Generation of Well-Defined Pairs of Silylamine on Highly Dehydroxylated SBA-15: Application to the Surface Organometallic Chemistry of Zirconium

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ABSTRACT

Generation of Well-Defined Pairs of Silylamine on Highly Dehydroxylated SBA-15: Application to the Surface Organometallic Chemistry of Zirconium

Joachim Azzi

Design of a new well-defined surface organometallic species [O-(=Si–NH)2Zr(IV)Np2] has been obtained by reaction of tetraneopentyl zirconium (ZrNp4) on SBA-15 surface displaying mainly silylamine pairs [O-(=Si–NH)22]. These surface species have been achieved by an ammonia treatment of a highly dehydroxylated SBA-15 at 1000°C (SBA-151000). This support is known to contain mainly strained reactive siloxane bridges (=Si-O-Si≡)[1] along with a small amount of isolated plus germinal silanols =Si(OH)2.

Chemisorption of ammonia occurs primarily by opening these siloxane bridges[2] to generate silanol/silylamine pairs [O-(=Si–NH2)(=SiOH)] followed by substitution of the remaining silanol. Further treatment using hexamethyldisilazane (HMDS) results in the protection of the isolated remaining silanol groups by formation of =Si-O-SiMe3 and =Si(OSiMe3)2 but leaves =SiNH2 untouched.

After reaction of this functionalized surface with ZrNp4, this latter displays mainly a bi-podal zirconium neopentyl organometallic complex [O-(=Si–NH)2Zr(IV)Np2] which has been fully characterized by diverse methods such as infrared transmission spectroscopy, magic angle spinning solid state nuclear magnetic resonance, surface elemental analysis, small angle X-ray powder diffraction (XRD), nitrogen adsorption and energy filtered transmission electron microscopy (EFTEM). These different characterization tools unambiguously prove that the zirconium organometallic complex reacts mostly with silylamine pairs to give a bi-podal zirconium bis-neopentyl complex, uniformly distributed into the channels of SBA-151000.

Therefore this new material opens a new promising research area in Surface Organometallic Chemistry which, so far, was dealing mainly with O containing surface. It is expected that vicinal amine functions may play a very different role as compared with classical inorganic supports. Given the importance in the last decades of N containing ligands in catalysis, one may expect important prospects…
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Thanks to you, I improved my communication, autonomy and knowledge in catalysis, characterization techniques and good laboratory practices. I discovered what research means: Passion, Work and Reflection and I am proud to have achieved my objectives which, I hope, will lead to new breakthroughs in a near future.
# TABLE OF CONTENTS

**EXAMINATION COMMITTEE APPROVALS FORM** .................................................. 2  
**COPYRIGHT** ................................................................................................. 3  
**ABSTRACT** .................................................................................................. 4  
**ACKNOWLEDGEMENTS** .............................................................................. 5  
**TABLE OF CONTENTS** ............................................................................... 6  
**LIST OF ABBREVIATIONS** ....................................................................... 8  

## I. Objectives and strategies .............................................................................. 9

## II. SBA-15 support .......................................................................................... 12  
1. Generalities ................................................................................................. 12  
2. Properties .................................................................................................... 13  

## III. Surface organometallic chemistry (SOMC) ............................................ 14  
1. Overviews ................................................................................................... 14  
2. Alkyl complexes grafting on oxide surface: example with Zirconium ........... 17  

## IV. Experimental section ............................................................................... 19  
1. Generalities ................................................................................................. 19  
2. Preparation of surface oxide ....................................................................... 21  
   a) Synthesis of hexagonal ordered mesoporous silica .................................. 21  
   b) Dehydroxylation of SBA-15: Generation of single silanols and strained siloxane bridges .............. 22  
3. Chemisorption of ammonia ....................................................................... 23  
   a) Reaction of $^{14}$NH$_3$ on SBA-15$_{1000}$ .................................................. 23  
   b) Reaction of $^{15}$NH$_3$ on SBA-15$_{1000}$ ............................................... 24  
4. Reactivity of ZrNp$_4$ on NSBA-15$_{1000}$: impregnation method ............... 25

