patterns of the ABLi₁₀₀₀, ABLi₁₄₅₀₀, ABLi₁₁₆₀₀ samples with temperature increase from 1000 to 1600 °C under N₂.
The XRD pattern of the ABLi1-1000 sample display a broad peak centered around 26.74° corresponding to the (002) reflection of BN with a lot of small peaks on the left and right sides between 2θ = 28° to 40° which are attributed to a Li·B·N phase. There are some peaks which are difficult to identify between 42° and 46°. Upon further annealing, the XRD pattern of the ABLi1-1450 sample was found to have a more intense and sharper peak at 26.74° as well as small broad peaks at around 43°, 54.5° and 75.9° which are all attributed to BN. The XRD peaks attributed to the Li·B·N phase disappear which can explain the weight loss we suggested to occur above 1000°C. Compared to the XRD pattern of the ABBN-1450 sample (See Fig. 3.3), a significant increase of the BN crystallinity occurred. At 1600 °C, we obtain a fully crystallized ABLi1-1600 sample with a sharp and intense peak at 26.4° (002) followed by small peaks at 41.6° (100), 43.87° (101), 50.15° (102), 55.1° (004), 75.93° (110) and 82.18° (112). The pattern was matched with JCPDS file number 04-003-6253 of the hexagonal phase of BN suggesting a centrosymmetric crystal structure and a P63/mmc space group. The crystallite size calculated using Scherrer formula at the dominant (002) peak increases from 5.1 nm for ABLi1-1000 to 12.5 nm at ABLi1-1450 and finally 16.15 nm at ABLi1-1600. Increase in degree of crystallization of BN due to addition of LiNH₂ to AB can be clearly seen upon comparing the crystallite sizes. For the ABBN-1450, we observed an
average crystallite size of 2.73 nm at (002) peaks. Hence we see a 7 fold increase in size of the crystal due to this process. Yuan et al reported a crystallite size of 9.27 nm at the same peak after addition of Li$_3$N powder to PB$^{46}$. The larger crystallite size in our case suggests the better efficiency of the intimate reaction between AB and LiNH$_2$, i.e., modification at a molecular level, over physical mixing of powders.

Two XRD peaks are also identified in the XRD pattern of the ABBN-1600 sample around 44°. The c-BN and the t-Li$_3$BN$_2$ phase displays a XRD peak around this position but an annealing at 1600°C is expected to decompose the t-Li$_3$BN$_2$ phase whereas the formation of c-BN from h-BN needs high pressure. As a consequence, it was not possible to attribute these two peaks.

Here, we successfully demonstrated the interest to modify BN precursors with LiNH$_2$ to significantly improve the BN crystallinity at high temperature. However, a temperature of 1600 °C can be still considered as too high to find this approach interesting. As a consequence and because both precursors, i.e., AB and LiNH$_2$, are solid, we tentatively applied a reactive ball-milling.

### 2.3.2 Reactive ball-milling

Ball milling (BM) is a simple and relatively inexpensive processing technique that is generally used for applying extensive plastic deformation to metallic powders through multiple impact events in a rotating vial containing hardened steel or ceramic balls. BM can produce extremely fine microstructures and form non-equilibrium phases (i.e. amorphous) or intermetallic compounds, when powder mixtures of different metals are used. Parameters that affect milling are particle size, compositional ratio of elements, ball-to-material ratio, rotation speed and milling time. Although BM has been carried out to mainly produce materials with superior high-temperature mechanical properties, there are only few reports on the preparation of BN by reactive ball-milling.

BN nanotubes have been produced by thermal annealing at 1000°C of elemental boron powders which were previously ball milled in NH$_3$ for 150 h at room temperature$^{47}$. As a proof of concept, we report for the first time the application of reactive BM to synthesize BN from single-source precursors. We performed the reaction between AB and LiNH$_2$ in a ball milling reactor (solid state reaction) at 200 rpm for 4 hours (See chapter 2 for more details). This process is called mechano-synthesis. The polymer (ABLi$_1$·BM) powders obtained after this
process have been pyrolyzed at 1000 °C under NH₃ then annealed up to 1450°C in flowing N₂. Figure 3.32 shows the XRD patterns of the ABLi₁•1000-BM and ABLi₁•1450-BM samples.

The ABLi₁•1000-BM sample is more crystalline as compared to its analog prepared by solution reaction. The crystallite size calculated at the dominant (002) peak using Scherrer equation was found to be 18.5 nm which upon annealing to 1450 °C (ABLı₁•1450-BM) increased to 25.9 nm. Values above 17 nm generally indicate good degree of crystallinity⁴⁸. More interesting, the ABLı₁•1450-BM sample crystallized as hexagonal boron nitride. The peaks were matched using JCPDS file number 04-003-6253. The most important peak which suggests the complete crystallization of BN at 1450 °C is the (102) peak. This peak did not crystallize for the previous ABLı₁•1450 sample in Figure 3.31. Therefore, we proved that reactive ball-milling is a promising approach to prepare highly crystallized BN at relatively low temperatures from single-source precursors. The process of mechano-synthesis also shows good promise in synthesizing polymers effectively. This process needs further investigation to understand its mechanism, advantages and drawbacks. Indeed, two unknown XRD peaks are still present in the XRD pattern of the ABLı₁•1450-BM sample.

We also applied BM using PB60 as a BN precursor using the same parameters. Pyrolysis was also done under NH₃ and annealing up to 1450 °C was performed under N₂. Figure 3.33 shows
the XRD for the \textbf{PB60Li1-1450} sample. Because of the strongly intense (002) peak, it is difficult to see other peaks. Therefore, Fig. 3.34 presents a zoom of the 2\(\theta\) range 35-90\(^\circ\). The majority of the peaks is attributed to the hexagonal phase of BN. However, it seems that the reactivity between \textbf{PB60} and LiNH\(_2\) is better to generate highly crystallized BN.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{xrd_pattern}
\caption{XRD pattern of the PB60Li1-1450-BM sample}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{xrd_pattern_zoom}
\caption{Zoom of the XRD pattern of the PB60Li1-1450-BM sample}
\end{figure}
By changing the chemistry of the Li-based compound and selecting LiH, we can observe a
same behavior in the XRD patterns of the samples prepared at 1450 °C with a better BN
crystallinity using PB60 as a BN precursor.

Figure 3.35 XRD patterns of the samples using LiH and LiNH₂ as Li-containing compounds.

4. Conclusion
In this chapter, we investigated the synthesis of boron nitride (BN) and B-M-N (M = Ti, Zr, Hf) ceramicts from two different BN precursor namely, ammonia borane (AB) and polyborazylene (PB). In the first part of the chapter, we briefly introduced the preparation of BN from these two precursors and showed that the formation of the hexagonal phase of BN was not possible using these two precursors which represents an advantage to prepare the nanocomposites with the nanostructural organization we targeted in the second part of the present chapter: MN nanophase distributed in an amorphous matrix. In the second part, the major part, we discussed on the introduction of transition metals such as titanium, zirconium and hafnium at molecular scale in BN precursor. The polymer synthesis and pyrolysis have been investigated through complementary tools such as FTIR, solid-state NMR and TGA. It has been shown that the synthesis of polymers occurred through two reactions involving NH and BH groups in BN precursors but such reactions occurred more efficiently with Hf-based
compounds. As a consequence, Hf-containing polymers displayed the highest crosslinking degree, thus resulting in a very high ceramic yield. After pyrolysis under NH₃ at 1000°C, samples were amorphous and the subsequent annealing to 1450°C under N₂ formed nanocomposites in which MN nanocrystals are dispersed in the BN matrix. We found out that increasing the Ti content in the polymer almost suppressed the crystallization of BN in the final nanocomposites at high temperature but only Hf is able to fully suppress the crystallization of BN for a B:Hf ratio of 3 resulting in the formation of highly stable nanocomposite structures. However, such nc-MN/a-BN nanocomposites especially with M = Ti and Hf may have some potential disadvantage due to the low BN crystallinity which can involve oxidation. To overcome this problem, we focused the last part of the present chapter on the investigation of the improvement of the BN crystallinity through the modification of BN precursors with LiNH₂ through a solution route and reactive ball-milling. Reactive ball-milling allowed generating a highly crystallized BN after pyrolysis under NH₃ at 1000 °C then annealed at 1450 °C under N₂.
References


CHAPTER 4
SILICON-BASED NON-OXIDE CERAMICS
1. Introduction

For most industrial purposes, technical ceramics are produced from conventional powder metallurgy routes which involve shaping and consolidation of inorganic powders. Although the process is well established at industrial scale, it has some limitations such as high operating temperatures, especially as non-oxide ceramics, inability to generate complex shapes and difficulties to design the porosity, at least the mesoporosity of materials. Furthermore, when the preparation of nanocomposites is targeted, a uniform distribution of elements is difficult to achieve, owing to the low diffusion coefficient of elements. One of the ways to design such materials is to control the structure at very small length scales in an early stage of their synthesis. Within this context, it appeared obvious to us that improving the control of compositional homogeneity, the purity as well as the processability of ceramics should be achieved using single-source precursors, polymers and/or solution techniques. This viewpoint focused on, the polymer-derived ceramics (PDC) route has been exploited in our work. As we observed in the chapter 3, the PDC route is well adapted to multi-element systems including MN/BN (M: Ti, Zr, Hf) nanocomposites.

This chapter is based on the same concept with the difference being change in the nature of the matrix from BN to Si$_3$N$_4$. It is divided in two parts: the first part deals with the chemistry, the polymer-to-ceramic conversion and the high temperature behavior of polysilazane-derived Si$_3$N$_4$. This study will allow us to understand the impact of the addition of a second phase, i.e., MN with M = Ti, Zr, Hf, in these ceramics to form nanocomposites which are discussed in the second (major) part of the present chapter. In this second part, we discuss the synthesis and properties of Si·M·N (M=Ti, Zr, Hf) ceramics using the PDC route. We firstly characterize the single-source polymetallosilazane, then document the polymer-to-ceramic conversion and finally characterize the microstructure of the ceramics, especially its evolution at high temperature.

The main objective behind the preparation of these nanocomposites is to understand the influence of the chemistry of precursor on the structural behavior of Si·M·N ceramics at high temperature.
2. Preparation of polysilazane-derived Si₃N₄

The objective of this part is to characterize the preceramic polymers like Si₃N₄ and Si-C-N which are used to prepare the Si-M-N (M: Ti, Zr, Hf) ceramics in the second part of this chapter. We investigate the chemistry, thermal behavior and study the microstructure evolution of the as-obtained ceramics at high temperature.

2.1 Perhydropolysilazane (PHPS)-derived Si₃N₄

PHPS is a highly reactive preceramic polymer containing two Si-H and one N-H functions in its structure as illustrated in Figure 4.1.

![Figure 4.1 Formula of perhydropolysilazane (PHPS)](image)

Figure 4.2a show the FTIR and ^1^H NMR spectra of PHPS.

![Figure 4.2 a) FTIR spectrum (taken using KBr windows) and b) ^1^H liquid NMR spectrum (in CDCl₃) of PHPS](image)

The FTIR spectrum of PHPS involves only three types of bonds corresponding to its structure shown in Figure 4.2, i.e., N-H, Si-N-Si, and Si-H. The bands in the range of 3200-3400 cm⁻¹ (stretching) and 1180 cm⁻¹ (bending) correspond to N-H bonds. The sharp nature of the band in the former range indicates the absence of hydrogen bonding in the system thus the polymer has a very open chain structure. The very strong band at 2150 cm⁻¹ corresponds to stretching of Si-H bonds whereas the strong band from 800 to 1000 cm⁻¹ corresponds to the Si-N-Si
network. A group of very weak signals can be seen in the range of 2900 to 3000 cm\(^{-1}\) which corresponds to the C-H bond. Although PHPS does not have any C in its backbone structure, the signal of C-H bonds can be attributed to protective end groups added to the main chain/backbone to stabilize PHPS and/or the presence of residual solvent as PHPS is commercially available as 20% solution in xylene. The doublet of sharp peaks at 2300 cm\(^{-1}\) is due to the CO\(_2\) and H\(_2\)O correction, so are the small bands in the range of 1500 to 1750 cm\(^{-1}\).

Apart from FT-IR, we investigated \(^1\)H liquid NMR on PHPS to determine the structure of the polymer (Figure 4.2b).

The liquid \(^1\)H NMR spectrum of PHPS shows signals at 7.26 ppm, 7.10 ppm, 4.8 ppm, 4.34 ppm, 2.4 ppm, 2.3 ppm, a broad peak from 0.5-2.0 ppm and 0.1 ppm Analysis of trace compounds in NMR done by Fulmer et al\(^1\) showed that the peaks at 7.26 ppm and 7.10 ppm are multiplet peaks of CH in \(m\)-xylene while the signals emerging at 2.4 ppm and 2.3 ppm belong to the CH\(_3\) in \(m\)-xylene. The rest of the signals belong to the proton in PHPS with the signals from 0.5 to 2.0 ppm attributing to Si\(_3\)NH, at 4.8 ppm (NSiH/NSiH\(_2\)), at 4.34 ppm (NSiH\(_3\)) and at 0.1 ppm (NSi(CH\(_3\))\(_3\)). Through pyrolysis under nitrogen, PHPS leads to a composite material composed of a majority of Si\(_3\)N\(_4\) and around 13 wt% of silicon (Si). Using ammonia as atmosphere, PHPS leads to Si\(_3\)N\(_4\) in a measured weight loss of 32 % (Figure 4.3); therefore, the ceramic yield is calculated to be 68 %. We particularly focused on the use of ammonia as atmosphere of pyrolysis because Si-M-N (M: Ti, Zr, Hf) ceramics designed in the second part of the chapter are prepared under ammonia.

![Figure 4.3 TGA of PHPS under NH\(_3\)](image)
Under ammonia the major weight loss occurs in the range of 100° to 350°C and is due to dehydrogenation of Si-H/N-H and Si-H/Si-H bonds leading to formation of Si-N and Si-Si bonds forming the backbone structure of the ceramic. There is no weight loss from 350°C to 550°C after which we have a drop of another 3% due to ceramization. There is loss dangling hydrogen from N-H groups in this range. Ideally, there is nitridation occurring in the temperature range of 350 to 450°C which should lead to weight gain as reported by Isoda et al but no such gain is observed. This contradictory result can be attributed to the fact that we use a commercial PHPS which generally has heavy carbon based end groups for stability which are lost in previously mentioned temperature range whereas Isoda et al used a homemade PHPS which did not have such groups. At 1000°C, the material labelled PHPS-1000 is amorphous as shown on XRD pattern represented in Figure 4.4. Further annealing in flowing nitrogen up to 1700°C involved the crystallization of α- and β-Si₃N₄. The major peaks start crystallizing at 1200°C and by 1400°C we achieved complete crystallization of Si₃N₄ which is a little higher than what was reported by Schwab et al, where they obtained a completely crystalline matrix at 1270 °C under N₂.
Figure 4.4 XRD patterns of ammonia-treated PHPS derived Si$_3$N$_4$ in the temperature range 1000-1700°C
2.2 Poly(vinylmethyl-co-methyl)silazane (HTT1800)-derived Si$_3$N$_4$

HTT1800 is a commercially available copolymer containing 20% of methyl/vinyl and 80% of methyl/hydride substituted silazane units (Figure 4.5).

![Figure 4.5 Structure for HTT1800](image)

The precursor can be used to prepare both Si$_3$N$_4$ and Si·C·N ceramics depending on the gaseous atmosphere used during the polymer-to-ceramic conversion.

The FTIR spectrum (Figure 4.6a) of HTT1800 shows the expected absorption bands of polyorganosilazanes, as reported in the literature\textsuperscript{6,7}: SiN-H stretching at 3382 cm$^{-1}$ coupled with Si-N vibrations at 1166 cm$^{-1}$, the stretching of C-H bonds in CH$_x$ units at 2957 cm$^{-1}$ (CH$_3$ asymmetric stretching), 2916 cm$^{-1}$ (CH$_2$ stretching), 2898 cm$^{-1}$ (CH stretching), and 2849 cm$^{-1}$ (CH$_3$ symmetric stretching), a typical absorption band arising from the stretching of C=C double bonds in vinyl groups and CH$_x$ deformations at 1593 and 1400 cm$^{-1}$, respectively as well as the corresponding C-H bond stretching at 3047 and 3005 cm$^{-1}$, respectively was also visible. The bands at 2126 and 1253 cm$^{-1}$ are attributed to the stretching of Si-H bonds and deformations of C-H bonds in SiCH$_3$ units, respectively. Below 1000 cm$^{-1}$, absorption bands attributed to stretching and deformation vibrations that involve Si·C, Si·N, C·H, and C·C bonds overlap and cannot be assigned unambiguously.
Figure 4.6 a) FTIR and b) $^1$H liquid NMR spectrum of HTT1800

The $^1$H NMR spectrum is typical of a vinyl-containing polyorganosilazane. $^1$H signals were detected at $\delta=0.20$ (SiCH$_3$), 0.5 to 1.1 (SiNH$_2$Si), 4.35 to 4.7 (SiH), 5.65 to 5.95 (SiCH=CH$_2$), and 6.00 to 6.25 ppm (SiCH=CH$_2$). In $^{13}$C NMR spectrum a broad signal was observed at $\delta = -4.0$ to 4 ppm which can be assigned to Si bonded CH$_3$ sites and signal relating to olefin carbon was observed from $\delta = 125$ to 142 ppm. For $^{29}$Si NMR spectra, a signal at $\delta = -21$ ppm was attributed to (CH$_3$)$_2$Si(=CH$_2$)N$_2$ units. Peak related to HSi(CH$_3$)$_2$N$_2$ units should appear at $\delta = -15$ ppm, but this component was superimposed by the main peak at $\delta = -21$ ppm.

The polymer-to-ceramic conversion of HTT1800 leads to either Si-C-N ceramics or Si$_3$N$_4$ depending on the pyrolysis atmosphere. Under N$_2$, HTT1800 exhibits three different weight losses during the pyrolysis (Figure 4.7). A first major weight loss occurs up to 250°C, which mainly corresponds to the volatilization of low-molecular-weight organosilicon species, but also crosslinking reactions of the precursor through transamination and bond redistribution. However, hydrogen is also identified as a gaseous byproduct, most probably due to the dehydrocoupling reaction of -SiH/-SiH and -SiH/=NH groups. The TGA profile after the first stage is nearly same for both N$_2$ and NH$_3$ as is evident from the figure. A second weight loss takes place between 250 and 450°C, which is possibly due to transamination because of the presence of NH groups, which removes ammonia. HTT1800 is converted into a ceramic through a third weight loss occurring between 450 and 1000°C, in which rearrangements occur through radical formation and recombination. Evolution of methane is mainly detected in this temperature range because of the decomposition of SiCH$_3$ groups or the cleavage of C=C bonds. However, the thermal decomposition of HTT1800 probably occurs through
mechanisms that are superimposed rather than well separated in clear temperature ranges as proposed.

Under ammonia (Figure 4.7), the weight loss is lower most probably because volatilization of low molecular weight species in the low temperature regime of the decomposition is reduced.