## V. Results and Discussions .............................................................................. 25  
1. Characterizations of surface species formed by reaction of ammonia on SBA-15$_{1000}$ ................................................................. 25  
   a) Infrared transmission characterizations .................................................. 25  
   b) Solid-state NMR spectroscopies .............................................................. 28  
   c) Analytical data ....................................................................................... 32  
   d) Conclusion ............................................................................................ 32  
2. Characterizations of the surface species formed by passivation on NSBA-15$_{1000}$ .......................................................... 33  
   a) Infrared transmission characterizations .................................................. 34  
   b) Analytical data ....................................................................................... 36  
   c) Conclusion ............................................................................................ 37
3. Characterizations of the surface species formed by reaction of ZrNp₄ on P-NSBA-15₁₀₀₀  
a) Infrared transmission characterizations  
b) Solid state NMR spectroscopies  
c) Analytical data  
d) Conclusion

4. Structural characterization
a) XRD and BET  
b) High Resolution Transmission Electron Microscopy  
c) Elemental mapping by Energy Filtered Transmission Electron Microscopy (EFTEM)

PROSPECTIVE AND APPLICATIONS

1. Industrial and environmental potential

CONCLUSION

REFERENCES

Appendix 1: Main chemical compounds used
Appendix 2: Calcination and dehydroxylation program of SBA-15
Appendix 3: Static versus Dynamic ammonia treatment at 500°C
Appendix 4: Optimal ammonia treatment temperature
Appendix 5: Ammonia treatment set up for ¹⁵NH₃
Appendix 6: SBA-15₁₀₀₀ Gas Analysis
Appendix 7: Zirconium Neopentyl Grafting

PERSONAL FEELING
# LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>HMDS</td>
<td>Hexamethyldisilazane</td>
</tr>
<tr>
<td>MeLi</td>
<td>Methyl Lithium</td>
</tr>
<tr>
<td>ZrNp₄</td>
<td>Zirconium Tetraneopentyl</td>
</tr>
<tr>
<td>MeH</td>
<td>Methane</td>
</tr>
<tr>
<td>NpH</td>
<td>Neopentane</td>
</tr>
<tr>
<td>SBA-15₁₀₀₀</td>
<td>Santa Barbara Amorphous type material (silica) dehydroxylated at 1000°C</td>
</tr>
<tr>
<td>NSBA-15₁₀₀₀</td>
<td>Santa Barbara Amorphous type material (silica) dehydroxylated at 1000°C after ammonia treatment</td>
</tr>
<tr>
<td>P-NSBA-15₁₀₀₀</td>
<td>Santa Barbara Amorphous type material (silica) dehydroxylated at 1000°C after ammonia treatment and passivation</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>MAS</td>
<td>Magic Angle Spinning</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>IR</td>
<td>Infra-Red</td>
</tr>
<tr>
<td>EFTEM</td>
<td>Energy-Filtered Transmission Electron Microscopy</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatography</td>
</tr>
<tr>
<td>HVL</td>
<td>High Vacuum Line</td>
</tr>
<tr>
<td>R</td>
<td>Gas constant = 8.3145 J/K/mol</td>
</tr>
<tr>
<td>T</td>
<td>Temperature in °C</td>
</tr>
<tr>
<td>RT</td>
<td>Room temperature</td>
</tr>
</tbody>
</table>
I. Objectives and strategies

There is an increasing interest into the immobilization of homogeneous catalysts onto supports that produce heterogeneous catalysts, which could maintain the selectivity of the former homogeneous catalytic system, and would be easily recycled.

The development of better catalysts has been hampered by the low concentration of many different active sites despite that chemical industry has often gave a preference to heterogeneous catalysis\textsuperscript{[3]}\textsuperscript{[3]}. These factors have to be offset by discovering new surface species and by improving our understanding of these surface reactions as well.

Catalysis is primarily a molecular phenomenon, and it must involve well-defined surface organometallic intermediates and/or transition states. Thus, in order to design better catalysts, one must be able to construct a well-defined active site, test its catalytic performance and assess a structure-activity relationship.

A first attempt will be aimed at creating a unique surface made up of two NH-metal bonds on a well-defined SBA-15 surface displaying silylamine pairs thanks to a perfect control and knowledge of the surface.

The use of nitrogen (N) - metal (Mt) bond has provided some significant improvements for the catalytic activity of several homogeneous systems \textsuperscript{[4]}\textsuperscript{[4]}. Thus, many transition metal complexes bearing N-Mt bonds could be active in heterogeneous catalysts.

The design of these unique and new surface organometallic complexes would allow us to better understand the heterogeneous catalysis and open a new way of research.

Extensive researches are usually needed with the purpose of improving and controlling the surface species, even though the basic mechanisms are often well known.

Therefore, this research has for goal to prepare a new surface bond with high concentration of active sites by a strategy of molecular design and by controlling each step in order to obtain a bi-podal zirconium bis-neopentyl complex grafted on well-defined SBA-15 surface displaying silylamine pairs.

As a result, the first objective is to develop a synthetic method to access to silica based mesoporous material (SBA-15) displaying well-defined silylamine groups (=SiNH\textsubscript{2}) surrounded by siloxane moities.

Then, create new Surface Organometallic Complexes where selected transition metals are grafted via at least one nitrogen-metal bond.
Finally, fully characterize these new organometallic surface species. Zirconium has been chosen because it is one of the most transition metal studied on silica \[^{[5]}\].

Our strategy is to use a highly dehydroxylated SBA-15\textsubscript{1000} displaying a small amount of single silanol and highly strained reactive siloxane bridges.

Each reaction step has been fully studied in order to obtain a fully characterized new surface species (scheme 1).

The formation of the zirconium complex 4 is in majority on the SBA-15 surface and we will prove and reinforce this assumption through this following work. Thus, we will consider that a surface bi-podal organometallic complex has been essentially formed thanks primarily to the formation of silylamine pairs on the surface (step 1-1).

All experiments were carried out under strict exclusion of air given that all surface species obtained are not air-stable and decompose rapidly.
Scheme 1: Main surface species after each step

**STEP 0**

- Controlled ammonia treatment

**STEP 1**

1. Scheme 1: Main surface species after each step

2. Scheme 1: Main surface species after each step

3. Scheme 1: Main surface species after each step

**STEP 2**

1. Scheme 1: Main surface species after each step

2. Scheme 1: Main surface species after each step

3. Scheme 1: Main surface species after each step

4. Scheme 1: Main surface species after each step

**STEP 3**

1. Scheme 1: Main surface species after each step

2. Scheme 1: Main surface species after each step

3. Scheme 1: Main surface species after each step

4. Scheme 1: Main surface species after each step

5. Scheme 1: Main surface species after each step

6. Scheme 1: Main surface species after each step

**Controlled ammonia treatment**

**Passivation HMDS**

**Complexation MLn**
II. SBA-15 support

1. Generalities

The development of porous materials with large specific surface areas is currently a subject of extensive research; particularly with regard to potential applications in different fields such as adsorption, chromatography, catalysis, sensor technology, and gas storage\textsuperscript{[6]}. Porous materials are divided into three classes, based on their pore diameter (table 1).

Table 1: Pore-Size regimes and representative porous inorganic materials\textsuperscript{[7]}

<table>
<thead>
<tr>
<th>Pore-size regimes</th>
<th>Definition</th>
<th>Examples</th>
<th>Actual size range</th>
</tr>
</thead>
<tbody>
<tr>
<td>macroporous</td>
<td>&gt; 500 Å</td>
<td>glasses</td>
<td>&gt; 500 Å</td>
</tr>
<tr>
<td>mesoporous</td>
<td>20–500 Å</td>
<td>aerogels</td>
<td>&gt; 100 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>pillared layered clays</td>
<td>10 Å, 100 Å\textsuperscript{[8]}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M41S</td>
<td>16–100 Å</td>
</tr>
<tr>
<td>microporous</td>
<td>&lt;20 Å</td>
<td>zeolites, zeotypes</td>
<td>&lt; 14.2 Å</td>
</tr>
<tr>
<td></td>
<td></td>
<td>activated carbon</td>
<td>6 Å</td>
</tr>
</tbody>
</table>

[a] Bimodal pore-size distribution.

Each of these porous materials can differ from the nature of their pore wall and pore distribution as well as their pore architecture (size, shape, connectivity), giving them specific and interesting properties.

In order to obtain such materials, various templates are employed such as individual molecules, micelles and emulsion or latex particles, to direct the synthesis of micro, meso or macro-pores respectively \textsuperscript{[8]}.