![Figure 4.7 TGA of HTT1800 under NH₃ and N₂](image)

After pyrolysis at 1000°C, ammonia-treated samples are X-ray amorphous as shown in Fig 4.8. By increasing the temperature up to 1700°C under nitrogen, ammonia-treated samples are shown to remain completely amorphous until 1400°C. After annealing at 1500°C, we can distinguish peaks attributed to α-Si₃N₄ and β-Si₃N₄. Major peaks for α-Si₃N₄ peaks are found at 20.62° (101), 31.02° (201), 34.617° (102), 35.376° (210) and 38.94° (-2-10) while β-Si₃N₄ peaks are found at 23.397° (110), 27.06° (200) and 33.693° (101). The crystallization temperature of HTT1800-derived Si₃N₄ is shifted by 230°C in comparison to PHPS-derived Si₃N₄. This is probably due to the more complex reaction sites which occur during pyrolysis because of the presence of carbon-based groups. After annealing to 1700°C, we obtained fully crystallized α-Si₃N₄ and β-Si₃N₄.
2.3 Conclusion

The objective of this part was to follow the thermal decomposition of PHPS and HTT1800, two commercially available preceramic polymers, into Si$_3$N$_4$ using ammonia as gaseous atmosphere. Then, we investigated the microstructural evolution at high temperature. Such a study was required to understand and highlight the effect of the introduction of a third element, \( i.e., M = \text{Ti, Zr, Hf} \) to these ceramics to form Si-M-N ceramics. This is the subject of the second part of the present chapter.
3. Preparation of Si-Ti-N ceramics

Ternary Si-M-N (M = early transition metal) materials have attracted the attention of researchers in recent years, especially as coatings with very interesting physical properties such as their hardness and wear resistance, their high-temperature stability and their oxidation resistance. Such materials form multiphase compounds with a uniform distribution of elements in which early transition metal nitride nanocrystals are homogeneously dispersed in a silicon nitride (Si₃N₄) matrix. They are denoted as nc-MN/α-Si₃N₄ films (nc for nanocrystalline, α for amorphous). CVD (chemical vapor deposition), ALD (atomic layer deposition) and reactive magnetron sputtering methods are reported to be applied in the fabrication of Si-M-N materials. However, these techniques are mostly applied to produce films whereas for many applications, there is a pressing need to generate other shapes and textures to make practical devices. This is the way to further explore the properties of these materials and exploit their widespread interest in industry, in cutting-edge technology and in our daily life. Here we used the previously described preceramic polymers, i.e., PHPS and HTT1800 to react with titanium containing precursor, tertakisdimethylaminotitanium (TDMAT), to prepare ternary Si-Ti-N materials using the procedure depicted in Figure 4.9 and already exploited in chapter 3 using BN precursors as matrix precursors.

![Figure 4.9 Schematic of PDC route to synthesize nanocomposites](image)
In the following sections we discuss the synthesis of the polytitanosilazanes from PHPS and HTT1800 by fixing a Si:Ti ratio of 2.5, the polymer-to-ceramic conversion, the crystallization behavior and the microstructural evolution of the ceramics and the nanostructure of ceramics. In particular, we will highlight that the polymer chemistry has a strong impact on the properties of the ceramics.

### 3.1. Polytitanosilazane synthesis

The liquid tetrakis(dimethylamido)titanium precursor (TDMAT, Figure 4.10) was used as the nanophase precursor to modify the polysilazanes such as PHPS and HTT1800. This modification leads to the synthesis of a *single source* Si-Ti-N precursor we call polytitanosilazanes.

![Figure 4.10 Molecular formula of TDMAT](image)

We already investigated the reaction between TDMAT and polyorganosilazanes such as polymethylsilazane (PMSZ) in the PhD thesis of Mirna Bechelany\(^3\). This work was recently published in *Chem. Eur. J.*\(^8\)

In particular, a series of polytitanosilazanes has prepared from PMSZ (Figure 4.11) through several ratios from 1 to 10 and the role of the chemistry behind their synthesis has studied in details.

![Figure 4.11 Molecular formula of polymethylsilazane (PMSZ)](image)
It has been demonstrated based on FTIR and solid-state NMR spectroscopies coupled with mass spectrometry and elemental analyses that the reaction of TDMAT and polyorganosilazanes involves N-H and Si-H bonds in polysilazanes as well as N(CH₃)₂ groups in TDMAT according to Eq. (1) and Eq. (2).

\[
\equiv Si - NH + Ti(N(CH₃)₂)₄ \rightarrow \equiv Si - N - Ti(N(CH₃)₂)₃ + H - N(CH₃)₂ \quad (1)
\]

\[
\equiv Si - H + Ti(N(CH₃)₂)₄ \rightarrow \equiv Si - N(CH₃)₃ - (Ti(N(CH₃)₂)₃) + CH₄ \quad (2)
\]

Figure 4.12 proposed a molecular structure for the polytitanosilazane prepared from PMSZ with a Si:Ti ratio of 2.5 based on chemical composition, FTIR, solid-state NMR and molecular weight measurements.

Titanium atoms allow increasing the crosslinking degree of the polymeric backbone. They are homogeneously distributed within the polysilazane structure as bridges linking silazane units as well as terminal units. There are two types of bridges *i.e.* those involving \(-(Si\cdot N)ₙ\cdot TiN₃\) units (Eq. (1)) which are built by HNMe₂ and NH condensation and those involving SiN(CH₃)TiN₃ units (Eq. (2)) which arise due to reaction between Si-H and (CH₃)₂NTi moieties. The proposed structure is consistent with the analyzed polymer structure although it shows a slight deviation in the nitrogen content in comparison to experimental chemical compositions.
We confirmed such reactions with the polytitanosilazanes prepared from PHPS (labeled \textbf{NCPTi2.5}) and HTT1800 (labeled \textbf{NCHTi2.5}) according to a Si:Ti ratio of 2.5 based on FTIR and solid NMR spectroscopies coupled with elemental analyses.

The FTIR spectra of the \textbf{NCPTi2.5} and \textbf{NCHTi2.5} samples are compared with PHPS and HTT1800, respectively. To better understand the chemistry behind the synthesis of polytitanosilazane from HTT1800, we compared its FTIR spectrum with the FTIR spectrum of HTT1800 and HTT1800 having undergone a similar synthesis procedure than polytitanosilazane but without TDMAT. It is labelled HTT1800-R120 (Figure 4.13).

At higher wavenumbers of around 3400-3300 cm\(^{-1}\) we observe the disappearance of the N-H stretching band after reaction between PHPS and TDMAT. The N-H vibration band at 1180 cm\(^{-1}\), marked by the black box, decreases in intensity in both systems. This confirms that NH groups participate to the building of the polytitanosilazane network as proposed in Eq. (1). The highly intense Si-H peak decreases in intensity after reaction of PHPS with TDMAT suggesting the occurrence of the reaction depicted through Eq. (2). In the \textbf{NCPTi2.5} sample, there is appearance of a set of broad bands in the range of 2800-3000 cm\(^{-1}\). This is attributed to the vibration of C-H bonds from the dimethyl group present in TDMAT. Another set of bands that can be attributed to deformation of C-H bands appears at around 1360 and 1450 cm\(^{-1}\). The band at 1280 cm\(^{-1}\) can be assigned to the N-C bonds in N(CH\(_3\)) groups. In the \textbf{NCHTi2.5} sample, the bands attributed to the vinyl groups at 1620 cm\(^{-1}\) present in HTT1800 disappeared. Interesting, they are still present in the HTT1800-R120 sample. This could
demonstrate that TDMAT reacts with the vinyl groups of HTT1800 but such a reaction cannot occur. We rather propose that TDMAT acts as a catalyst for the polymerization of the vinyl groups (Eq. (3) and/or hydrosilylation reactions (Eq. (4).

\[
n \cdot \text{HC} = \text{CH} \cdot \text{Si} \rightarrow \cdot \left(\text{CH}_2 \cdot \text{CH}_2\right)_n \cdot \text{Si} \equiv (3)
\]

\[
\equiv \text{Si} \cdot \text{H} + 2 \cdot \text{HC} = \text{CH} \cdot \text{Si} \rightarrow \equiv \text{Si} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{Si} \equiv (4)
\]

In order to obtain a complete view of the polytitanosilazane structure, we investigated solid-state NMR spectroscopy to probe the local carbon, nitrogen and silicon environments of the samples. The CP technique has been used to obtain spectra with a reasonable signal-to-noise (S/N) ratio. Solid-state $^{13}$C CP MAS NMR spectra of the NCPTi2.5 and NCHTi2.5 samples (Figure 4.14a) exhibit signals which can be simulated into two and four signals, respectively. The spectrum of the NCHTi2.5 sample (Figure 4.14a) is similar to the spectrum of polytitanosilazanes prepared from PMSZ8. The signal emerging at 6 ppm is very broad with a shoulder emerging at 0 ppm. $^{13}$C NMR signals at around 0 ppm are generally assigned to carbon atoms of aliphatic groups bonded to a silicon atom, i.e. in this case SiCH$_3$ units as identified in HTT1800. In NCPTi2.5, such units are logically absent (Figure 4.15b). Therefore, the resonances at 39 and 45 ppm, present in both systems, have been assigned to TiNCH$_3$ groups. In particular, the peak at 45 ppm can tentatively be attributed to NCH$_3$ groups linked to titanium, i.e., Si$_2$N·Ti[NCH$_3$]$_2$ units, resulting from reaction between NH units and N(CH$_3$)$_2$ groups with dimethylamine elimination (Eq. (1)). Indeed, its position is similar to the position of the signal of TDMAT being thermolyzed at toluene reflux for 3 days identified in the liquid-state $^{13}$C NMR spectrum (Figure 4.15).
The signal at 39 ppm has been therefore assigned to N$_2$Si(CH$_3$)$_2$·N(CH$_3$)$_2$·TiN$_3$ units resulting from the reaction between SiH units and N(CH$_3$)$_2$ groups with methane elimination (Eq. (2)).

Regarding the signal around 0 ppm deconvoluted into two components centered at 0 and 6, it is possibly due to CH$_3$ groups linked to SiN$_2$H (Eq. (1)) and SiN$_3$ (Eq. (2)) environments.

The solid-state $^{15}$N CP MAS NMR spectra (Figure 4.16) of the NCPTi$_{2.5}$ and NCHTi$_{2.5}$ samples display two broad signal centered at -350 and -370 ppm. The signal at -350 ppm corresponds to HN$_2$Si environments whereas the additional signal centered around -370 ppm is assigned to NCH$_3$ environment based on our data collected for polytitanosilazanes prepared from PMSZ.$^8$
29Si CP MAS NMR spectra are shown in Figure 4.17. The 29Si MAS NMR spectrum of the NCPTi2.5 sample (Figure 4.17a) exhibits a broad line with a maximum around -36 ppm assigned to both $N_{2}SiH_{2}$ and $N_{3}SiH$ environments. Their presence highlights reactions between Si-H units and N(CH$_{3}$)$_{2}$ groups. The NCHTi2.5 sample (Figure 4.17b) exhibits a main broad resonance centered around -24 ppm that can be simulated with two components at -21 and -29 ppm similarly to polytitanosilazanes prepared from PMSZ$^8$. The signal at -21 ppm is related to CH$_{3}$-$Si(H)N$_{2}$. This 29Si chemical shift value is consistent with those published previously for a boron-modified polyhydridovinylsilazane which exhibited broad signals at -13 ppm, attributed to silicon atoms in a $SiHC(sp^{3})N_{2}$ environment$^{10}$. The other signal at -29 ppm could correspond to a $SN_{3}C$ group and more precisely to CH$_{3}$-$Si(NCH$_{3}$-)N$_{2}$ resulting from the reaction between SiH units and NCH$_{3}$ groups present in Ti[N(CH$_{3}$)$_{2}$]$_{4}$ (Eq. (2)). It definitely approves the occurrence of this reaction. Finally, the signal at -7 ppm can be attributed to SiC$_{2}N_{2}$ environments. Indeed, the 29Si chemical shift depends on the conformation of the silazane$^{13}$. For example, a 29Si chemical shift value of -5 ppm is expected for SiC$_{2}N_{2}$ units within six-membered cyclosilazanes$^{14}$ while those of SiC$_{2}N_{2}$ groups in four- or eight-membered rings would appear at 3.3 ppm or -8.7 ppm, respectively$^{14}$. In conclusion, the NCHTi2.5 sample is preferentially composed of six- and eight-membered Si-N rings as well as Si-N chains.
As suggested by FTIR and solid-state NMR spectra, the synthesis of polytitanosilazanes gives rise to a large variety of structural components which are formed by the mechanism described in Eq. (1)→(4). Even though highly suitable for probing the local chemical environment of NMR-active nuclei, NMR spectroscopy does not give information on the chemical composition of the polymers. Such data are, however, strictly required for having a complete view of the polymer synthesis.

Polytitanosilazanes synthesized from PMSZ displayed a chemical composition of \( \text{Si}_{1.0} \text{Ti}_{0.37} \text{C}_{2.0} \text{N}_{0.7} \text{H}_{7.1} \) (20.3 wt% of Ti for a Si:Ti ratio of 2.5)\(^8\). In comparison, the presence of two SiH groups (one more in comparison to PMSZ) and one NH group (like PMSZ) in the monomeric unit of PHPS did not allow significantly increasing the Ti content in polytitanosilazanes prepared from PHPS, i.e., \( \text{NCPTi}_{2.5} \) sample. A chemical composition of \( \text{Si}_{1.0} \text{Ti}_{0.4} \text{C}_{2.0} \text{N}_{1.0} \text{H}_{5.0} \) has been calculated for \( \text{NCPTi}_{2.5} \). This corresponds to 20.6 wt% of Ti which has been introduced in PHPS. These results prove that the precursor synthesis occurs in the expected manner since they agree reasonably well with the fixed Si:Ti ratio. HTT1800, in its given structure, contains a lower SiH site content (0.8) than in PMSZ (1) and PHPS (2) while the NH group content is the same. However, the steric hindrance imposed by vinyl groups can reduce the reactivity of this polymer with TDMAT in comparison to PMSZ and PHPS. This is confirmed through the Ti content of the \( \text{NCHTi}_{2.5} \) sample: a chemical composition of \( \text{Si}_{1.0} \text{Ti}_{0.3} \text{C}_{3.0} \text{N}_{1.6} \text{H}_{8.5} \) has been calculated corresponding to only 12.9 wt% of Ti which has been introduced in HTT1800 taking into account a Si:Ti ratio of 2.5. This proves that the reactions described in eqs (1) to (4) occur more effectively under PHPS and PMSZ.
This will have clearly an effect on the polymer-to-ceramic conversion as well as on the microstructural evolution and crystallization behavior of the ceramics.

### 3.2. Polytitanosilazane-to-amorphous ceramic conversion

The thermal conversion of preceramic polymers into ceramics occurs through the evolution of gaseous byproducts involving a weight loss upon the heat treatment. The ceramic yield, which is the share of $(m_{\text{ceramic}}/m_{\text{precursor}}) \times 100 \%$ is a subject of major importance as it proves the general applicability of preceramic polymers as ceramic precursors. A common method for monitoring the progress during pyrolysis and for determining ceramic yields is thermogravimetric analysis (TGA). Here, we firstly discuss the polymer-to-ceramic conversion of the $\text{NCPTi}_2.5$ and $\text{NCHTi}_2.5$ samples from room temperature (RT) to 1000 °C in flowing ammonia as followed by TGA (Figure 4.18). Results are compared data recorded from PHPS and HTT1800.

In both cases, the weight loss of the $\text{NCPTi}_2.5$ and $\text{NCHTi}_2.5$ samples are higher than the native polymer, i.e., PHPS and HTT1800, respectively.

![Figure 4.18 TGA of a) NCPTi2.5 and b) NCHTi2.5 samples under NH3](image)

As a first speculation, this is mainly attributed to the presence of dimethylamino groups in the $\text{NCPTi}_2.5$ and $\text{NCHTi}_2.5$ samples that form NH$_2$ groups by reaction with ammonia (transamination reactions$^{15,16}$) and release dimethylamine (Eq. (5)). Then, the NH$_2$ groups immediately condense to form NH groups by releasing ammonia (Eq. (6)).

$$\equiv Ti - N(CH_3)_2 + H - NH_2 \rightarrow \equiv Ti - NH_2 + H - N(CH_3)_2 \quad (5)$$
However, only speculations can be made at this stage on the mechanisms governing the polymer-to-ceramic conversion. Within this context, spectroscopic analyses (FTIR and solid-state NMR) of intermediates isolated during pyrolysis have been carried out to learn more about the chemistry involved in each step of the polymer-to-ceramic conversion and to set up the procedure parameters. This is discussed in details below.

FTIR and solid-state NMR spectroscopies were performed on both NCPTi2.5 and NCHTi2.5 samples heat-treated at 200, 450, 700 and 1000 °C in an ammonia atmosphere with a dwelling time of 2 hours at each temperature. Pyrolysis intermediates are labeled NCPTi2.5-Y/NCHTi2.5-Y (Y being the temperature at which the sample was exposed: Y = 200 for 200 °C and 1000 for 1000 °C). On the basis of the structural assignment of the spectral features, the pyrolytic decomposition pathways are outlined. Representative FTIR spectra recorded from the two samples are shown in Figure 4.19.

![Figure 4.19 FTIR spectra of pyrolysis intermediates derived from NCPTi2.5 and NCHTi2.5 under NH3](image)

Upon pyrolysis under NH3 up to 200°C (NCPTi2.5-200/NCHTi2.5-200), there is a main decrease in intensity of the C-H vibration bands in both systems which tend to confirm the occurrence of transamination reactions (Eq. (5)) during the decomposition of the NCPTi2.5 and NCHTi2.5 samples in the low temperature regime of the pyrolysis. There are no major changes between 200 and 450°C as shown on the FTIR spectra. Only the band assigned to the stretching of N-H bonds increases in intensity, in particular in the NCPTi2.5-450 sample.
most probably because of the condensation of as-formed –NH$_2$ groups forming NH units (Eq. (6)).

From 450°C (NCPTi2.5-450/NCHTi2.5-450) to 700°C (NCPTi2.5-700/NCHTi2.5-700) the N·H, C·H and Si·H bond stretching bands disappear which indicates that the conversion of the polymer into ceramic is almost achieved. At 1000°C, we finally have an amorphous Si·N·Si network with N-Ti-N bridges.

FTIR spectroscopy gives a good overview of the evolution of chemical structure of preceramic polymers during their pyrolytic conversion but is not sufficient to fully understand the reactions taking place. Multinuclear solid-state NMR spectroscopy is another extremely helpful tool to investigate the structural rearrangements of the pyrolysis intermediates at the atomic scale during the polymer-to-ceramic transformation, by probing the local environment of the various NMR-active nuclei. Here, we give a detailed picture of the structural changes of both NCPTi2.5 and NCHTi2.5 samples during their ceramic conversion up to 1000 °C under ammonia, based on $^{29}$Si, $^{14}$N and $^{13}$C solid-state NMR spectroscopies. The samples pyrolyzed at 450°C (NCPTi2.5-450 and NCHTi2.5-450) and 1000°C (NCPTi2.5-1000 and NCHTi2.5-1000) have been investigated.

$^{29}$Si MAS spectra of NCPTi2.5-450 and NCHTi2.5-450 samples (Figure 4.20) result in a small shift of the main signal. For the NCPTi2.5-450 sample, this suggests a predominantly covalent material in which silicon is mainly present in SiN$_4$ environments. For the NCHTi2.5-450 sample, the main signal shifts toward the resonance at -28 ppm (SiN$_3$C) suggesting that the chemical environment of the silicon atoms is not strongly affected by the pyrolysis under ammonia. Whereas the silicon environment is similar for the NCPTi2.5-1000 sample, more changes occur in the NCHTi2.5-1000 sample. Obviously, nucleophilic substitutions and rearrangements occur in the temperature range 450-1000°C that cause a modification of the chemical environment of the silicon atoms: The signal corresponding to SiCHN$_2$ environments almost disappears while a broad signal centered at -48 ppm appears. It suggests a predominantly covalent material in which silicon is mainly present in SiN$_4$ environments like in the NCPTi2.5-1000 sample. As a consequence, the $^{29}$Si MAS NMR signals confirm the formation of silicon nitride.
The experimental $^{13}$C CP MAS NMR spectra of NCPTi2.5-450/NCHTi2.5-450 samples are reported in Figure 4.21. The experimental $^{13}$C CP MAS NMR spectra of NCPTi2.5-10/NCHTi2.5-10 samples could not be recorded with CP due to the low amount of remaining protons. The signals at 39 and 45ppm which have been attributed to TiNCH$_3$ units in different environment almost disappear. This points to the fact that such units react during the first step of the pyrolysis under ammonia. The spectra of NCPTi2.5-450/NCHTi2.5-450 samples show one main signal in the aliphatic region that can be assigned to CH$_3$Si$_{4-x}$ units (with $x = 0, 1, 2, 3$) in the NCHTi2.5-450 sample.
FTIR and solid state NMR spectroscopies allow us to understand the pyrolysis behavior of polytitanosilazanes prepared from PHPS and HTT1800.