Zeolite is one of the most important microporous materials so far, but shows some shortcomings due especially to their small pores size. Indeed, Zeolite can lead to coke formation in some chemical reaction such as catalytic cracking, degrading its catalytic activity, but also can experience problems in mass transfer.

Moreover, the use of bulky molecules restricts their usage in important chemical processes. However, theses drawbacks have been bypassed or reduced by synthesizing materials with larger pores size.
A next generation of silica nanoparticles with much larger nanometer pores was produced at the University of California, Santa Barbara\(^9\) under the name of Santa Barbara Amorphous type material, or SBA-15.

2. Properties

SBA-15 exhibits a hexagonal ordered array of pores (called as honeycomb) ranging between 25 and 300Å (figure 1). SBA-15 possesses a large BET surface area (>650m\(^2\)/g) with large pores diameter and large pores wall thickness which result in higher hydrothermal stability than M41S materials.

![Figure 1: Mesoscopic honeycomb structure of SBA-15](image)

Consequently, the area of periodic mesoporous materials has exploded due to their unique properties (table 2) and promising applications of these materials.

Table 2: Physical properties of SBA-15/d (d indicates the pore diameter)\(^{10}\)

<table>
<thead>
<tr>
<th>Porous silica</th>
<th>Pore diameter (Å)</th>
<th>BET Surface area (m(^2)/g(^{-1}))</th>
<th>Total pore volume (cm(^3)/g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15/50</td>
<td>50</td>
<td>695</td>
<td>0.56</td>
</tr>
<tr>
<td>SBA-15/92</td>
<td>92</td>
<td>810</td>
<td>0.94</td>
</tr>
<tr>
<td>Silica gel</td>
<td>20-200</td>
<td>451</td>
<td>0.85</td>
</tr>
</tbody>
</table>
In this research, SBA-15 has been chosen as an oxide support. It is one of the most attractive host materials due to its distinctive mesostructure features, such as high surface area (650-1000 m²/g), large uniform pore size (5–35 nm), thicker silica walls (3-6.5 nm) and high thermal stability (up to 1000 K)\cite{9,11}.

Furthermore, this high surface area allows to obtain an important nitrogen and metal loading on the SBA-15 surface which is very important for industrial applications and catalytic performance.

In addition, a high nitrogen loading is necessary to analyze the sample by $^{15}$N solid-state NMR spectroscopy but also to graft as much metals as possible in order to get a high metal loading as well.

This will lead, most likely, to very interesting properties and efficiency of diver catalytic reactions.

III. Surface organometallic chemistry (SOMC)

1. Overviews

One of the main objectives of Surface OrganoMetallic Chemistry (SOMC) is the creation of “single site catalysts” onto well-defined surfaces.

This concept was first proposed in the field of catalytic polymerization when well-defined “homogeneous” metallocene catalysts were found to behave in a tunable way, and have been slowly replacing the “black box” of classical heterogeneous Ziegler–Natta catalysis\cite{3}.

Compared to the molecular organometallic chemistry and homogeneous catalysis, the level of understanding of heterogeneous catalysis is still limited. Indeed, one of the main reasons are the small number of active sites and the complex description of the mechanism occurring at these latter (elementary steps)\cite{12}. This makes more difficult getting a structure-activity relationship in heterogeneous catalysis.

Indeed, in a metal particle the surface heterogeneity is governed by the properties and nature of various surface atoms in different crystallographic positions (e.g., corners, faces, edges, kinks, steps) and, in principle, there is no simple reason why they should behave in the same way to activate the incoming, first “physisorbed” and then “chemisorbed” molecule.
Understanding the reaction of organometallic complexes with a support, which can be considered as a rigid ligand, can bring molecular insight to the design of new catalysts and even allow the discovery of new reactions (Ziegler–Natta depolymerization\textsuperscript{[13]} and alkane metathesis\textsuperscript{[14]} for instance).

It is to meet this challenge, which is a century old and yet strategic (90% of the chemical industry is based on heterogeneous catalytic processes), that surface organometallic chemistry has recently been developed.

In the last 20 years or so a variety of surface organometallic complexes have been synthesized by creating one to several bonds between transition metal elements and the surface of oxides and metals (scheme 2).