Mutin *et al.*\(^7\) showed that Si·H and Si·CH\(_3\) as well as Si·CH\(_2\)·Si units in polycarbosilane are easily modified by ammonia according to Eq. (7). This mechanism is quite favored with polymers containing Si·H units which are sensitive to nucleophilic substitution.

\[
\equiv \text{Si} \cdot \text{R} + \text{NH}_3 \rightarrow \equiv \text{Si} \cdot \text{NH}_2 + \text{RH} \ (\text{R} = \text{H}, \text{CH}_3, \text{CH}_2\cdot\text{Si}\equiv)
\]  

(7)

Homolytic cleavages probably occur in a parallel way according to Eqs (8)-(10).

\[
\equiv \text{Si} \cdot \text{R} \rightarrow \equiv \text{Si} \cdot + \text{R} \cdot \ (\text{R} = \text{H}, \text{CH}_3, \text{CH}_2\cdot\text{Si}\equiv)
\]  

(8)

\[
\text{R} \cdot + \text{NH}_3 \ (g) \rightarrow \text{RH} + \cdot \text{NH}_2
\]  

(9)

\[
\equiv \text{Si} \cdot + \cdot \text{NH}_2 \rightarrow \equiv \text{SiNH}_2
\]  

(10)
Such mechanisms have also been proposed by Interrante et al. for vinyl-substituted polysilanes\textsuperscript{18}, and by Mutin et al. for polysilazanes\textsuperscript{17}. They probably occur below 500 °C. In the presence of N-CH\textsubscript{3} groups in the preceramic network, e.g. in N-CH\textsubscript{3} polysilazanes\textsuperscript{17}, release of methylamine is detected around 450 °C. It arises from the substitution of N-C H\textsubscript{3} groups by ammonia, \textit{i.e.}, a \textit{trans} amination according to Eqs (11)-(12).

\[
\equiv\text{Si-NCH}_3\equiv + \text{NH}_3(g) \rightarrow \equiv\text{Si-NH}_2 + \equiv\text{Si-NCH}_3\text{H} \quad (11)
\]

\[
\equiv\text{Si-NHCH}_3 + \text{NH}_3(g) \rightarrow \equiv\text{Si-NH}_2 + \text{CH}_3\text{NH}_2 \quad (12)
\]

Si-NMe-Si units are thus cleaved by formation of Si-NH\textsubscript{2} and Si- N-CH\textsubscript{3}H entities. The latter are subsequently transformed into SiNH\textsubscript{2} and CH\textsubscript{3}NH\textsubscript{2} which is released. Si-NH\textsubscript{2} groups condense with formation of Si-NH-Si and N(Si)\textsubscript{3} units by release of ammonia according to Eqs (13) and (14).

\[
\equiv\text{Si-NH}_2 + \equiv\text{Si-NH}_2 \rightarrow \equiv\text{Si-NH-Si} \equiv + \text{NH}_3 \quad (13)
\]

\[
\equiv\text{Si-NH-Si} \equiv + \equiv\text{Si-NH}_2 \rightarrow \equiv\text{N(Si)}_3 + \text{NH}_3 \quad (14)
\]

We suggest that \textit{trans} amination reactions of internal Si-NCH\textsubscript{3}Si units as depicted in Eqs (11) and (12) forming Si-NH\textsubscript{2} groups (Eq (7)) occur during the pyrolysis under ammonia up to 450 °C. Besides, we cannot exclude the possibility of an ammonolysis of SiCH\textsubscript{3} groups according to Eqs (7) to (10) resulting in the elimination of methane and the formation of Si-NH\textsubscript{2} units. As-formed Si-NH\textsubscript{2} units self-condense during further heat treatment to release ammonia according to Eqs (13) and (14) forming the ceramic network at 1000 °C.

### 3.3. Crystallization behavior:

Si-Ti-N materials prepared from \textbf{NCPTI2.5/NCHTI2.5} samples after pyrolysis at 1000°C under ammonia (\textbf{NCPTI2.5-10/NCHTI2.5-10}) are predominantly amorphous according to the extremely diffuse peaks in the corresponding XRD pattern (Figure 4.22). Through annealing at higher temperatures, crystallization occurred in both systems. The X-ray diffraction patterns of the samples annealed between 1200 and 1600 °C, \textit{i.e.}, \textbf{NCPTI2.5-12/NCHTI2.5-12}, \textbf{NCPTI2.5-14/NCHTI2.5-14}, \textbf{NCPTI2.5-15/NCHTI2.5-15} and \textbf{NCPTI2.5-16/NCHTI2.5-16} samples, are given in Figure 4.24. Phase identification is achieved by locating the characteristic diffraction peaks of the respective phases in the XRD spectra.
The XRD pattern of the NCPTi2.5-12/NCHTi2.5-12 and NCPTi2.5-14/NCHTi2.5-14 samples show broad peaks corresponding to the nucleation of the face-centered cubic (fcc) TiN phase (The peaks match with the JCPDS: 00-038-1420, corresponding to cubic structure of TiN.). TiN is identified by the presence of peaks at $2\theta = 36.5^\circ$, $42.63^\circ$ and $62.11^\circ$ which are attributed to the (111), (200) and (220) reflections. The $2\theta$ values indicated above are based on the CuKα radiation. The XRD patterns of the NCPTi2.5-15/NCHTi2.5-15 samples are different. The XRD pattern of the NCPTi2.5-15 sample show sharper and more intense TiN peaks with two
additional broad peaks attributed to TiN at and 74.00° and 78.30° corresponding to the (311) (222) reflections, respectively. As we move up to 1500°C with the NCHT2.5-15 sample, sharper TiN XRD peaks appear at 36.5°, 42.4°, 61.3°, 73.4° and 77.2°C. In addition, the matrix starts crystallizing as peaks corresponding to α-Si₃N₄ appear at 21.5°, 23.5°, 26.5°, 31°, 34.5°, 35.5°, 38.9°, 43.48°, 44.62°, 50.51°, 51.72°, 57.82°, 62.44°, 64.92°, 65.86°, 69.68° and 84.2°. As the annealing temperature was increased to 1600 °C, i.e., the NCPTi2.5-16/NCHT2.5-16 samples, crystallization of α-Si₃N₄ proceeded together with an increased extent of the crystallization of the TiN phase. The β phase is difficult to identify in those samples. Only by increasing the temperature to 1700°C with the NCHT2.5-17 sample, we could identify the β-Si₃N₄ phase appearing at 23.6°, 32.8°, 33.8°, 52.5°, 56.5°, 60.2°, 70.3° and 75.9° along with the previous peaks of α-Si₃N₄. As a confirmation of the marked improvement of the extent of crystallization and TiN crystallite growth from 1500 to 1600°C, the average TiN nanocrystal size has been calculated by applying the Scherrer formula to measure the FWHM of the dominant TiN peak (111) in the XRD patterns. It increases from 2.6/1.9 nm (NCPTi2.5-14/NCHT2.5-14) to 27.6/22.4 nm (NCPTi2.5-16/NCHT2.5-16). Hence, we have shown that the amorphous matrix in TiN/Si₃N₄ nanocomposites is more stable using PHPS than HTT1800 as matrix precursors. The crystallization behavior of materials prepared from PHPS is similar to those prepared from PMSZ. This clearly shows that the chemistry of the polyorganosilazane plays a key role in the crystallization behavior at high temperature. Let’s discuss on the reactivity of these polyorganosilazanes.

As a consequence, and in contrast to other systems, Si₃N₄ nucleation already occurred at 1500 °C in the HTT1800·derived NCPTi2.5-15 sample because of the lowest reactivity of HTT1800 with TDMAT in comparison to PMSZ and PHPS. As a consequence, the TiN volume fraction increases from HTT1800·derived Si·Ti·N ceramics to PMSZ and PHPS·derived Si·Ti·N ceramics. We observed that this shifts the onset of the crystallization of the Si₃N₄ phase to higher temperatures from HTT1800·derived Si·Ti·N ceramics to PMSZ and PHPS·derived Si·Ti·N ceramics. The XRD results allowed us to demonstrate that PHPS offers more latitude in the control of the crystallization of the Si₃N₄ matrix in Si·Ti·N ceramics. After pyrolysis up to 1600°C and 1700°C, we confirm the formation of nanocomposites with three crystallized phases: the fcc TiN and the α/β-Si₃N₄ in the three systems.
To highlight the interest of PHPS to limit or even suppress the crystallization of Si$_3$N$_4$, the effect of the Si:Ti ratio on the high temperature structural evolution of PHPS-derived nanocomposites has been studied.

The X-ray diffraction patterns of the samples with Si:Ti ratios of 5 (NCPTi5-14 $\rightarrow$ NCPTi5-17) and 1 (NCPTi1-12 $\rightarrow$ NCPTi1-18) have been investigated in the temperature range 1400-1700°C (Figure 4.23) and 1200-1800°C (Figure 4.24), respectively. We performed XRD of the NCPTi1-12 sample because it can be already considered as a nc-TiN/a-Si$_3$N$_4$ nanocomposite (Figure 4.24). After a pyrolysis at 1400°C, all samples are nanocomposites made of a TiN nanophase and an amorphous Si$_3$N$_4$ matrix. At a pyrolysis temperature $>$ 1400°C, the crystallization behavior changed: the XRD peaks attributed to Si$_3$N$_4$ showed a progressive decrease in intensity as the Si:Ti ratio of the sample decreased. Indeed, Si$_3$N$_4$ nucleation already occurred at 1500°C in the NCPTi5-15 samples (Figure 4.23). This confirms the strong influence of the Ti content in SiTiN ceramics on the onset of the crystallization of Si$_3$N$_4$.

Interestingly, a mixture of $\alpha$- and $\beta$-phases is identified in the NCPTi5-17 sample while only the $\alpha$-phase is identified in the NCPTi5-16 sample (Figure 4.23).

*Figure 4.23* XRD patterns depicting evolution of phases for the NCPTi5 sample with temperature
In comparison, a $\beta$-$\text{Si}_3\text{N}_4$ phase is obtained in the the NCPTi1-16 sample (Figure 4.24). This showed that the Si:Ti ratio has also a strong effect on the nature of the $\text{Si}_3\text{N}_4$ phases even by using a same polyorganosilazane, i.e., PHPS.

Figure 4.24 XRD depicting evolution of phases for NCPTi1 sample with temperature

However, the crystallization of the $\text{Si}_3\text{N}_4$ phase is significantly reduced in the NCPTi1-17 and NCPTi1-18 samples. Indeed, it is remarkable to observe that the crystallization of $\text{Si}_3\text{N}_4$ is extremely limited even after a pyrolysis at 1800°C for a Si:Ti ratio of 1, i.e., the NCPTi1-18 sample (Figure 4.24). A semi-quantitative estimation of the extent of crystallization has been done by calculating the integrated intensity of the selected diffraction (111)$_{\text{TIN}}$ line. The crystallite size of TiN increased from (a) NCPTi1-12 (6.2 nm) to NCPTi1-18 (60 nm) samples.

Based on this detailed XRD study on Si-Ti-N ceramics, we demonstrated that $n\sigma$-TiN/$\alpha$-$\text{Si}_3\text{N}_4$ nanocomposites prepared from a series of polyorganosilazanes can be prepared after a pyrolysis performed under ammonia at 1000 °C then under nitrogen at 1400 °C. By increasing the temperature of pyrolysis to 1500 °C, a strong effect of both the polysilazane chemistry and the Si:Ti ratios is identified. PHPS offers more latitude in the control of the crystallization of the $\text{Si}_3\text{N}_4$ matrix in Si-Ti-N ceramics and could produce nanocomposites with a limited crystallization of the $\text{Si}_3\text{N}_4$ phase at 1800 °C with a Si:Ti ratio of 1.
We confirmed the growth of the TiN nanophase by Raman spectroscopy. The Raman spectra from the NCPTi2.5-10 to NCPTi2.5-16 samples are presented in Figure 4.25. We can really identify the TiN phase in the NCPTi2.5-14, NCPTi2.5-15 and NCPTi2.5-16 samples.

![Figure 4.25 Raman spectra from the NCPTi2.5-10 to NCPTi2.5-16](image)

The peaks below 400 cm$^{-1}$ can be attributed to acoustical phonons whereas those in the high frequency mode, above 500 cm$^{-1}$, can be attributed to optical phonons. The peaks corresponding to 296.6 cm$^{-1}$ belong to longitudinal acoustic (LA) node. This node is generally accompanied by transverse acoustic (TA) node at around 210 cm$^{-1}$ but due to poor signal strength the node seems to be absent. The 2A mode of vibration which is centered around 410 cm$^{-1}$ becomes visible only at 1500°C. For temperatures below 1500°C the peak is not visible although its contribution to the adjacent broad peak can be seen upon deconvolution of the broad peak. The peak at 540 cm$^{-1}$ along with a very slight shoulder at 600 cm$^{-1}$ (visible only at 1600°C) corresponds to the transverse optic/longitudinal optic (TO/LO) mode. The phonon bands in the lower acoustic range correspond to the heavier Ti$^{4+}$ ions while in the higher optical range they correspond to the lighter N$^{3-}$ ions. The two broad peaks in the 817-1075 cm$^{-1}$ wavenumber range can be assigned to the A+O and 2O modes.

No contribution from Si$_3$N$_4$ is visible for this system. α-Si$_3$N$_4$ has close to 20 peaks in the wavenumber range of 400 to 1000 cm$^{-1}$. The absence of these peaks can be attributed to the fact that they may be covered by TiN peaks.
Interestingly, D and G peaks corresponding to free carbon emerge in the NCPTi2.5-10 and NCPTi2.5-12 samples. The peaks disappear in the NCPTi2.5-14 and NCPTi2.5-15 samples then tend to re-appear in the NCPTi2.5-16 sample. The presence of free carbon at 1000°C goes contrary to the observations of elemental analysis at the same temperature. The chemical composition of the NCPTi2.5-10 sample as calculated by elemental analysis is Si1.9N3.8Ti1.0C0.01O0.03. This shows that only a very negligible amount of carbon is present in the system. The Raman bands attributed to free carbon then can be attributed to carbon impurity arising from the graphite furnace used for high temperature (>1000°C) treatment of the samples.

As we move to the lowest Si:Ti ratio of 1 (Figure 4.26), we see a stark difference between the Raman spectra for this system and the previous systems at 1600°C. The modes corresponding to both transverse acoustic/longitudinal acoustic and transverse optical/longitudinal optical phonons are shifted by nearly 75 cm⁻¹. While the A+O and 2O bands are completely missing at 1600°C, 2A band centered around 410 cm⁻¹ is very sharp at 1600°C while it is just visible as a shoulder at lower temperatures.

3.4 Microstructural characterization using Transmission Electron Microscopy

The microstructure of the NCPTi2.5 derived ceramics was observed by a HRTEM for samples crystallized at 1400°C (NCPTi2.5-14) and 1500°C (NCPTi2.5-15). From XRD, it was observed
that the matrix (Si₃N₄) is amorphous and the TiN nanocrystals were crystallized out from the amorphous system. The TEM images confirm this observation. The HRTEM image showed that the NCPTi₂.₅･₁₄ sample (Figure 4.27) consists of nanocrystals with sizes ranging from 2 to 5 nm embedded in a bright-appearing network which revealed the typical phase contrast of amorphous materials. The low magnification TEM image (inset) demonstrated the homogeneous distribution of nanocrystals in the matrix. Based on the selected area electron diffraction (SAED) pattern, the indexation of \textit{fcc} TiN is confirmed but the continuous rings demonstrated the relatively low degree of crystallinity of TiN nanocrystals as shown by X-ray diffraction.

![HR-TEM image for NCPTi₂.₅･₁₄ with SAED pattern inset](image)

Figure 4.27 HR-TEM image for NCPTi₂.₅･₁₄ with SAED pattern inset

The TEM observation results of the NCPTi₂.₅･₁₅ sample (Figure 4.28) also shows small nuclei (around 8 nm); again embedded in a bright-appearing network which reveals the typical phase contrast of amorphous materials (inset). We can clearly distinguish the \textit{fcc} structure of TiN nanocrystals with a fringe spacing of 0.225 nm, corresponding to the $d$-
spacing of the lattice plane of the TiN structure *i.e.* the [111] direction of the *fcc* cubic rocksalt TiN structure. As in Fig, the low magnification TEM image (inset) demonstrated the homogeneous distribution of nanocrystals in the matrix. The SAED pattern (inset) is in general composed of continuous rings (but spots can be identified) demonstrating an extent of the TiN crystallization similar to the sample prepared at 1400°C as shown by X-ray diffraction.

![Image of HR-TEM image with SAED pattern inset](image)

**Figure 4.28** HR-TEM image for NCPTi2.5-15 with SAED pattern inset

The macro/microstructure was observed by a HRTEM for samples crystallized at 1400°C (NCHTi2.5-14) and 1500°C (NCHTi2.5-15). From XRD it was already known that at 1400°C the matrix of Si₃N₄ was still amorphous and the TiN nanocrystals were crystallizing out from the amorphous system while at 1500°C the matrix was also crystallizing as α-Si₃N₄ and TiN crystals have crystallized sufficiently and are growing in size. The TEM images confirm this observation. The HRTEM image showed that the NCHTi2.5-14 sample (Figure 4.29) consists of nanocrystals with sizes ranging from 1.5 to 4 nm embedded in a bright-appearing network which revealed the typical phase contrast of amorphous materials. The low magnification TEM image (inset) demonstrated the homogeneous distribution of nanocrystals in the matrix.
Based on the selected area electron diffraction (SAED) pattern (inset in Figure 4.29), the indexation of \textit{fcc} TiN is confirmed but the continuous rings demonstrated the relatively low degree of crystallinity of TiN nanocrystals as shown by X-ray diffraction. The average $d_{(200)}$ for TiN nanocrystal was found to be 0.26 nm.

In the \textbf{NCHTi2.5-15} sample we can see crystallization of alpha phase of Si$_3$N$_4$ along with TiN nanocrystals (Figure 4.30). The $d_{(100)}$ for Si$_3$N$_4$ (green arrows) was matched with literature and found to be 0.66 nm while $d_{(200)}$ (red arrows) for TiN was gain confirmed to be 0.25 nm. The TEM image agrees with the XRD study for the system at 1500°C.
4 Preparation of Si-Zr-N and Si-Hf-N ceramics

Zirconium (Z=40) and Hafnium (Z=72) lie below Titanium in the same group IVB. Having similar electronic configuration in the outermost shell, ZrN and HfN are expected to have similar electronic and thermal properties than TiN. The section is divided into two groups, first modification of polysilazanes, PHPS and HTT1800, with tetrakisdiethylamidoZirconium(IV) (TDEAZr) and second modification of the same polysilazanes with tetrakisdimethylamidoHafnium(IV) (TDMAHf).

4.1 Si-Zr-N ceramics

4.1.1 Synthesis and characterization of Zr modified polysilazanes

As discussed in chapter 2, Si-Zr-N are synthesized using tetrakisdiethylamidoZirconium(IV) (TDEAZr). In this case an alkyl amino group with a bigger ethyl group is considered instead of methyl as in TDMAT. TDEAZr is in liquid state thereby facilitating easy handling, although steric hindrance can occur due to larger size of side chain. After the reaction, a yellowish-orange powder is obtained using PHPS and HTT1800 as Si₃N₄ precursors and Si/Zr molar ratio of 2.5.
The polymer systems **NCPZr2.5** (PHPS with TDEAZr) and **NCHZr2.5** (HTT1800 with TDEAZr) have the following elemental composition in wt%.

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>Si</th>
<th>Zr</th>
<th>N</th>
<th>C</th>
<th>O</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NCPZr2.5</strong></td>
<td>14.45</td>
<td>24.7</td>
<td>14.35</td>
<td>27.55</td>
<td>13.85</td>
<td>6.5</td>
</tr>
<tr>
<td><strong>NCHZr2.5</strong></td>
<td>19.55</td>
<td>19.3</td>
<td>16.25</td>
<td>31.19</td>
<td>6.5</td>
<td>7.2</td>
</tr>
</tbody>
</table>

The compositional analysis brings up some interesting observations. Firstly, the Si:Zr ratio of 2.5 fixed before the reaction is obtained with the NCPZr2.5 sample. It shows a ratio of 2.69 which is very close to the theoretical value. In contrast, the **NCHZr2.5** sample displays a ratio of 3.26. This implies that the extent of reaction in **NCPZr2.5** sample is higher than in the **NCHZr2.5** sample. This is attributed to the high steric hindrance faced by the vinyl groups in HTT1800 as we demonstrated for the **NCHTi2.5** sample. The presence of small amount of oxygen is due to the highly volatile and sensitive nature of TDEAZr precursor. Figure 4.31 shows FTIR spectra of **NCPZr2.5** and **NCHZr2.5** with comparison to PHPS and HTT1800. For the **NCPZr2.5** sample it can be clearly seen that the reaction has occurred at both N-H (3400 cm\(^{-1}\) and 1180 cm\(^{-1}\)) and Si-H (2100 cm\(^{-1}\)) bonds as the intensity of these bonds decreases. The extent of reaction in **NCHZr2.5** sample is lower as the N-H bonds at 3400 cm\(^{-1}\) and 1180 cm\(^{-1}\) are still visible in the polymer. Even the intensity of Si-H bonds between the **NCHZr2.5** and HTT1800 does not decrease much.
Figure 4.31 FTIR spectra of a) NCPZr2.5 and b) NCHZr2.5 samples

4.1.2 Polymer to ceramic conversion

The ceramic yield of both polymers was investigated under NH$_3$ using TGA and compared with the native polymer (Figure 4.32).

Figure 4.32 TGA under NH$_3$ of NCPZr2.5 and NCHZr2.5 samples and comparison with native polymers

The NCPZr2.5 sample displays a ceramic yield of 46% while the NCHZr2.5 sample exhibits a higher ceramic yield of about 53.5%. This is contrary to what was expected as in case of the NCPTi2.5 and NCHTi2.5 samples. The latter had a lower ceramic yield. We can suggest that the NCHZr2.5 sample has less Zr-based groups that NCPZr2.5 sample due to lower extent of reaction between TDEAZr and HTT1800 as explained in the previous section. The behavior
of decomposition for NCHZr2.5 sample is very similar to HTT1800-R120 as shown in the Figure 4.32. It should be noted that the TGA of HTT1800-R120 is performed under N\(_2\) but we expect the profile under NH\(_3\) to be similar but with a higher weight loss. The polymer to ceramic conversion mechanism for NCPZr2.5 and NCHZr2.5 systems under ammonia is similar to those for Ti modified PHPS and HTT1800 and hence are not discussed again.

### 4.1.3 Microstructural evolution and high temperature behavior

The microstructural evolution of both NCPZr2.5·10 and NCHZr2.5·10 system with annealing temperature was studied using XRD.

After thermal decomposition under NH\(_3\), the samples labelled NCPZr2.5·10 and NCHZr2.5·10 are x-ray amorphous as shown in Figure 4.33. The following section investigates the annealing treatment of these samples. As we move up to 1400°C, sharp peaks corresponding to nanocrystalline phase appear at 33.8°, 39.3°, 56.75°, 67.75°, 71.15° and 84.5°. The peaks matched with cubic ZrN phase (JCPDS file: 04-004-2860) with space group Fm-3m(225). The crystallite calculated at the dominant (111) peak was found to be 28.92 nm. Small peaks corresponding to alpha phase of Si\(_3\)N\(_4\) start appearing at this temperature. This tends to suggests that the interaction of Zr at the molecular scale does not shift the crystallization of the matrix to higher temperature as Ti can do it. This can be attributed to the fact that with the same Si/M ratio, the quantity of Zr introduced in PHPS is lower than the quantity of Ti introduced in the same polymer. Upon further annealing for NCPZr2.5·15 sample we observe an increase in the crystallite size of the nanophase along with a leftward shift for the peaks. After annealing at 1600°C (NCPZr2.5·16) the nanophase peak shift to 33.36°, 38.74°, 56.06°, 66.89°, 70.32° and 83.42° which correspond to cubic ZrC\(_{0.5}\)N\(_{0.5}\) cubic phase (JCPDS file: 04-001-6512). The crystallite size calculated at dominant (111) peak of ZrCN was found to be 32.82 nm.
Figure 4.33 XRD depicting the phase evolution for NCPZr2.5-10 with temperature above 1000°C

This movement of nanophase peaks with temperature can be clearly seen in the inset of Figure 4.33. The observation is very contrary to what was expected. This implies that due to the large size of the ethyl side chain in TDEAZr, some carbon is trapped in the polymer network and does not react with NH$_3$ during the pyrolysis up to 1000°C. Above 1400°C the carbon in the matrix dissolves in the crystallizing nanophase and forms carbonitride via solid solution mixing and reactions.

The annealing behavior of NCHZr2.5-10 sample was different (Figure 4.34). The NCHZr2.5-12 sample is x-ray amorphous; followed by appearance of peaks for both ZrN nanophase and α-Si$_3$N$_4$ for NCHZr2.5-14, similar to NCPZr2.5-14. Upon further annealing up to 1600°C (NCHZr2.5-16), β-Si$_3$N$_4$ crystallizes along with increase in intensity for the ZrN nanophase. The peaks for ZrN were obtained at same positions as for NCPZr2.5-14 sample from 1400°C to 1600°C; these were matched with JCPDS file: 04-004-2860. The crystallite size calculated at the dominant (111) peak varies from 16.2 nm at 1400°C to 21.58 nm at 1600°C. Crystallite size of the nanophase is markedly different for both NCPZr2.5-16 and NCHZr2.5-16. This may be due to the bigger size required for ZrCN crystals formed in the former case.
The Si·Zr·N ceramics derived from using PHPS and HTT1800 are compared to those derived from PMSZ. The nanophase at 1500°C for PMSZr2.5-15 is similar to NCHZrzr2.5-15, i.e., ZrN (Figure 4.35). It was observed that the crystallization of both matrix and nanophase in for the PMSZ derived Si·Zr·N ceramic begins only at 1500°C while for the HTT1800 and PHPS derived systems it begins at a lower temperature, i.e., 1400°C. The average crystallite size for ZrN nanophase calculated at (111) peak at 1500°C was 52 nm. Comparing with other Zr modified polysilazanes, PMSZr2.5-15 has the biggest average crystallite size. Also at 1500°C, PMSZr2.5-15 has the most crystallized matrix in comparison to other two polysilazanes based systems implying that the quantity of Zr introduced at molecular level in PMSZ is the least compared to PHPS and HTT1800 for the same Si/M ratio.
Raman spectroscopy was performed on both systems to confirm the formation of carbonitride/nitrides of the nanophase and the atom vacancies in the nanophase system. Figure 4.36 shows the Raman spectra for NCPZr2.5-10 and NCHZr2.5-10 sample above 1000°C.

For the NCPZr2.5-10 sample the Raman spectra shows no peaks. The appearance of TA/LA and TO/LO peaks for NCPZr2.5-12 is at similar positions as observed for NCPTi2.5 sample thus signifying presence of nitrogen and zirconium vacancies. The D and G bands at 1320 cm\(^{-1}\) and 1605 cm\(^{-1}\) respectively show the presence of graphitic carbon. The presence of carbon
in this case can be due to carbon from the ethyl group of TDEAZr trapped in the matrix during polymer to ceramic conversion. Upon further annealing to 1400°C (NCPZr2.5-14), the TA/LA peaks deconvolute with the appearance of 2A peak due to second order Raman scattering appears at 320.9 cm⁻¹ and the TO/LO peak centered at 441.2 cm⁻¹ with shoulders at 397.8 cm⁻¹, 479.2 cm⁻¹ and 640.43 cm⁻¹ match with the work of Constable et al²⁰ confirming the formation of ZrN as the nanophase. Surprisingly the D and G bands disappear. For the NCPZr2.5-16 sample the second order scattering peaks disappear completely, TA/LA convolutes into one broad peak and TO/LO separates into two peaks signifying the formation of ZrCₓN₁₋ₓ system. The disappearance of graphitic peaks can thus be attributed to formation of solid solution of Zr-C-N system.

The Raman spectrum NCHZr2.5-12 (Figure 4.36b) is quite different from its PHPS derived analog. The appearance of deconvoluted TA/LA and TO/LO peaks for NCHZr2.5-14 sample suggests the formation of ZrN nanophase. Thus the formation of vacancies of Zr and N occur simultaneously. Upon further annealing at 1600°C the system does not change much and retains the same ZrN nanophase unlike NCPZr2.5-16 sample.

4.1.4 Microstructure analysis using TEM

TEM analysis for the microstructure was performed on a representative sample of NCPZr2.5-14. Figure 4.37 shows the formation of ZrN nanophase crystals with the SAED pattern in the inset (top right corner) confirm the formation of ZrN. The d-spacing between planes marked by the blue lines was found to be 0.25 nm which was found to be in close agreement with that reported for (111) peak for ZrN in the JCPDS file 04-004-2860. On an average the crystallite size calculated at 111 peak as 28 nm is confirmed by the crystals observed in TEM.
As the XRD suggests that there is crystallization of matrix as well at this temperature; we find this to be true as shown in the following Figure 4.38. We can see the crystallized matrix for alpha silicon nitride with the d-spacing calculated for the planes marked with blue lines to be 0.42 nm which matches with d-spacing for silicon nitride calculated at (101) plane in the JCPDS file 04-013-5606. The inset figure shows the homogeneous distribution of ZrN nanocrystals in a crystallizing Si$_3$N$_4$ matrix.

*Figure 4.37 HR-TEM image for NCPZr2.5-14 with SAED pattern for ZrN as inset*
Figure 4.38 HR-TEM image for NCPZr2.5-14 showing crystallizing matrix
4.2 Si-Hf-N ceramics

As discussed in chapter 2, the Si-Hf-N ceramics are synthesized using tetrakis(dimethylamido)Hafnium. After the reaction a whitish-green powder was obtained using PHPS and HTT1800 as Si₃N₄ precursor and a Si/Hf molar ratio of 2.5

4.2.1 Synthesis and characterization of Hf modified polysilazanes

The polymer systems NCPHf₂.₅ (PHPS with TDMAHf) and NCHHFf₂.₅ (HTT1800 with TDMAHf) have the following elemental composition (Table 4.2)

<table>
<thead>
<tr>
<th>Table 4.2 Elemental analysis for NCPHf₂.₅ and NCHHFf₂.₅</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>NCPHf₂.₅</td>
</tr>
<tr>
<td>NCHHFf₂.₅</td>
</tr>
</tbody>
</table>

The Hf content in the polymers is very close to the ratio we set implying good reaction of TDMAHf with both PHPS and HTT1800 which was not the case with TDEA Zr due to issues of steric hindrance. The polymers have a slightly higher content of O because of highly reactive nature of Hf precursor.

Figure 4.39 compares the FTIR spectra of the polyhafnosilazanes with their native polymers. For NCPHf₂.₅ we see that the reaction takes place at both N-H (3400 cm⁻¹ and 1180 cm⁻¹) and Si-H (2100 cm⁻¹) bonds by reactions similar to that occurring in NCPTi₂.₅ polymer. Ionescu et al have done studies on the Si-Hf-N ceramics derived from PHPS albeit with higher Si/Hf ratios, i.e., lower Hf content in the polymer. They found that in case of Hf modified PHPS, the Si-H bond is more involved in the reaction as compared to in Ti modified PHPS via equation (1) mentioned below. For the NCHHFf₂.₅ sample the reaction seems to occur more prominently at the N-H bond rather than the Si-H bond.

\[
\begin{align*}
\equiv Si - H + Hf(N(CH₃)₂)₄ & \rightarrow \equiv Si - N(CH₃) - (Hf(N(CH₃)₂)₃) + CH₄ \quad (1) \\
\equiv Si - NH + Hf(N(CH₃)₂)₄ & \rightarrow \equiv Si - N - Hf(N(CH₃)₂)₃ + H - N(CH₃)₂ \quad (2)
\end{align*}
\]
The extent of this reaction is higher in case of NCPf2.5 as compared to NCHf2.5 because there are 2 moles of Si-H bonds per one mole of PHPS while there is only one mole of Si-H in one mole of HTT1800. Also any group approaching Si-H in HTT1800 will face higher steric hindrance as compared to those approaching in PHPS because of the presence of larger vinyl and methyl groups on Si.

Figure 4.39 FTIR spectra of a) NCPHf2.5 and b) NCHHf2.5 samples

This was confirmed by the $^{13}$C MAS NMR (Figure 4.40) for NCPHf2.5. NCPHf2.5 has signals quite similar to NCPTi2.5 suggesting occurrence of similar type of reactions. The intensity of the signal at 43.5ppm is greater than in the case of NCPTi2.5 sample suggesting higher reaction at the Si-H bond (equation 1) as also suggested by Ionescu et al.

Figure 4.40 $^{13}$C MAS NMR for NCPHf2.5

Figure 4.41 shows the $^{29}$Si MAS for the polymer. It is very similar to that observed for NCPTi2.5. Around -36 ppm we have signals due to presence of proton rich environments of
N\textsubscript{2}SiH\textsubscript{2} and N\textsubscript{3}SiH. These signals confirm the reaction sites of Si-H and N(CH\textsubscript{3})\textsubscript{2}. Another very weak signal at -48ppm suggests the presence of SiN\textsubscript{4} environment.

![Figure 4.41 29Si MAS for NCPHf2.5 polymer](image)

For the NCHHf\textsubscript{2.5} sample (Figure 4.39b) the reaction occurs mainly at N-H (3400 cm\textsuperscript{-1} and 1180 cm\textsuperscript{-1}) and only slightly at Si-H bond. The disappearance of vinyl bonds after the reaction can be attributed to hydrosilylation reaction facilitated by presence of Hf (as explained in case of NCHTi2.5 system).

### 4.2.2 Polymer to ceramic conversion analysis with TGA

The polymer to ceramic conversion for both NCPHf\textsubscript{2.5} and NCHHF\textsubscript{2.5} samples was carried out under ammonia atmosphere at 1000°C. Figure 4.42 compares the TGA profile and ceramic yield for both systems along with their precursor polysilazane.

![Figure 4.42 TGA under NH\textsubscript{3} for NCPHf2.5 and NCHHf2.5](image)
The NCPHf2.5 has a ceramic yield of 69.26% while NCHHf2.5 has a ceramic yield of 66.33%. The overall higher yield in this case as compared to Zr modified polysilazanes is due to presence of methyl groups instead of ethyl in the metal precursors and higher degree of cross-linking as a result of more reaction at Si-H bonds. These Hf based single source precursors have ceramic yields even higher than their Ti based analogues due to similar reason. Upon comparing NCPHf2.5 sample with PHPS we observed an increase in ceramic yield by 1.2%; this implies that presence of Hf enhances the cross-linking due to higher reaction at Si-H bonds which decreases the loss of low molecular oligomers after 250°C as reported by Ionescu et al also. According to solid-state NMR and FTIR studies done by Ionescu et al.\textsuperscript{21} the reaction forms a Si-N-Hf bond (equation 1) with removal of methane via reaction at Si-H bond along with reaction at N-H. This lead to higher degree of cross-linking which in turn leads to lower loss of low weight oligomers. Even though the initial weight loss for NCPHf2.5 sample is higher compared to PHPS, the profile changes once the conversion reaches temperatures where we have hydrosilylation taking place and the latter crosses over the former with a less slope. The rest of the mechanism is very similar in both.

While for NCHHf2.5 sample, the profile all along the conversion is very much similar to HTT1800 except in the very beginning where it experiences a sudden drop. There is difference of 1% in the ceramic yield of NCHHf2.5 sample and pure HTT1800.
4.2.3 High Temperature microstructural analysis

The microstructural evolution of both \textit{NCPHf2.5} and \textit{NCHf2.5} sample with annealing temperature was studied using X-Ray.

At 1000°C, the \textit{NCPHf2.5-10} is mostly x-ray amorphous with four broad peaks centered at 30.5°, 35.1°, 51.2° and 60.5° as shown in Figure 4.43.

![Figure 4.43 XRD patterns depicting phase evolution for NCPHf2.5 with temperature](image)

Upon further annealing, the \textit{NCPHf2.5-14} sample had peaks which became sharper along with appearance of other peaks at 33.99°, 39.47°, 57.02°, 68.08°, 71.48° and 84.87°. By comparing with X-ray patterns in the literature and database it was found that the first of peaks belonged to Hafnium nitride (HfN; JCPDS file: 01-079-5779) while the second set of peaks could be attributes to HfC\textsubscript{0.5}N\textsubscript{0.5} phase (JCPDS file: 04-001-6516). The presence of nitride and carbonitride of the same metal in nanophase with the matrix still being amorphous was an unexpected result as it deviates from the previous discussed Si-Ti-N and Si-Zr-N ceramics. Ionescu et al have studied the Hf modified PHPS system with various mass ratios between Si and Hf but did not report formation of such phase at high temperature. They reported that with increasing Hf content in the polymer the crystallization of silicon nitride matrix was pushed up. Our system, with Si/Hf molar ratio of 2.5 confirms the trend as the amount of Hf in our system is higher than that present in their systems. We observe that the crystallization of the matrix beings at 1500°C with just peaks of α-Si\textsubscript{3}N\textsubscript{4} appearing as marked in the Figure 4.43. The intensity of the matrix peaks is dwarfed as the nanophase
becomes highly crystalline and hence has high intensity. At 1500°C for the NCPHf2.5-15 sample, HfN has the most intense peaks with dominant (111) peak at 30.53° with a crystallite size of 32.59 nm while the crystallite size for HfCN calculated at the dominant (111) peak at 33.99° was found to be 21.72 nm. For the NCPHf2.5-16 sample the HfCN peaks became more intense than HfN with crystallite size increasing to 26.31 nm for HfCN while for HfN the crystallite size decreases to 26.07 nm. For NCPHf2.5-15, the matrix starts crystallizing as α-Si₃N₄. The intensity of the matrix peaks is low even after crystallization at 1600°C due to the highly intense nanophase peaks. The increase in HfCN peak intensity can be attributed to consumption of free carbon in the system in to the Hf-C-N solid solution as is indicated by the Raman spectra for NCPHf2.5-16 sample (Figure 4.44).

The Raman spectrum for NCPHf2.5-16 sample displays two distinct peaks for optical phonons around 500 cm⁻¹ and 600 cm⁻¹ along with decrease in intensity of D and G bands of graphitic free carbon suggesting formation of a metal carbonitride system, thereby confirming the results obtained by XRD.

Following the trend from previous metal modifies HTT1800 polymers we expected the formation of HfN and crystallization of silicon nitride matrix by 1500°C. Figure 4.45 shows the XRD for NCHHf2.5-10 → NCHHf2.5-16.
Figure 4.45 XRD patterns depicting phase evolution for NCHHf2.5 with temperature

The system upon annealing to 1400°C (NCHHf2.5-14) gave sharp peaks corresponding to the HfN having a zinc blende structure as expected (JCPDS file: 01-079-5779). It is a non-centrosymmetric crystal structure. The crystallite size calculated at the dominant (111) peak was found to be 12.84 nm. Upon further annealing till 1500°C under N₂ the existing peaks become sharper along with appearance of a new set of intense peaks at 34.3°, 39.85°, 57.65°, 68.85° and 72.35°. The positions of the peaks were found to be similar to carbonitride belonging to Hf as was observed in the previous system but upon further investigation the peaks were found to belong to another cubic phase of HfN with a rock salt structure. (JCPDS file: 00-033-0592). The two HfN phases differ from each other in terms of their space groups. The crystallite size in NCHHf2.5-15 for ZB·HfN(100) was calculated to be 17.22 nm while for RS·HfN(100) was calculated to be 21.72 nm. In NCHHf2.5-16, we observe the disappearance of ZB·HfN phase while the RS·HfN phase peak increase in intensity and sharpness. The crystallite size for RS·HfN(100) was calculated to be 21.72 nm. The disappearance of the second phase, ZB·HfN, can be explained by looking at the work of Jiang and Chen on 4d and 5d transition metal nitride. They simulated the metal nitrides of the 4d and 5d series in the rock salt and zinc blende structure and compared the calculated values of properties like elastic modulus, bulk modulus and lattice parameters with those obtained experimentally.
They compared the cohesive energy of the various metal nitrides in their rock salt and zinc blende structure. For HfN, it was found that rock salt has higher cohesive energy than zinc blende implying that zinc blende structure is more energetically stable. Also they estimated that under 5GPa of pressure ZB coverts to RS structure. Thus the disappearance of ZB at 1600°C may attributed to the energy provided by increases temperature and the pressure encountered by the nanophase from the surrounding matrix as it tries to grow.

The Raman spectroscopy analysis of NCHHf2.5 samples at temperatures above 1000°C allows us to confirm the difference in crystallization behavior of this system and the previous system. Figure 4.46 shows a number of extra peaks as compared to the previous system. Figure 4.46 Raman spectra for NCHHf2.5 system from 1000°C to 1600°C

For NCHHf2.5-14, a broad peak centered around 500 cm\(^{-1}\) can be attributed to the first order optical phonon scattering caused due to N\(^3\) ions. The presence of first order peaks confirms our result of the presence of non-symmetric\(^{25}\) HfN phase (Zinc Blende structure). Second order acoustic scattering peaks 2TA, LA+TA and O·A are visible around 230 cm\(^{-1}\), 262 cm\(^{-1}\) and 360 cm\(^{-1}\) respectively. For NCHHf2.5-15, the previously mentioned second order acoustic peaks are still visible but the optical phonon peak appears broadened. After annealing at 1600°C for NCHHf2.5-16 sample, we see reappearance of TO/LO peak centered around 500 cm\(^{-1}\) and the second order optical phonon peak A+O centered around 630 cm\(^{-1}\). The XRD suggests the presence of symmetric HfN crystal at this temperature which implies that the first order scattering peaks should disappear. The retention of the first order peaks in
NCHHf2.5-16 sample can be attributed to two things: either the presence of small amount of non-symmetric ZB structured HfN or the crystallization of small amount of Si₃N₄ matrix.

The two systems were compared with PMSZHf2.5-15 sample at 1500°C to see the microstructural difference between them. It was expected that since addition of carbon based groups in the polysilazane does not affect the appearance of the two different HfN structures same would be expected in PMSZHf2.5-15 but the XRD comparison (Figure 4.47) shows that the only one phase of HfN crystallizes at 1500°C in case of Hf modified PMSZ. The HfN crystallizes only in high energy rock salt structure with the matrix nearly amorphous. Thus it is observed that presence of carbon in the polysilazane leads to formation of nitride while a polysilazane without carbon in its structures results in formation of a carbonitride contrary to what would be expected.

Figure 4.47 Comparison between PMSZHf2.5-15, NCPHf2.5-15 and NCHHf2.5-15
4.2.4 Microstructural analysis through TEM

The microstructure of the nanocomposite system was studied using TEM for the representative system NCPHf2.5-14. The Figure 4.48 shows the microstructure of NCPHf2.5-14. The TEM image shows the presence of two different nanocrystals in an amorphous matrix. The set of planes depicted by pink color belong to HfN (JCPs file: 01-079-5779) with a d-spacing calculated at the (200) set of planes as 2.21 Å while the set HfCN of planes depicted by green lines at (111) set of planes was found to be 2.68 Å. The inset figure on bottom right shows the SAED pattern for both HfN and HfCN. The inset top right image shows the continuous rings for an amorphous Si$_3$N$_4$ phase.

Figure 4.48 HR-TEM image for NCPHf2.5-14 with SAED for HfN and HfCN (bottom right) and SAED for Si$_3$N$_4$ (top right)
4. Conclusion

In this chapter we focused on Si₃N₄ and Si-M-N (M = Ti, Zr, Hf) ceramics. We firstly sequenced a one-step synthetic method to obtain polymetallosilazanes. The synthesis consisted to perform the reaction between commercially available polysilazanes such as PHPS and HTT1800 and the low molecular weight metal-containing molecules (which have been already used in chapter 3) with controlled Si:M ratios. The role of chemistry behind their synthesis was studied by FTIR, solid-state NMR and elemental analyses. Two mechanisms involving N-H and Si-H bonds in polysilazanes as well as N(CH₃)₂ groups in metal-containing precursors have been identified. It has been shown that PHPS is the most reactive polysilazane while Hf-based molecules were highly reactive with SiH groups of polysilazanes. Such a difference has an effect on the ceramic conversion and the high temperature behavior of ceramics. Thus, we provided a comprehensive mechanistic study of the polymetallosilazane to Si-M-N ceramic transformation under ammonia based on solid-state NMR coupled with TG experiments. Pyrolysis under ammonia generated X-ray amorphous ceramics.

The subsequent annealing of ammonia-treated samples under nitrogen at 1400 °C led to nanocomposites made of MN nanocrystals dispersed in an amorphous or crystallized matrix depending on the nature of the metal and the Si:M ratio fixed at molecular scale. After annealing to 1500°C, the effect of the chemistry of the polysilazane on the matrix crystallization was demonstrated. We found that the addition of Ti or Hf to PHPS in the correct Si:M molar ratio led to suppression of the matrix crystallization up to 1800°C. This generates a system where we have controlled growth of nanostructured metal nitride crystals within an amorphous ceramic matrix. These materials have been prepared as mesoporous components in the chapter 5.
References


33. PhD. Thesis Mirna Bechelany, University of Lyon, 2011
CHAPTER 5
SHAPING AND APPLICATION
1. Introduction

The emerging hydrogen economy addresses environmental and energy challenges faced by society by envisaging the production of electricity using fuel cells. The success of this approach relies heavily on the broad availability of high-purity hydrogen (H₂). However, hydrogen is mainly produced by methane reforming; a high temperature process yet expensive and requiring separation techniques to purify it. This is one of the first issues which limit the large scale development of these technologies. Furthermore, the mature technologies for fuel cells involve platinum-based nanoparticles (Pt-NPs) dispersed on a carbon substrate as electrode catalysts for performing the electrochemical reactions (oxygen reduction reaction ·ORR·, hydrogen evolution reaction ·HER·, alcohol oxidation reaction ·AOR·, hydrogen oxidation reaction ·HOR·). But, platinum is a rare, strategic and expensive material and classical carbon supports having a low graphitization degree are sensitive to corrosion at low and medium potentials, which limits the large scale development of these technologies because of cost (catalysts represents 50% of a fuel cell cost and more than 20% of the whole system) and durability issues. Moreover, carbon supports are inactive. Within this context, a major part of the present chapter deals with the processing of the materials developed and characterized in chapters 3 (Si-C-N, Si₃N₄, Si-Ti-N(C)) and 4 (BN, B-Ti-N). These materials are prepared as mesoporous compounds for use as supports of platinum (Pt) nanoparticles: i) in the hydrolysis of sodium borohydride (NaBH₄) to produce hydrogen as an alternative to methane reforming. For these applications, highly stable and catalytically active materials are expected. This is the reason of using Si- and B-based ceramics such as SiC, Si-C-N, Si₃N₄ and BN compounds. Furthermore, TiN has a number of desirable properties that make it uniquely suited as a catalyst support, especially when synthesized at nanoscale¹⁻⁴. However, TiN may suffer from corrosion in harsh environments. Therefore, TiN alone may not propose the necessary stability for the application we target. The design of mixed nitrides in the Si-Ti:N and/or B-Ti:N systems can provide useful properties derived from their component nitrides such as catalytic properties, robustness and chemical stability for catalysis-assisted reactions in harsh environment. In addition, there is a particular interest in controlled synthetic approaches for monolithic structures that provide nanosized materials (because they show improved properties compared with bulk materials), three-dimensional (3D) porosity, connectivity and accessibility. In particular, we pay attention to
tailor the pore size in the mesoscale range (2-50 nm), namely mesopores, to warrant high surface area in order to maximize the contact of catalyst with the fuels such as NaBH₄.

With the structural viewpoints focused on, we describe the synthesis and characterization of monoliths that bear mesopores and provide a very high specific surface area through the template-assisted Polymer-Derived Ceramics (PDCs) route in the systems explored in chapters 3 and 4. We start with the preparation and detailed characterization of mesoporous ceramics including binary (SiC, Si₃N₄, BN) and ternary/quaternary (Si·C·N, Si·Ti·N(C), B·Ti·N) materials using activated carbon monoliths as templates. Supported platinum (Pt) catalysts were prepared by reduction of Pt precursors with hydrogen as a reducing agent and the different systems as supports. A 1 wt% of Pt was targeted. The catalytic behavior of the nanocomposite supported Pt catalyst for the hydrolysis of NaBH₄ was investigated and compared.
2. Design of mesoporous components

The possibility to develop materials bearing tailored mesoporosity can be envisioned by coupling the PDCs route with a templating approach. This process is in general applied to prepare mesoporous PDC powders through impregnation of hard template powders such as ordered mesoporous silica (SBA-15), derived carbon (CMK-3) or zeolite-derived carbon. However, powders have limited practical use. One of the solutions could be to sinter these powders at low temperature by Spark Plasma Sintering (SPS) and generate 3D structures as the preferred configuration. However, this strategy reduces the micro/mesoporosity and develops the macroporosity of the materials. Here, we propose to i) impregnate the porous structure of monolith-type templates (activated carbon monoliths labeled ACM) with particular mesoporosity with a preceramic polymer solution, (ii) performing the subsequent pyrolysis to achieve the precursor-to-ceramic conversion, and then (iii) removing the mold while generating a monolith with tailored mesoporosity.

Firstly, we use three different commercial organosilicon polymers including the PHPS (Si₃N₄ precursor) and HTT1800 (Si-C-N precursor) already detailed in chapter 3 and AHPCS (SiC precursors) to form mesoporous 3D structures. Then, we will briefly speak about mesoporous BN monoliths. In the third section, we will describe Si-Ti-N and B-Ti-N ceramics designed as mesoporous components. The pore architecture of all samples has been assessed at the mesoscopic scale by nitrogen gas adsorption-desorption measurements at 77 °K.
2.1. Preparation of mesoporous SiC, Si-C-N and Si$_3$N$_4$ monoliths

Herein, we used three commercially available liquid precursors to produce mesoporous 3D structures (Fig. 5.1).

AHPCS (SiC precursor) has a nominal structure of \([\text{Si(CH}_2\text{CH=CH}_2\text{HCH}_2]}_{0.1}[\text{SiH}_2\text{CH}_2]_{0.9}\) (Fig. 5.1)$^{10}$. The presence of allyl groups in its structure results in a precursor with improved thermal cure characteristics, as well as enhanced ceramic yield. AHPCS exhibits a three-step decomposition starting from 70 °C to provide SiC and free carbon in a weight loss of 28 % corresponding to 72.0 wt% ceramic yield. The polycarbossilazane HTT1800 (Si-C-N precursor) is a copolymer containing 20 % of methyl/vinyl and 80 % of methyl/hydride substituted silazane units (Fig. 5.1)$^{11}$. HTT1800 can be crosslinked by heating to 180–200 °C then pyrolyzed under nitrogen to produce Si-C-N ceramics with free carbon with a weight loss of 32 % corresponding to a ceramic yield of 68 %. PHPS (Si$_3$N$_4$ precursor, Fig. 5.1) is a highly
reactive preceramic polymer containing two Si-H and N-H functions in its structure\textsuperscript{12,13}. Through pyrolysis under nitrogen, PHPS leads to a composite material composed of a majority of Si\textsubscript{3}N\textsubscript{4} and around 13 wt\% of silicon (Si). Using ammonia as atmosphere, PHPS leads to Si\textsubscript{3}N\textsubscript{4} in a measured weight loss of 30 \%; therefore, the ceramic yield is calculated to be 70 \%.

In the present paper, nanocasting provides access to mesopores by replicating the nanostructure of activated carbon monoliths labeled ACM into mesoporous 3D structures. Two key factors need to be appropriately selected during the processing of the mesoporous 3D structures from AHPCS, HTT1800 and PHPS. They are the mass ratio between the preceramic polymers and the template as well as the heat treatment conditions to convert the corresponding ceramics and remove the template. These two factors have a strong impact on the structural properties of the final materials and the cohesion of the materials after pyrolysis and template removal. The most appropriate processing parameters have been selected based on the specific surface area (SSA) and the structural stability of the well representative mesoporous 3D Si\textsubscript{3}N\textsubscript{4} structure after pyrolysis of PHPS/ACM and the template removal step. Table 5.1 shows the effect of the mass ratio for the sample mSi\textsubscript{3}N\textsubscript{4}10.
Table 5.1 Effect of the mass polymer-to-template ratio fixed during impregnation of PHPS in ACMs

<table>
<thead>
<tr>
<th>Mass Ratio (PHPS:ACMs)</th>
<th>Specific surface area (m² g⁻¹)</th>
<th>Pyrolysis and template removal step</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 (product collapsed during processing)</td>
<td>511.0</td>
<td>1°C min⁻¹ heating rate till 1000°C, dwell time of 10 hours and cool to RT at 1°C min⁻¹; atmosphere NH₃</td>
</tr>
<tr>
<td>1</td>
<td>216.3</td>
<td>1°C min⁻¹ heating rate till 1000°C, dwell time of 10 hours and cool to RT at 1°C min⁻¹; atmosphere NH₃</td>
</tr>
<tr>
<td>1.4</td>
<td>494.1</td>
<td>1°C min⁻¹ heating rate till 1000°C, dwell time of 10 hours and cool to RT at 1°C min⁻¹; atmosphere NH₃</td>
</tr>
<tr>
<td>1.8</td>
<td>501.7</td>
<td>1°C/min heating rate till 1000°C, dwell time of 10 hours and cool to RT at 1°C/min; atmosphere NH₃</td>
</tr>
</tbody>
</table>

Based on the values of the SSA, a mass polymer-to-template ratio of 1.4 has been fixed. It represents the minimal ratio to avoid the collapse of the structure of monoliths during the pyrolysis. Above this ratio, the monoliths display low SSA values. This means that a mass polymer-to-template ratio of 1.4 brings about an appropriate combination of voids in the pore walls which can generate a large porosity and in turn a large pore volume without altering the mechanical robustness of the materials. Based on the results obtained with PHPS, we apply the same ratio using AHPCS and HTT1800 as SiC and Si-C-N precursors, respectively.

The composites **AHPCS/ACM**, **HTT1800/ACM** and **PHPS/ACM** have been subjected to various final pyrolysis programs and pyrolysis temperatures to select the ideal ones which allowed obtaining 3D structures with a sufficient structural integrity, high SSA as well as pore volumes after template removal. Here, we need to distinguish the couple **AHPCS/ACM** and **HTT1800/ACM** from **PHPS/ACM**. Within this context, we discuss firstly on the characterization of SiC and Si-C-N 3D structures then on the characterization of Si₃N₄ 3D
structures combining nitrogen gas adsorption-desorption measurements, X-ray diffraction and/or SEM. Complete characterization is done at mesoscale. The objective is to select the best material in terms of SSA and pore volume in each composition.

2.1.1 Mesoporous SiC and Si-C-N monoliths:

2.1.1.1 Synthesis strategy
For \textit{AHPCS/ACM} and \textit{HTT1800/ACM}, the formation of mesoporous 3D structures is achieved within two steps including the pyrolysis to convert AHPCS into SiC and HTT1800 into Si-C-N ceramics and the template removal step. The determination of the final pyrolysis temperature in the first step is crucial because it is expected to produce a material which is sufficiently stable (thermally and chemically) for the second heat treatment performed under air (template removal step). Within this context, the samples \textit{AHPCS/ACM} and \textit{HTT1800/ACM} are heat-treated at different temperatures in the range 1000-1600 °C before the template removal step which has been fixed at 600 °C for 5 hours. The temperature is selected after performing TGA on the sample in which a sudden drop in weight is observed in the temperature range 500-600 °C due to oxidation of carbon template.

2.1.1.2 Characterization:
The monoliths prepared by nanocasting were characterized using BET technique to measure the specific surface area of the samples and to confirm the type of porosity created in the system. XRD on the crushed monoliths was done to confirm the formation of intended ceramic phase.

The pore architecture of samples m\text{SiCX} (from \textit{AHPCS/ACM}) and m\text{Si-C-NX} (from \textit{HTT1800/ACM}) (X being the two first numbers of the final temperature, \textit{e.g.}, 12 for 1200) is assessed at the mesoscopic length scale by nitrogen gas adsorption-desorption measurements at 77 K (Figure 5.2. (for m\text{SiCX}) and Figure 5.5. (for m\text{Si-C-NX})).
As expected, the structure of monoliths as well as the pore dimensions may be tailored by the choice of the final temperature. This is highly reflected through the shapes of the isotherms of the mSiCX samples. The mSiC10 and mSiC12 samples show two similar IV type-curves in
which the adsorption and desorption curves do not coincide over the region of relative pressure \( P/P_0 = 0.4-0.99 \) indicative of \( \text{H}_2 \) hysteresis loops for these samples. The IV-type isotherms suggest that the samples have uniform mesoporous channels\(^{13,14} \) while \( \text{H}_2 \) hysteresis loops are generally found in disordered porous materials or in ordered mesoporous material with 3-D cage-like pores and interconnected pores\(^{15} \). Based on the structure of ACM, we can consider that \( \text{mSiC}_{10} \) and \( \text{mSiC}_{12} \) are mesoporous materials bearing interconnected porosity. The specific BET surface area is 396.5 m\(^2\) g\(^{-1}\) for the sample \( \text{mSiC}_{10} \) and 581.4 m\(^2\) g\(^{-1}\) for the sample \( \text{mSiC}_{12} \). The SSA of the sample \( \text{mSiC}_{12} \) is close to that one reported by Zhao \textit{et al.} on ordered mesoporous PCS-derived SiC powders when temperature of pyrolysis of 1200 °C\(^{16} \). The micropore area for \( \text{mSiC}_{10} \) is 244.2 m\(^2\) g\(^{-1}\), whereas there are no micropores in the sample \( \text{mSiC}_{12} \). The total pore volume determined from the amount of nitrogen adsorbed at \( P/P_0 = 0.97 \) for \( \text{mSiC}_{10} \) is 0.34 cm\(^3\) g\(^{-1}\) and it increases to 0.76 cm\(^3\) g\(^{-1}\) for the fully mesoporous \( \text{mSiC}_{12} \). The pore size distribution (PSD) calculated from desorption branch by means of the Barett-Joyner-Halenda method gives an average pore diameter of 5.26 nm (Figure 5.3). It should be mentioned that the SiC composition of the sample \( \text{mSiC}_{10} \) cannot be retained under the air-treatment to remove ACM. Silica is generated. A treatment at 1200 °C before template removal enhances the thermal stability during the subsequent air-treatment.

Figure 5.4 shows that the profiles of isotherms significantly change for the samples \( \text{mSiC}_{14} \) and \( \text{mSiC}_{16} \) and correspond to II-type isotherms suggesting the formation of macroporous or non-porous samples. The samples exhibit specific BET surface areas ranging from 63 m\(^2\) g\(^{-1}\) to 83 m\(^2\) g\(^{-1}\) which significantly decrease in comparison to \( \text{mSiC}_{10} \) and \( \text{mSiC}_{12} \). The total pore volume determined from the amount of nitrogen adsorbed at \( P/P_0 = 0.97 \) decreases to 0.36 cm\(^3\) g\(^{-1}\) and 0.24 cm\(^3\) g\(^{-1}\) for \( \text{mSiC}_{14} \) and \( \text{mSiC}_{16} \), respectively. We suggest that the possible reason is the mesostructural/framework shrinkage of the ACM host accompanied by a tremendous decrease in the volume of the pores due to the high-temperature treatment. The high-temperature treatment involves the crystallization of the \( \beta \)-SiC phase above 1200 °C as shown in the X-ray diffraction patterns of these materials. The samples \( \text{mSiC}_{10} \) and \( \text{mSiC}_{12} \) are X-ray amorphous whereas the samples \( \text{mSiC}_{14} \) and \( \text{mSiC}_{16} \) show the main diffraction peaks of the \( \beta \cdot \text{SiC} \) phase ((111) at 35.6°, (220) at 59.9° and (311) at 71.7°) as well as of \( \beta \cdot \text{SiC} \) and \( \beta \cdot \text{SiC} \) through the two poorly intense peaks at 41.5° and 76°.
Figure 5.4 XRD patterns of mSiCX monoliths with temperature

The same behavior is observed with the samples \( \text{mSi-}$C\cdot\text{NX} \) (\( X = \) first two numbers of annealing temperature for eg. At 1200°C the sample is labelled \( \text{mSi-}$C\cdot\text{N12} \)) in the nitrogen adsorption desorption isotherms (Fig. 5.5).
Figure 5.5 BET isotherm for mSi-C-NX monoliths with temperature

Figure 5.6 Pore size distribution of mSi-C-N12 monolith
The isotherms of mSi-C-N\textsubscript{10} and mSi-C-N\textsubscript{12} show IV type-curves in which the adsorption and desorption curves do not coincide over the region of relative pressure $P/P_0=0.4-0.99$. We can suggest that the adsorption hysteresis represents a H2-type for both samples. Therefore, we suggest that the samples mSi-C-N\textsubscript{10} and mSi-C-N\textsubscript{12} are mesoporous materials with interconnected pores similarly to mSiC\textsubscript{10} and mSiC\textsubscript{12}. A specific BET surface area as high as 623.7 m\textsuperscript{2} g\textsuperscript{-1} is measured for the sample mSi-C-N\textsubscript{12} which is significantly higher than the values reported by Kim et al. on HTT1800-derived Si-C-N powders using CMK-3 and CMK-8 as templates\textsuperscript{17}. The total pore volume determined from the amount of nitrogen adsorbed at $P/P_0 = 0.97$ is 0.77 cm\textsuperscript{3} g\textsuperscript{-1}. The pore size distribution (PSD) is calculated from the desorption branch (Figure 5.6) by means of the Barrett-Joyner-Halenda method. A uniform diameter of 4.9 nm is found. In contrast, the sample mSi-C-N\textsubscript{14} proposes II-type isotherms suggesting the formation of macroporous or non-porous samples. The specific BET surface area decreases to 111.4 m\textsuperscript{2} g\textsuperscript{-1} in line with the total pore volume decreasing to 0.36 cm\textsuperscript{3} g\textsuperscript{-1}. These results confirm the behavior observed with the samples mSiC\textsubscript{14}. However, the sample mSi-C-N\textsubscript{14} is X-ray amorphous as shown on the corresponding X-ray diffraction patterns. This confirms that the decrease of the SSA in the samples mSiC\textsubscript{14} and mSi-C-N\textsubscript{14} is mainly due to the high temperature heat-treatment which probably involves framework shrinkage. Surprisingly, the sample mSi-C-N\textsubscript{16} shows a IV-type curve suggesting that the sample displays uniform mesoporous channels. Furthermore, at relative pressures below 0.1, the relatively high uptake implies the presence of micropores. The shape of the isotherm is asymmetrical with a desorption branch steeper than the adsorption branch at a relative pressure ($P/P_0$) from 0.4 to 0.99 indicative of H2 hysteresis loop. The sample displays a SSA of 490.7 m\textsuperscript{2} g\textsuperscript{-1} and a pore volume of 0.74 cm\textsuperscript{3} g\textsuperscript{-1}; the reason of this behavior may be understood through the XRD patterns (Figure 5.7). Like the samples mSiCX, the heat-treatment of the samples mSi-C-NX at high temperature involves the nucleation of the $\beta$-SiC phase as shown in the X-ray diffraction patterns of these materials. The samples mSi-C-N\textsubscript{10}, mSi-C-N\textsubscript{12} and mSi-C-N\textsubscript{14} are X-ray amorphous whereas mSi-C-N\textsubscript{16} shows the main diffraction peaks of $\beta$-SiC and small peaks of mixture of $\beta$-Si\textsubscript{3}N\textsubscript{4} and $\alpha$-Si\textsubscript{3}N\textsubscript{4} phases. $\beta$-SiC is formed through the carboinduction of Si\textsubscript{3}N\textsubscript{4} in the sample mSi-C-N\textsubscript{14}. This involves the removal of nitrogen from the volume of the component while SiC is formed. As a consequence, we suggest that nitrogen leaves pores in the samples mSi-C-N\textsubscript{16} to increase its SSA and pore volume. The main disadvantage is the lack of control over total mesoporosity.
2.1.2 Mesoporous Si₃N₄ monoliths

2.1.2.1 Synthesis strategy
Three strategies are investigated to prepare mesoporous Si₃N₄ 3D structures. Firstly, we should mention that heat-treatment in air to remove ACM after the polymer-to-ceramic conversion systematically leads to silica. As a consequence, the template removal step is performed under ammonia according to our previous work. The first strategy consists to pyrolyze PHP/ACM under nitrogen at 1000 °C for 2 h followed by removal of template under ammonia at 1000 °C for 5 h. In the second strategy, conversion and removal of template are achieved in the same step under ammonia. In the third strategy, the pyrolysis is first performed under nitrogen up to 400 °C then under ammonia up to 1000 °C.

The first strategy does not allow fully removing the template whereas the second strategy is effective in both conversions of PHPS into Si₃N₄ and removal of the carbonaceous template. However, it leads to the formation of a monolith with a very poor robustness. As a consequence, we applied the third strategy which involves the use of both nitrogen and ammonia in the same heat treatment process. This leads to the best results in terms of SSA.

Figure 5.7 XRD patterns of mSi-C-NX monoliths with temperature.
(653.8 m² g⁻¹), structural integrity and template removal. Such a SSA value is close to the values we got for ordered mesoporous PHPS-derived Si₃N₄ powders using CMK3 as a template. The system is first treated in flowing nitrogen up to 400 °C to ensure sufficient conversion of the preceramic polymer to a cross-linked state which has some structural stability and then the gas is changed to ammonia through a continuous pyrolysis up to 1000 °C. A dwell time of 1 h at 400 °C is employed to switch the gas and a dwell time of 5 h is employed at 1000 °C for effective conversion and template removal. The pore architecture of the sample mSi₃N₄₁₀ by BET (micropores and mesopores scale) is discussed below based on the BET isotherms reported in Figure 5.8.

The sample mSi₃N₄₁₀ demonstrates mesoporosity according to the nitrogen sorption isotherms (Fig. 5.8). Analysis of the isotherms allows identifying a IV type curve typical for mesoporous adsorbents with distinct capillary condensation branches. The shape of the isotherms is asymmetrical with a desorption branch steeper than the adsorption branch at a relative pressure (P/P₀) from 0.4 to 0.9 indicative of H₂ hysteresis loops.

It is observed that the sample mSi₃N₄₁₀, which is X-ray amorphous is not stable though heat-treatments at temperatures higher than 1000 °C under nitrogen. Its specific surface area (as well as mesoporosity) falls drastically with the increased temperature. The reason for this is attributed to the formation of Si₃N₄ nanowires in the porosity starting from 1200 °C (Figure 5.9) while crystallization of α-Si₃N₄ occurs.
Figure 5.9 XRD patterns of mesoporous Si$_3$N$_4$ monoliths with temperature

Figure 5.10 SEM image for mSi$_3$N$_4$412 to mSi$_3$N$_4$416 depicting the growth of nanowires

The formation of nanowires at these temperatures for silicon nitride made via polymer derived ceramic route has been well documented$^8$. Hence for Si$_3$N$_4$ supports, the optimum specific surface area of 653.8 m$^2$ g$^{-1}$ was obtained for the sample mSi$_3$N$_4$410.
2.2. Preparation of mesoporous BN monoliths

The design of mesoporous BN monoliths has been submitted for publication to *J. Mater. Chem. A* and was demonstrated in the PhD thesis of Chrystelle Salameh. Here, we briefly described the process and the main characterization of samples.

2.2.1 Synthesis strategy

We used polyborazylene (PB) (synthesized through thermolysis of borazine at 60°C in an autoclave) to produce the mesoporous 3D BN structures (Fig. 5.11).

It has the nominal structure $[\text{B}_{3.0}\text{N}_{3.5}\text{H}_{4.0}\text{O}_{0.04}]_n$. In the present work, we have prepared a series of mesoporous samples in the temperature range 1000-1450 °C to tune the textural and structural properties. We labeled as-obtained samples mBNX (with X being the temperature), *i.e.*, mBN1000, mBN1200 and mBN1450. Based on the different attempts, a polymer-to-template ratio, *i.e.*, a PB:AC ratio of 0.75, has been fixed during the impregnation step. It represents the minimal ratio to avoid the collapse of the structure of monoliths during the pyrolysis. Above this ratio, the monoliths display low SSA values. After 2 days of aging, washing and drying of the impregnated AC, a two-step pyrolysis allows transforming PB into BN while removing the template. An appropriate heat-treatment procedure consists in a pyrolysis under N$_2$ then under ammonia at 1000 °C (dwelling time of 5 h) delivering the
sample labeled mBN1000. Then the latter is annealed at different temperatures under N\textsubscript{2} up to 1450°C to generate the mBN1450 sample. An intermediate sample labeled mBN1200 has been isolated after annealing at 1200 °C.

2.2.2 Characterization
All the BN samples discussed have an excellent cylinder-like appearance and replicate the monolithic shape of AC (Fig. 5.11). More interestingly, the samples did not reveal any shrinkage and retained the dimension of the template. We investigated Raman spectroscopy to provide information about the lattice vibration modes of the samples and to confirm that AC was removed during the ammonia treatment. The Raman spectrum of the mBN1450 sample shows a signal at 1366 cm\textsuperscript{-1} which indicates the presence of BN (Fig. 5.12). The D and G peaks related to carbon are not identified indicating the complete removal of the carbon template.

We used the semi-quantitative EDX to characterize the elemental composition of the BN samples. A nearly stoichiometric composition (42.5 at% (N) and 57.2 at% (B)) is confirmed with a neglected oxygen content (0.32 at%). We then characterized the mBN1000, mBN1200 and mBN1450 samples at mesoscopic length scale by N\textsubscript{2} physisorption measurements at 77K (Fig. 5.13).
As expected, the structure of the monoliths as well as the pore dimensions may be tailored by the annealing temperature. This is not reflected through the shapes of the isotherms of the BN samples because they display similar isotherms that follow the typical behavior of type IV. This suggests that the samples have uniform mesoporous channels (Fig. 5.13 a). Above a relative pressure $P/P_0$ of 0.4-0.45 and up to 1, the distinct hysteresis loops observed between the adsorption and desorption curves confirm the presence of mesopores. It is identifiable to a H2-type which is generally found in disordered porous materials or in ordered mesoporous material with 3-D cage-like pores and interconnected pores. Based on the structure of ACM, we can consider that the BN samples are disordered mesoporous materials bearing interconnected porosity which was targeted for an efficient nanoconfinement.

The BET SSA (Fig. 5.13 b) and the pore volume (less than 78.08 nm determined from the amount of nitrogen adsorbed at $P/P_0 = 0.975$) are very high. In particular, the pore volume changes from 0.93 (mBN1000) to 0.75 (mBN1450) cm$^3$.g$^{-1}$ (Fig. 5.13 b). The SSA and pore volume values of the BN samples decrease with the increase of the temperature. We suggest

![Figure 5.13](image-url)
that the possible reasons are the crystallization of the BN phase from 1000 to 1450 °C concomitantly with the mesostructural/framework shrinkage of the materials accompanied by a decrease in the volume of the pores due to the high-temperature treatment. The samples exhibit uniform mesopore dimensions according to the \( \text{N}_2 \) desorption calculated from desorption branch by means of the \textit{Barett-Joyner-Halenda} method (Fig. 5.13 c). The TEM images of the \textbf{mBN1000} and \textbf{mBN1450} samples are presented in Fig. 3 and well reflect the above discussion.

A high porosity level is particularly revealed by HRTEM and the local pore diameter matches the pore diameter calculated by the BJH method (See above). The low-magnification TEM (Figure 5.14 a) of the \textbf{mBN1000} sample confirms its porous character made of randomly distributed voids surrounded by a very thin wall. The corresponding SAED pattern which reveals diffuse haloes, as a general feature, has been indexed as the \( P6_3/mmc \) space group and suggests a poorly crystallized BN structure. HRTEM observations (Fig. 5.14 b) reveal the presence of BN layers with a lack of a long range ordering confirming that the structure is rather turbostratic (t-BN). The average number of layers in the walls is comprised between 5 and 10. The HRTEM investigations also confirm the locally high degree of porosity of the \textbf{mBN1450} sample (Fig. 5.14 c). However, a significant change in the crystallinity occurs. The \textbf{mBN1450} sample is made of strongly faceted nanopolyhedral shapes comprising highly crystalline BN layers (Fig. 5.14 d). The degree of crystallinity of the walls appears to be very high in contrast to the observations made by XRD. Figure 5.14d shows that there is a clear continuity between layers of adjacent facets even if locally a discontinuity in the walls and a mismatch within the wall structure can be encountered for this sample. The polyhedron wall thickness has been found to vary from 6 to more than 30 layers with an interlayer spacing found to be 0.34 ± 0.05 nm which is highly constant throughout the sample. The SAED pattern exhibits spots that indicate the formation of a highly crystalline structure presuming a well-ordered B and N-alternating hexagonal pattern belonging to the \( P6_3/mmc \) space group. Such a nanocrystalline quality made of highly crystallized hexagonal BN polyhedra is unusual for polymer-derived BN. The reason is difficult to explain but the use of activated carbon most probably promoted the crystallite growth of BN.
A value of the helium density was found to be equal to 1.95 and 2.03 for mBN1000 and mBN1450 samples, respectively. This is relatively close to the theoretical value of 2.27. The bulk density determined through the ratio of the mass of the monolith samples and its total volume (ten replicate determinations was achieved for the determination of this property) was calculated to be 0.52 (mBN1000) and 0.57 (mBN1450) which indicate 73.3 and 71.9% of porosity, respectively. Interestingly, through this high porosity, mesoporous BN monoliths can be compressed. As an illustration, the mBN1450 sample exhibits a load bearing capacity of the order of 14 N. The calculated values of the ultimate compressive stress are found to be 3.3 MPa which is around 6 times lower than the value found for AC. This is inherently due to the significantly higher porous volume found in the BN samples. However, such a value is the highest ever reported for a monolith of BN with high SSA and pore volumes.\textsuperscript{23}
2.3. Preparation of mesoporous Si-Ti-N monoliths

2.3.1. Synthesis strategy:
Mesoporous Si-Ti-N ceramics are prepared by impregnation of ACM with the NCPTi2.5 (synthesized from PHPS) and NCHTi2.5 (synthesized from HTT1800) polytitanosilazanesexperimentally described in chapter 2 and studied in chapter 4. The Si:Ti ratio of 2.5 is chosen for various reasons. As seen in chapter 3, the NCPTi2.5 and NCHTi2.5 samples are able to produce a nanocomposite at 1400°C where the matrix is still amorphous while the nanophase of TiN starts to crystallize out of the matrix. Any Si:Ti ratio greater than 2.5 does not lead to such a tailored microstructure at high temperature. Although a Si:Ti ratio 1 leads to highly stable amorphous matrix as shown in chapter 4: the viscosity of the polymer increases thereby making it more difficult to impregnate in activated carbon.

To prepare the mesoporous components, we applied the strategy used for mesoporous Si3N4 monoliths. The system is first treated in flowing nitrogen up to 400 °C to ensure sufficient conversion of the preceramic polymer to a cross-linked state which has some structural stability and then the gas is changed to ammonia through a continuous pyrolysis up to 1000 °C. A dwell time of 1 h at 400 °C is employed to switch the gas and a dwell time of 5 h is employed at 1000 °C for effective conversion and template removal.

2.3.2. Characterization:

2.3.2.1. PHPS-derived Si-Ti-N ceramics:
Figure 5.15 shows the evolution of BET isotherm with temperature for mesoporous Si-Ti-N ceramics prepared from NCPTi2.5 precursors (synthesized from PHPS) we label mNCPTi2.5-X (X being the two first numbers of the temperature: 10 for 1000°C).

We note that the samples display similar complex isotherms which represent a mixture of type IV and type II suggesting the presence of microporosity at lower relative pressures and mesoporosity at higher values of relative pressures with 3-D cage-like pores and interconnected pores being disordered16. Above a relative pressure P/P0 of 0.45 and up to 1, the distinct hysteresis loops observed between the adsorption and desorption curves confirmed the presence of mesopores. It is identifiable to a type H2 which is generally found in disordered porous materials or in ordered mesoporous material with 3-D cage-like pores and interconnected pores. Based on the structure of AC, we can consider that the samples
are a micro-/mesoporous material bearing interconnected porosity which was targeted for an efficient use as a catalyst support.

The Table 5.2 shows the SSA values along with the pore volume and pore size for monoliths. SSA values are very high for such compounds and are the highest values reported in the literature for mesoporous PDCs. Furthermore, there is no specific trend observed in the values but unlike previously reported for Si₃N₄ made using similar procedure there is no drop in the SSA values with the increased annealing temperature. To understand such high values, we investigated SEM and, although it is difficult to observe, it appeared that the template is still present in monoliths which means that the general procedure we applied for Si₃N₄ ceramics does not work with Si-Ti-N ceramics whereas the matrix precursor is the same, i.e., PHPS. This means that the extremely high SSA of these samples are attributed to the retention of the template. In this case, the Si-Ti-N material forms a coating over the template and surrounds it preventing its decompositions. Because this phenomenon does not occur with mesoporous Si₃N₄ samples, we decided to prepare mesoporous TiN sample.
using the same strategy from TDMAT (TiN precursor that has been used to react with matrix precursors, \textit{i.e.}, PHPS and HTT1800 forming the polytitanosilazanes).

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>SSA (m(^2)/g)</th>
<th>Pore volume (cm(^3).g(^{-1}))</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
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<td>3.4</td>
</tr>
<tr>
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<td>0.63</td>
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</tr>
<tr>
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<td>0.67</td>
<td>3.3</td>
</tr>
<tr>
<td>mNCPTi2.5-16</td>
<td>1143</td>
<td>0.66</td>
<td>3.2</td>
</tr>
</tbody>
</table>

\textbf{Figure 5.16} Nanocomposite coating over activated carbon template

\textbf{2.3.2.2. TDMAT-derived TiN:}

As described before the monoliths were prepared using the same heat treatment as Si\(_3\)N\(_4\) monoliths. The monoliths obtained after pyrolysis were black in color with a golden tinge on the surface. The pore architecture of the mesoporous TiN sample was assessed at the mesoscopic scale by nitrogen gas adsorption-desorption measurements at 77 °K. Figure 5.17 shows the BET isotherm for the TiN monoliths prepared at 1000°C and 1400 °C.
The BET isotherm for TiN (Figure 5.17) prepared at 1000°C, i.e., mTiN-10, is a mixture of type II and type IV isotherms. At low pressures (below $P/P_o = 0.4$) the curve represents type II isotherm indicating a presence of micropores in the system. While in the higher pressure regime it looks like type IV isotherm with H2 hysteresis suggesting the presence of disordered interconnected mesopores. The BET adsorption isotherm of the mTiN-14 sample, although distorted with a thinner hysteresis, still retains its character as a mixture of type II and IV isotherms with H2 hysteresis. The SSA and pore volume for the former is found to be 1088 m$^2$ g$^{-1}$ and 0.58 cm$^3$ g$^{-1}$ while for the later the SSA decreased to 872 m$^2$ g$^{-1}$ and the pore volume to 0.46 cm$^3$ g$^{-1}$. Values for SSA at 1000 °C exceed that of the activated carbon template by close to 100 m$^2$ g$^{-1}$. The average pore diameter calculated using the desorption branch of BJH curve is found to be 3.33 nm in the mTiN-10 sample and 3.8 nm in the mTiN-14 sample. Therefore, the behaviour of the mesoporous TiN sample is close to that of the mesoporous Si-Ti-N ceramics and different from the mesoporous Si$_3$N$_4$ sample. We therefore suggest that TiN can act as a diffusion barrier for NH$_3$, as it acts as barrier diffusion for metals$^{19-22}$. Thus it is possible that the initial treatment performed under N$_2$ during the preparation of TiN...
and Si-Ti-N ceramics forms a coating over the surface of activated carbon to protect it from being eaten away by NH₃. TGA of activated carbon under NH₃ revealed the beginning of mass loss to be above 500°C. This supports our hypothesis that the activated carbon is protected by a coating over it.

2.3.2.3. HTT1800-derived Si-Ti-N ceramics:
The adsorption–desorption isotherms of the Si-Ti-N ceramics prepared from NCHTi2.5 precursors (synthesized from HTT1800) we label mNCHTi2.5-X (X being the two first numbers of the temperature: 10 for 1000°C) are similar to mNCPTi2.5-X samples (Figure 5.18). The SSA value for the mNCHTi2.5-10 sample is obtained to be 1326 m².g⁻¹ with a pore volume of 0.69 cm³/g. The pore size distribution (PSD) calculated from desorption branch by means of the BJH method gives an average pore diameter of 3.45 nm. Although there is a small drop in the SSA value in the mNCHTi2.5-14 sample (1028 m².g⁻¹), the isotherm profiles still remain the same with mixture of types II and IV with H₂ hysteresis and a similar pore size of 3.5 nm.

2.3. Preparation of mesoporous B-Ti-N monoliths

2.3.1. Synthesis strategy
The preparation of mesoporous components in the B·Ti·N system was only possible with polytitanoborazine synthesized from ammonia borane (AB). In particular, they have been prepared using the ABTi₃ precursor (synthesized from ammonia borane with a B·Ti ratio of 3). The BET isotherms (Figure 5.19) are similar to those of Si based nanocomposite. The SSA
and pore volume for the 1000°C and 1400 °C systems are 1326 m².g⁻¹, 0.7 cm³.g⁻¹ and 1028 m².g⁻¹, 0.55 cm³.g⁻¹, respectively. The nature of the porosity is same as the previous case, a complex mix of type IV and type II isotherms representing microporosity at low pressure (P/P₀<0.45) and mesoporosity at high pressures (P/P₀>0.45) with a H2 type hysteresis curve suggesting interconnected porosity, and the retention of the activated carbon template can be attributed to the presence of titanium nitride in the system. The evolution is studied only till 1400°C as BN matrix is known to crystallize at 1450°C and we prefer a system with an amorphous matrix and crystallizing nanophase. Such a system is preferred since the amorphous matrix protects the metal nitride nanocrystal and hinders grain growth. These metal nitride nanocrystals are known to exhibit interesting catalytic and photocatalytic properties at such low sizes⁵³ as discussed in chapter 1.

![BET isotherm and PSD for mABTi3 at 1000°C and 1400°C](image)

As-obtained high SSA and pore volume mesoporous samples have been used as platform to grow catalytically-active platinum nanoparticles (NPs). Then, to assess the catalytic activity
of the Pt-supported mesoporous samples, these systems are tested for hydrolysis of NaBH\textsubscript{4} to generate hydrogen in aqueous medium: the performances have been finally compared.

### 3. Design of Pt-supported mesoporous Components-Catalytic application

Catalytic activity of metal nanoparticles is dependent on their shape, size, crystal structure and textural parameters. Furthermore, it can be suitably increased by selecting a support system on which nanoparticles are preferentially synthesized with tailored shapes, sizes and crystalline structure without agglomeration. Because the transport of materials to active sites of catalyst is controlled by diffusion through the pores of the support system\textsuperscript{24}, the support is expected to be prepared with tunable pore morphologies, accessible porosity\textsuperscript{25}. In particular, the high specific surface area (SSA) of mesopores in the samples prepared in their previous part should provide selectivity and active sites to be effectively accessed for catalysis.

Pt NPs are deposited on mesoporous samples using hexahydrated chloroplatinic acid as Pt precursor by wet impregnation followed by chemical reduction in hydrogen/argon flow (See experimental part in chapter 2). The attractiveness of a supported catalyst lies in the low amount of Pt loaded. We supported 1 wt% of Pt only. The successful loading of Pt on the supports has been verified by BET and ICP/EDXS. The activity of Pt-supported mesoporous samples for the hydrolysis of sodium borohydride is investigated at 80 °C, in a very alkaline solution (pH > 10; 2% NaOH), and with the presence of water (1 mL such as 1 mol NaBH\textsubscript{4} for 17.5 mol H\textsubscript{2}O; water excess of 438%) according to Eq. (1a and 1b).

\[
\text{BH}_4^-(aq) + 2\text{H}_2\text{O}(l) \rightarrow \text{BO}_2^-(aq) + 4 \text{H}_2(g) \quad (1a)
\]
\[
\text{BH}_4^-(aq) + 4\text{H}_2\text{O}(l) \rightarrow \text{B(OH)}_4^-(aq) + 4 \text{H}_2(g) \quad (1b)
\]

By hydrolysis, molecular hydrogen is spontaneously released by reaction of one hydric hydrogen (H\textsuperscript{d-}) of NaBH\textsubscript{4} with one protic hydrogen (H\textsuperscript{d+}) of H\textsubscript{2}O, which thus provides half of the H\textsubscript{2} generated. The volume of hydrogen generated during the synthesis is calculated. The by-product, sodium tetrahydroxyborate, may be recycled back into NaBH\textsubscript{4} via a complex process but this is not the subject of the present study. The imposed conditions are considered as being harsh for any catalyst support. It should be mentioned that we synthesized a Pt-supported activated carbon monoliths for comparing the performance of the mesoporous
samples we prepared in the first part of the present chapter. However, the mesoporous BN and B·Ti·N samples have been no longer investigated because their performance as catalytic support was poor. In the following section, we firstly describe the preparation, characterization and catalytic activity of Pt·supported SiC, Si·C·N and Si₃N₄ samples before investigating Pt·supported Si·Ti·N samples.

3.1. Catalytic activity of Pt-supported SiC, Si-C-N and Si₃N₄ samples

3.1.1. Pt impregnation

Based on the previous results and discussion, the samples \( m\text{SiC}_{12}, \text{mSi}-\text{C·N}_{12}, \text{mSi₃N₄}_{410} \) have been selected according to their high BET SSA values, large pore volume and tailored mesoporous structure. These characteristics are positive features for the growth of Pt NPs which is investigated in the following section of this paper. Pt NPs are deposited on \( m\text{SiC}_{12}, \text{mSi}-\text{C·N}_{12} \) and \( \text{mSi₃N₄}_{410} \) to form nanocatalysts labelled \( \text{Pt·mSiC}_{12}, \text{Pt·mSi-C·N}_{12} \) and \( \text{Pt·mSi₃N₄}_{410} \). These materials are used to catalytically activate the hydrolysis of NaBH₄. The successful loading of Pt on the supports has been verified by BET (Figure 5.20) and EDXS.
As mentioned previously, we targeted 1 wt% of Pt. This was confirmed by EDXS: EDXS spectroscopy indicates the presence of 1.54 wt%, 1.79 wt% and 1.12 wt% for Pt-mSiC12, Pt-mSi-C-N12 and Pt-mSi3N410, respectively. Since the loading content is low, it is necessary to continuously ultra-sonicate the solution containing the platinum salt and the support system for 24 h. The heat treatment of the supported samples under hydrogen to reduce the palatinate to metallic platinum is done at 450 °C\textsuperscript{26}. The process does not affect the structural stability in any way and allows keeping the mesoporosity of the support with a decrease of the SSA values as shown in Figure 5.20 and Table 5.3.

**Table 5.3 SSA values of samples Pt-mSiC12, Pt-mSi-C-N12 and Pt-mSi3N410.**

<table>
<thead>
<tr>
<th>Samples</th>
<th>SSA (m\textsuperscript{2} g\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before impregnation</td>
</tr>
<tr>
<td>mSiC12</td>
<td>581.4</td>
</tr>
<tr>
<td>mSi-C-N12</td>
<td>623.7</td>
</tr>
<tr>
<td>mSi3N410</td>
<td>653.8</td>
</tr>
</tbody>
</table>
After Pt growth, the shape of the isotherms and the hysteresis loop of the Pt-mSiC\textsubscript{12}, Pt-mSi-C\textsubscript{N12} and Pt-mSi\textsubscript{4410} samples are similar to the isotherms of the parent mSiC\textsubscript{12}, mSi-C\textsubscript{N12} and mSi\textsubscript{4410}. It can be observed that growth of Pt NPs decreases the SSA to reach values that are close for all the samples as indicated in Table 5.3. This suggests the encapsulation of NPs inside the pore channels. However, the relatively high SSA value after Pt impregnation further proves that the pores of the support are not blocked by nanoparticles larger than the pore size of the support, revealing that the mSiC\textsubscript{12}, mSi-C\textsubscript{N12} and mSi\textsubscript{4410} samples hinder the agglomeration or migration of the nanoparticles. This is also fundamental to allow diffusion of borates through the porosity during hydrolysis of NaBH\textsubscript{4}.

### 3.1.2. Hydrolysis of NaBH\textsubscript{4}

The activity of Pt-mSiC\textsubscript{12}, Pt-mSi-C\textsubscript{N12} and Pt-mSi\textsubscript{4410} for the hydrolysis of sodium borohydride is investigated at 80 °C, in a very alkaline solution (pH > 10), and with the presence of water. The hydrogen generation results are presented in Figure 5.21. It should be mentioned that we synthesized a Pt-supported activated carbon monoliths labelled Pt-ACM through the same process we applied to prepare Pt-mSiC\textsubscript{12}, Pt-mSi-C\textsubscript{N12} and Pt-mSi\textsubscript{4410}.

Figure 5.21 demonstrated the highest performance obtained with the Pt-mSi\textsubscript{4410} sample. A hydrogen generation rate (slope of the curves at a conversion < 50 %) of 4.3 mL min\textsuperscript{-1} was measured. Expressed per gram of Pt, the rate is as high as 24.2 L min\textsuperscript{-1} gPt\textsuperscript{-1} which is the maximum value reported in the literature\textsuperscript{2,3}. The hydrolysis starts immediately; no induction period is observed, which is in agreement with the metallic state of Pt. This is also the case for the Pt-mSiC\textsubscript{12} and Pt-mSi-C\textsubscript{N12} samples but the hydrogen evolution rate is significantly lower: at 50 % conversion, 2.016 mL min\textsuperscript{-1} and 0.68 mL min\textsuperscript{-1} are measured for the Pt-mSiC\textsubscript{12} and Pt-mSi-C\textsubscript{N12} samples, respectively. The results obtained with the Pt-ACM sample is comparable to those obtained with the Pt-mSiC\textsubscript{12} and Pt-mSi-C\textsubscript{N12} samples. During the first minutes, hydrogen release is fast because ACM is well known to contain acid groups available on the surface which can contribute to the generation of hydrogen. However, this fast step is rapidly followed by a process with slow kinetics most probably due to absorption of water that affects the diffusion of the anions BH\textsubscript{4}\textsuperscript{-} and B(OH)\textsubscript{4}\textsuperscript{-}.
Whereas the SSA of the $\text{Pt-mSiC}_{12}$, $\text{Pt-mSi-C-N}_{12}$ and $\text{Pt-mSi}_{3}\text{N}_{410}$ samples are close, we may suggest that silicon-based nitride ceramics are the most appropriate candidates to be used as supports of platinum for the hydrolysis of an alkaline solution of sodium borohydride. This can be due to the interactions with the adsorbed reacting species. Theoretical and computational investigations should make tremendous advances in the understanding of the interest to use silicon nitride as catalytic supports. Further works are under investigation to study the beneficial effect of silicon nitride on the catalytic activity of Pt in comparison to other Si-based supports. Because it displays the highest performance, the microstructure and composition of the $\text{Pt-mSi}_{3}\text{N}_{410}$ sample has been analyzed by elemental mapping and TEM (Figure 5.22a-b), EDXS and elemental mapping (Figure 5.22 c-g).
The $\text{mSi}_3\text{N}_4\text{410}$ sample exhibits a mesoporosity with a lack of ordering as expected. It does not show any crystallinity in the Selected Area Electron Diffraction (SAED) pattern (not shown) confirming its amorphous structure as previously observed by XRD. After Pt growth (Figure 18a), HRTEM investigation allows observing Pt NPs with a spherical shape and we clearly observe their homogeneous distribution on the surface of the $\text{mSi}_3\text{N}_4\text{410}$ sample forming the $\text{Pt}\cdot\text{mSi}_3\text{N}_4\text{410}$ sample. We observe spots belonging to Pt, which crystallizes in
the fcc system (Figure 5.22a). Figure 5.22b shows that a few ones tend to be agglomerated. Then cross-sections have been prepared by using a focused ion beam unit, and EDXS maps were superimposed on the cross-sectional images (Figure 5.22g). Elemental mapping (Figure 5.22c–f) reveals the uniform distribution of silicon and nitrogen from the support as well as Pt on Pt-mSi₃N₄₁₀. The sample mSi₃N₄₁₀ displays a typical chemical formula determined by Energy Dispersive X-ray Spectroscopy (EDXS) of Si₃₀·O₈·N₄₁. The relatively low O content level is mainly associated with physisorbed/chemisorbed water from the internal and external surface of the samples.

However, we should point to the fact the hydrogen production under the reaction conditions we imposed was very vigorous. The Pt-mSi₃N₄₁₀ sample collapsed after reaction and in fact, none of the three catalyst support systems were able to withstand the vigorous bubbling of hydrogen and collapsed after reaction. The Pt-mSiC1₂ and Pt-mSi-C·N1₂ samples (which survived the platinum impregnation) collapsed into coarse powders which mostly settled at the bottom of the reaction chamber even with stirring. In contrast, the Pt-mSi₃N₄₁₀ sample formed a suspension with stirring and was stable for a long time even after the stirring was stopped.

Although all materials collapsed after reaction, the performance of the Pt-mSi₃N₄₁₀ sample is significantly superior to platinum-supported silicon carbide and carbonitride confirming the interest of nitride for heterogeneous catalysis. Indeed, nitrides as catalytic supports (or even as co-catalysts) are an exciting and vibrant field with a number of significant advances reported recently. In terms of catalysis, it is clear that nanostructuration is an important aspect. Furthermore, surface area considerations play a key role. Finally, the design of multi-element-containing nitrides displaying synergetic effects with the metal catalyst is one of the best strategies to optimize the catalytic properties we present in the following section.

3.2. Catalytic activity of Pt-supported Si-Ti-N samples

In the previous section we demonstrated the superior performance of silicon nitride over carbonitride and carbide counterparts. As mentioned in the introduction, we focus on the Si-Ti-N system because of the presence of TiN that can act as a co-catalyst in some reactions, reducing the required quantity of Pt.
3.2.1. Pt impregnation

The change in the pore architecture of the Pt-supported Si-Ti-N samples including those prepared from NCPTi2.5 precursors (synthesized from PHPS) labelled Pt·mNCPTi2.5·X (X being the two first numbers of the temperature: 10 for 1000°C) and from NCHTi2.5 precursors (synthesized from HTT1800) labeled Pt·mNCHTi2.5·X (X being the two first numbers of the temperature: 10 for 1000°C) has been assessed at the mesoscopic scale by nitrogen gas adsorption-desorption measurements at 77 °K. Figure 5.23 and 5.24 show the BET isotherms of Pt·mNCPTi2.5·10, Pt·mNCPTi2.5·14, Pt·mNCPTi2.5·16, Pt·mNCHTi2.5·10 and Pt·mNCHTi2.5·14. The isotherms retain the types II and IV with a H2 hysteresis.

Figure 5. 23 BET isotherm of Pt·mNCPTi2.5·X samples with temperature
3.2.2. Hydrolysis of NaBH₄

The hydrogen generation results are shown in Figure 5.25. The figure shows hydrolysis curve obtained for the Pt-supported Si-Ti-N materials prepared from NCPTi2.5 precursors (synthesized from PHPS) labelled Pt-mNCPTi2.5-X (X being the two first numbers of the temperature: 10 for 1000°C) and from NCHTi2.5 precursors (synthesized from HTT1800) labeled Pt-mNCHTi2.5-X (X being the two first numbers of the temperature: 10 for 1000°C).
Figure 5.25 Volume of hydrogen measured after 180 min during hydrolysis of NaBH₄ using Pt-mNCPTi2.5-10, Pt-mNCPTi2.5-14, Pt-mNCPTi2.5-16, Pt-mNCHTii2.5-10 and Pt-mNCHTii2.5-14

Although the Si-Ti-N system is the same, the catalytic activity is different between Pt-mNCPTi2.5-X and Pt-mNCHTii2.5-X (X being the two first numbers of the temperature: 10 for 1000°C) samples. This proves that the chemistry of the precursor has a strong impact on the properties of the derived ceramics. In these cases, along with total amount of hydrogen released from the given fuel, the rate of hydrogen generation per gram of platinum used is also important. It is observed that the system labelled Pt-mNCPTi2.5-14 has the highest rate with a value of 39.3 L.min⁻¹ .g⁻¹. This reported rate is the highest for low noble metal content catalyst systems reported in the literature¹²,²⁷. Table 5.5 shows the hydrogen evolution rate calculated from other samples.
Table 5.5 Rate of hydrolysis of NaBH₄ with different nanocomposite catalyst systems

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Rate of H₂ production (L.min⁻¹ g⁻¹ Pt⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mNCPTi2.5·10</td>
<td>14.85</td>
</tr>
<tr>
<td>mNCPTi2.5·14</td>
<td>39.3</td>
</tr>
<tr>
<td>mNCPTi2.5·16</td>
<td>14.35</td>
</tr>
<tr>
<td>mNCHT2.5·10</td>
<td>8.28</td>
</tr>
<tr>
<td>mNCHT2.5·14</td>
<td>3.26</td>
</tr>
</tbody>
</table>

This Pt·mNCPTi2.5·14 sample has a significantly better performance than the previously reported Pt supported-mesoporous Si₃N₄ monoliths studied in the previous section, i.e., the Pt·mSi₃N₄410 sample. In addition, the Pt·mNCPTi2.5·14 sample solves the problem of structural integrity of the Pt·mSi₃N₄410 sample which collapses during hydrolysis. This higher structural stability can be attributed to the presence of the activated carbon monolith.

To understand the reasons for the different catalytic behaviors between the Pt·mNCPTi2.5·X and Pt·mNCHT2.5·X (X being the two first numbers of the temperature: 10 for 1000°C) samples, we compare their X-ray diffraction pattern. We already mentioned the effect of the chemistry of the precursor on the crystallization behavior of nanocomposites in chapter 3. Here, the figure 5.26 compares the NCPTi2.5·10 and NCPTi2.5·14 samples to NCHT2.5·10 and NCHT2.5·14 samples as mesoporous components.
The difference between both systems arises in the crystallization of the matrix phase. The Si₃N₄ matrix has started to crystallize along with TiN nanocrystals in the NCHTi2.5-14 samples whereas it remains amorphous in the NCPTi2.5-14 sample. Furthermore, the extent of crystallization of TiN nanocrystals is lower in the NCPTi2.5-14 sample. The extent of crystallization of TiN in mesoporous monoliths is different from that in powders for the same system at the same temperature. This can be attributed to the porous nature of the system and the activated carbon template acting as a heat sink. The heat sink drains more heat from the nanocomposite layer thereby delaying the crystallization whereas the porous structure decreases the thermal conductivity of the overall system hence the heat transfer is lowered. Also this can be due to different pyrolysis procedure applied in both cases during the polymer to ceramic conversion. The amorphous structure formed in both cases can be different leading to different crystallization behavior.

To understand the catalytic behavior of the Pt-NCPTi2.5-14 sample, we investigated the catalytic activity of mesoporous TiN samples prepared previously but after Pt deposition, *i.e.*, Pt-mTiN10 (prepared at 1000°C) and Pt-mTiN14 (prepared at 1400°C) and compared in the sample graph (Fig. 5.27), the volume of hydrogen evolved per gram of Pt for the Pt-NCPTi2.5-14, Pt-mSi₃N₄10, Pt-mTiN10 and Pt-mTiN14 samples.
Upon comparing the hydrolysis behavior of all these systems we observe that both Pt-mTiN10 and Pt-mTiN14 have the lowest (and nearly similar) amount of hydrogen evolved per gram of platinum nanoparticles deposited. While the nanocomposite system has the highest value for the same and Pt-mSi₃N₄110 lies between the two. In the two mesoporous TiN monoliths, the TiN crystals are not nanostructured (<10 nm) as in case of the nanocomposite system. The crystallite size differs by an order of magnitude in both cases. This Nano structuration of TiN in an amorphous Si₃N₄ matrix seems to be a crucial factor which leads to the nanocomposite acting as co-catalyst in the presence of Pt. For the synergistic effect between Pt and TiN to occur the particle size of both should be less than 10 nm²⁸–³¹. In case of the Pt-mTiN14 sample the calculated average crystallite size using scherrer equation was 17 nm and for deposited Pt nanoparticles was 8 nm. While for Pt-mNCPTi2.5-14 the TiN crystallite size was calculated to be around 3.8 nm and the Pt nanoparticles were calculated to be in the range of 6.8 nm.

Then, we investigated the same samples without Pt (Fig. 5.28).
For samples without Pt, \( m\text{SiN}_4\text{410} \) has the highest activity in hydrolyzing NaBH\(_4\) among all investigated systems suggesting a catalytic nature to this nitride. Surprisingly \( m\text{NCHTi2.5\text{-}14} \), which has the highest rate of hydrolysis in presence of Pt, shows lower catalytic activity. This suggests that we need some amount of Pt in the Si-Ti-N system so that the nanocomposite can act as a co-catalyst. The catalytic activity of \( m\text{TiN}_{14} \) and \( m\text{TiN}_{10} \) alone is the lowest. The reason for this can be absence of nanoscale TiN in these monoliths. In case of the nanocomposite system, the secondary metal nitride phase is trapped inside an amorphous matrix which leads to its nanostructuration. Any such process is absent here; hence we do not obtain any nanoscale metal nitride leading to loss of catalytic properties associated with size. Although, all these systems alone can act as good supports due to sufficient strengths; they cannot act as efficient co-catalyst. The nanocomposite with a low loading of Pt shows drastic increase in its catalytic behavior as shown previously.

Leaching of active particles from such systems after successive cycles of hydrolysis is one of the biggest problems in such materials\(^{32}\). Hence a recyclability test was performed on this system. The same monolith was used for 5 successive cycles (sample name Pt·mNCPTi2.5·
R1 to R5; last to symbols denoting the cycle number) and its hydrogen generation rate was studied (Figure 5.29). It was observed that there was no decrease in the activity even after 5 cycles. This observation suggests that there is no loss in catalytic activity due to leaching of Pt nanoparticles and/or poisoning by borate sorption.

![Figure 5.29 Recyclability test for Pt-mNCPTi2.5-14 system](image)

The apparent activation energy was calculated for the system. The rate was calculated at 4 different temperatures of 80°C, 65°C, 50°C and 35°C and the logarithmic reaction rate values were plotted against inverse of temperature and AAE was calculated by comparing the equation of the line to the Arrhenius rate equation.

\[
\ln(k) = \ln(A) - \frac{(E_a)}{RT}
\]

The AAE was found to be 62 kJ / mole. This value lies in intermediate range of AAE for such type of systems.
4. Conclusions:
In this chapter we focused on as the design of mesoporous monoliths in the systems investigated in chapters 3 and 4 using the nanocasting process based on activated carbon monoliths as templates. We were able to generate monoliths with very high specific surface area, significant pore volume and interconnected mesoporosity. This is particularly the case of Si-Ti-N ceramics for which it was impossible to remove the activated carbon template most probably because TiN acted as a thermal barrier coating against ammonia. As a consequence, SSA values above 1200 m².g⁻¹ have been generated. Such compounds have been used to support platinum nanoparticles (1 wt%) to be used in the hydrolysis of sodium borohydride at 80°C. Mesoporous Si₃N₄-based ceramics including Si₃N₄ monoliths and TiN/Si₃N₄ nanocomposites displayed the best performance in terms of volume of hydrogen released from sodium borohydride and structural stability. We achieved and reproduced hydrogen generation rate of up to 39000 L.min⁻¹.g⁻¹Pt, which is one of the highest reported rates in the literature for the used conditions. This is most probably due to the catalytic activity of PHPS-derived amorphous Si₃N₄ combined with the presence of nanoscaled TiN and the synergetic effect between Pt with both TiN and Si₃N₄.
References:


3. Cui, Z., Yang, M. & Disalvo, F. J. Mesoporous Ti0.5Cr0.5N supported PdAg nanoalloy as highly active and stable catalysts for the electro-oxidation of formic acid and methanol. *ACS Nano* **8**, 6106–6113 (2014).


12. Salameh, C. *et al.* Monodisperse platinum nanoparticles supported on highly ordered


CONCLUSION AND PERSPECTIVES
The work presented in this manuscript has dealt with investigation of the synthesis, processability into mesoporous components and pyrolytic conversion of “single source” precursors to generate mainly BN and Si₃N₄-based ceramics as single phase materials and nanocomposites with in-situ growth of MN (M= Ti, Zr, Hf) nanocrystals in the BN and Si₃N₄ matrix. The high temperature behavior of the final materials has been investigated whereas their use as catalyst support for the hydrolysis of sodium borohydride has been explored.

The first chapter proposes a bibliographic study on different electrochemical power sources and the issues which limit their commercialization. We provided a state of the art on the synthesis of Si- and B-based carbide, carbonitride, nitride and their derived nanocomposites using the polymer derived ceramic (PDC) route. We focused our attention on the PDC route in this thesis due to its advantages to control the ceramic composition precisely, its ability to synthesize complex shapes and the relatively low processing temperature.

The second chapter was focused on the description of materials and experimental protocols for synthesis, shaping and pyrolysis processes.

The third chapter was focused on boron nitride (BN) and the derived B·M·N (M = Ti, Zr, Hf) ceramics. We described the development of BN from two different precursors, i.e., ammonia borane (AB) and polyborazylene (PB60), and detailed their pyrolytic conversion as well as the high temperature crystallization of BN to better understand the chemistry behind the process to elaborate B·M·N (M = Ti, Zr, Hf) ceramics in the second part of the chapter. Thus, we discussed on the synthesis and characterization of B·M·N (where M = Ti, Zr, Hf) ceramics through the reaction between BN precursors and MN precursors. The polymer synthesis was studied by FTIR and solid-state NMR spectroscopies which allowed us to identify the mechanisms that govern the polymer synthesis. Then, we focused on the polymer-to-ceramic conversion and we found that polymers containing Hf displayed the highest ceramic yield because of their high degree of crosslinking. Ammonia-treated samples are poorly crystallized and it was necessary to anneal samples at 1450°C to form nanocomposites in which MN nanocrystals are distributed in a BN matrix. Through the investigation of the microstructural evolution and the crystallization behavior at high temperature, we particularly demonstrated that the gradual increase of the transition metal nitride content in the B·M·N ceramics shifts the crystallization of the BN matrix to higher temperatures and can be even suppressed using hafnium as a metal. Thus, B·Ti·N ceramics with a B·Ti ratio of
1 and B-Hf-N ceramics with a B:Hf ratio below 2.5 form highly stable nanocomposite structures. However, such nc-MN/a-BN nanocomposites may have some potential disadvantages in some applications due to the low BN crystallinity which can involve a low oxidation resistance. To overcome this problem, we focused the last part of the present chapter on the investigation of the improvement of the BN crystallinity using AB and PB as BN precursors. We investigated two strategies using syntheses in solution and reactive ball-milling through the reaction of BN precursors with lithium amide (LiNH₂). We successfully demonstrated that a reactive ball-milling between AB and LiNH₂ according to a certain ratio allowed us to generate highly crystallized BN at 1450°C. The materials have been characterized at each step of their process.

The second solution to overcome the low oxidation resistance of the BN matrix in MN/BN nanocomposites is to change the nature of the matrix. Within this context, the fourth chapter was focused on Si₃N₄ and Si·M·N(C) (M = Ti, Zr, Hf) ceramics. We firstly sequenced a one-step synthetic method to obtain polymetallosilazanes. The synthesis consisted to perform the reaction between commercially available polysilazanes such as PHPS and HTT1800 and the low molecular weight metal-containing molecules (which have been already used in chapter 3) with controlled Si:M ratios. The role of the chemistry behind their synthesis was studied by FTIR, solid-state NMR and elemental analyses. Two mechanisms involving N-H and Si-H bonds in polysilazanes as well as N(CH₃)₂ groups in metal-containing precursors have been identified. It has been shown that PHPS is the most reactive polysilazane while Hf-based molecules were highly reactive with SiH groups of polysilazanes. Such a difference has an effect on the ceramic conversion and the high temperature behavior of ceramics. Thus, we provided a comprehensive mechanistic study of the polymetallosilazane to Si·M·N ceramic transformation under ammonia based on solid-state NMR coupled with TG experiments. Pyrolysis under ammonia generated X-ray amorphous ceramics

The subsequent annealing of ammonia-treated samples under nitrogen at 1400 °C led to nanocomposites made of MN nanocrystals dispersed in an amorphous or crystallized matrix depending on the nature of the metal and the Si:M ratio fixed at molecular scale. After annealing to 1500°C, the effect of the chemistry of the polysilazane on the matrix crystallization was demonstrated. We found that the addition of Ti or Hf to PHPS in the correct Si/M molar ratio led to suppression of the matrix crystallization up to 1800°C. This generates a system where we have controlled growth of nanostructured metal nitride crystals
within an amorphous ceramic matrix. We also explored the effect of modification of a polysilazane with two different metallic precursors simultaneously. We obtain a new TiZr(C)N phase which crystallizes in an amorphous matrix.

Finally, in chapter 5, we focus on as the design of mesoporous monoliths in the systems investigated in chapters 3 and 4 using the nanocasting process based on activated carbon monoliths as templates. We were able to generate monoliths with very high specific surface area, significant pore volume and interconnected mesoporosity. This is particularly the case of Si-Ti-N ceramics for which it was impossible to remove the activated carbon template most probably because TiN acted as a thermal barrier coating against ammonia. As a consequence, SSA values above 1200 m².g⁻¹ have been generated. Such compounds have been used to support platinum nanoparticles (1 wt%) to be used in the hydrolysis of sodium borohydride at 80°C. Mesoporous Si₃N₄-based ceramics including Si₃N₄ monoliths and TiN/Si₃N₄ nanocomposites displayed the best performance in terms of volume of hydrogen released from sodium borohydride and structural stability. We achieved and reproduced hydrogen generation rate of up to 39000 L.min⁻¹.g⁻¹, which is one of the highest reported rates in the literature for the used conditions. This is most probably due to the catalytic activity of PHPS-derived amorphous Si₃N₄ combined with the presence of nanoscaled TiN and the synergetic effect between Pt with both TiN and Si₃N₄.

These very interesting results demonstrated the functionality of the materials prepared in chapters 3 and 4. However, the development of novel solutions and system integration concepts constitutes the role of ceramics-based energy converters in future energy scenarios. The breakthrough in this field consists in providing and tuning specific properties by developing new formulations and structures/morphologies (nanoparticles, mesoporous or 2D structures) from dedicated chemistry. Within this context, our perspectives are focused on the design of composites and nanocomposites, in particular those we present in this manuscript, to envision energy storage based on electrochemical reactions in fuel cells and supercapacitors, and conversion of renewable energy sources.

We firstly consider the design and physico-chemical characterization of functional nanostructured ceramics as electrode materials. Fuel cells and supercapacitors are important electrochemical energy storage/production devices but state-of-the-art supercapacitors and fuel cells are not able to meet the requirements for energy-efficient use in transportation,
grid, and commercial technologies. Both technologies seek new materials design concepts for higher energy densities, higher power densities, and longer cycle life.

For **fuel cells**, our perspectives are concerned by direct formic acid fuel cells (DFAFCs) and in particular on new fuel cell catalysts. FA is a liquid at room temperature with volumetric and gravimetric energy densities of 53 g/L and 4.3 wt%, respectively. However, there are still several challenges that hinder fuel cell commercialization, including insufficient durability/reliability of catalysts. The corrosion of carbon supports (cathodes and anodes) is identified to be the major contributor to the catalyst failure. To address the issue of carbon corrosion, alternative materials should be explored. Metal nitrides (MN) display noble-metal-like properties which result from their similar electronic structure. However, they need to be nanostructured and they suffer from wear and corrosion in highly acidic environments. Therefore, MN alone may not possess the necessary stability to replace carbon as supports. Confined in a Si-C-N matrix through the concept we applied in chapter 4, we expect a significant improvement of the chemical stability of the resulting materials in acid and alkaline media while proposing the electrocatalytic activity of nanostructured MN. **MN (M = Ti/Cr/Nb/Co)/Si-C-N electrodes for DFAFCs** obtained through the Polymer-derived ceramic route with an *in-situ* controlled growth of MN nanocrystals (~5 nm in diameter) during the formation of the Si-C-N matrix will be therefore considered in a close future. They will be prepared as capsules with hollow macroporous core/mesoporous shell structures, nanofibers and monoliths with tailored mesoporosity. The design of their porosity will be achieved using templating approaches as we planned in chapter 5 and additive manufacturing routes at the Research Institute of Ceramics in Limoges. Pt will be deposited as nanoparticles through impregnation of the support in a Pt salts then reduction in H₂ furnace in a controlled amount. A synergetic effect between Pt and MN is expected to optimize the electrocatalytic activity of the material investigated. We already started such experiments through the deposition of Pt NPs on mesoporous Si-Ti-N(C) supports (the carbon coming from the activated carbon template and/or free carbon present in the Si-C-N ceramics).

For **supercapacitors**, we already investigated the design of MXenes/Si-C-N composites as electrode materials and got interesting results. MXene are promising materials for use as electrodes in supercapacitors but are limited by oxidation/corrosion. It needs to be protected by a coating which will not decrease its electrical conductivity and also provide mechanical stability to the system. Under harsh condition of electrochemical cell most oxide based
coatings will fail, hence we need a non-oxide ceramic coating for this purpose. In the previous sections we discussed various ceramic non-oxides which can withstand harsh conditions. Out of those discussed earlier only HTT1800 derived Si·C·N system can provide electrical conductivity. Rest all are either semiconductors (SiC) or insulators (Si₃N₄). SiCN/MXene composites were synthesized as discussed in chapter 2 and tested as electrode materials in supercapacitors.

The CV (cyclic voltammogram) curve (Figure 1) of the 50 wt.% and 90 wt.% SiCN in MXenes is larger than that of the neat materials (Si·C·N and MXene). This indicates the 50 wt.% and 90 wt.% Si·C·N in MXene electrode has a higher capacitance which may be due to the modification of Si·C·N with MXene. In addition, the rectangular-shaped CV curve of the 50 wt.% and 90 wt.% Si·C·N in MXene electrode suggests the charge storage mechanisms of both materials is dominantly non-faradaic. According to Eqn. 1, the 90 wt.% Si·C·N in MXene displays the highest areal capacitance (137.17 mF/cm²); which is comparable to the areal capacitance of similar 2D materials.

\[
C_A = \frac{2\int_{v_2}^{v_1} I(v) \, dv}{A \Delta v} \quad \text{Eqn. 1}
\]

More so, the CV displays a quasi-rectangular shape with no redox peaks which suggest the charge storage mechanism of the 90 wt.% Si·C·N in MXene is dominantly non-faradaic. Further work needs to be done to optimize the chemistry and properties of the composite. A
detailed study need to be performed to study the interaction between MXene and Si-C·N and to investigate the effect of the nature of the ceramic matrix.

Secondly, we will focus on **nanostructured ceramics as catalysts in the production of hydrogen**. The H₂-PEMFC is mainly limited by the high cost of miniaturised hydrogen containers. Liquid-phase **hydrogen carriers** are an interesting alternative. For the application of FA as a liquid organic hydrogen carrier or as an energy source for fuel cells, its dehydrogenation is highly desired, and the catalytic selectivity for dehydrogenation depends on the catalytic surface, temperature, pH value in reaction system, FA concentration and so on [S. Moret, et al.. Nat. Commun. (2014) 5, 4017]. The limitation of homogeneous catalysts involved the development of heterogeneous catalysts using various supports and metals. However, new materials investigations are required to propose highly efficient and effective for decomposition. Because of their co-catalytic property, the MN/Si₃N₄ nanocomposites will be evaluated as support of Pd and binary Ag/Pd nanoparticles for the production of hydrogen from FA. They would be also explored to recycle CO₂ into FA.

The key for successful applications as catalyst is the chemically inert support and the strong interactions between the metal nanoparticles and the support to allow for the stabilization of ultra-small metal nanoparticles. Our proposal consists in the synthesis of processable metal-containing polymer followed by their pyrolysis into nanocomposites during which an *in-situ* growth of active metal sites occurs within the matrix. This reduces the number of steps to prepare metal-supported ceramics and should increase the interaction with the fluid is the metal is accessible. We investigated such a route to prepare Co/Si₃N₄ nanocomposites in collaboration with Prof. Yuji Iwamoto (NITech, Japan) and Pt/Si-C·N nanocomposites in collaboration with the group of Rhett Kempe (University of Bayreuth) and as a proof of concept, we applied such materials for the hydrolysis of sodium borohydride.

*Figure 3 Hierarchically porous SiCN ceramics with surface Pt NPs were fabricated by the self-assembly and subsequent pyrolysis of an in situ generated block copolymer whose inorganic block (Si-N backbone) was modified with Pt (II) ions. The as-obtained catalysts*
Such materials display great potential as nanocatalysts and also as electrocatalysts. The hydrolysis behavior of the such systems is demonstrated in the figure 3. Further work on these materials aims to reduce the platinum content in the system and shape these systems as monoliths thereby making them easier to use.

Figure 4 Volume of hydrogen (in mL) measured during the hydrolysis of sodium borohydride over the mass of nanocomposites containing the same amount of Pt. (0.35 mg) at 80°C. Under these conditions the amount (in mg) of nanocomposites used were different.