\textbf{Scheme 2 : Preparation of well-defined single site catalyst}

As we can see, the methodology for single site synthesis is based on three important constituents: a support as a ligand, an active site (containing a crucial ligand for catalysis) and spectator ancillary ligands (scheme 3).

The support serves as a basis for grafting any organometallic complexes made up of different or identical ligands (homoleptic). In this research, SBA-15 will be the support, zirconium will be the transition metal and can constitute an active center upon hydrogenation for instance, and finally the neopentyl group act as ligand in the coordination sphere of the zirconium.
Therefore, the ultimate aim of this chemistry is to use all the above concepts to construct on the surface the active sites, uniform in composition and distribution, by a true molecular engineering approach, so as to achieve single-site heterogeneous catalysts\textsuperscript{[15]}.

Hence, as in molecular chemistry, surface organometallic chemistry relies on both chemical and spectroscopic methods to understand the structure of surface entities and the accuracy of the grafting directly onto the surfaces of oxides and metals.

\textit{Scheme 3 : Metal and oxide support considered as a same entity}

Here, as already said, the surface is considered as a ligand, “similar” to classical ligands in organometallic chemistry (X, L, Z…). One of the concepts derived from such an approach is to consider the metal and the oxide support, whose metal is grafted as a same entity (cluster), to which one applies the rules of coordination and organometallic chemistry.

IR spectroscopy is an essential tool for understanding and evaluating the grafting step as well as assessing the modification of the surface species upon various treatments. It has been widely used in this research for each step and modification on the surface.

Thus, spectroscopy, in combination with quantitative measurements of product evolution during grafting and upon further chemical treatments can provide a quick, yet clear, picture of the surface complex through mass-balance analysis.

Typically, the latter aspect has been mainly addressed by using hydrolysis and hydrogenolysis reactions.

The key component in surface organometallic chemistry is the support.
It is therefore of prime importance to understand the support in order to control its reactivity and the potential structure of the supported organometallic complexes. In this work, SBA-15 surface is composed mostly of siloxane bridges (≡Si-O-Si≡) and silanol groups (≡Si-OH). Silanol groups are either isolated, geminal or vicinal (scheme 4). Their concentration and their nature will depend on the temperature of the pretreatments.

Scheme 4 : Surface silanol groups

2. Alkyl complexes grafting on oxide surface: example with Zirconium

The first step in the design of a single site catalyst consists on the reaction of an organometallic complex (generally homoleptic alkyl complex) with a silica oxide surface.

This approach has lead to single organometallic complexes surface well characterized. It concerns essentially transition elements as, Cr, Zr, V, Mo, Ti, Ta W, Re, Rh, Ni and Mn. In the case of tetra-neopentyl zirconium, the surface organometallic complexes depicted on scheme 5 have been obtained and characterized.
When silica is dehydroxylated at temperature below 500°C, the reaction with (M(CH$_3$Bu)$_4$), M = Ti or Zr, leads to the formation of a bi-podal organometallic complexes on the silica: ((≡SiO)$_2$M(CH$_3$Bu)$_2$) as well as a monopodal species: ((≡SiO)M(CH$_3$Bu)$_3$).

Nevertheless, bi-podal zirconium bis-neopentyl complexes have never been obtained at 100% on the silica surface.
IV. Experimental section

1. Generalities

All experiments were performed under controlled atmosphere by using standard air-free methodology in an argon-filled vacuum atmosphere glove box, in a Schlenk or in a Schlenk-type apparatus interfaced to a High Vacuum Lines HVL (10^-5 Pa).

Pentane and ether was distilled on Na-benzophenone and degassed through freeze pump thaw cycles.

Pluronic (P123, PEO_{20}PPO_{70}PEO_{20}), Tetraethyl Orthosilicate (TEOS), Hydrochloric acid, HMDS and ^{15}\text{NH}_3 were purchased from Aldrich (see appendix 1). Ammonia was purchased from Abdullah Hashim Industrial Gases & Equipment Co. Ltd.

- **Gas phase analysis** of alkanes was performed on Agilent 6850 gas chromatography with split/splitless injector and FID. 10 µl was injected by the hot needle technique (thermospray) at an injector temperature of 180°C using the split mode (split ratio 10:1; 30 ml/min split flow).

A HP-PLOT/U 30m × 0.53mm; 20.00µm capillary column coated with a stationary phase divinylbenzene/ethylene glycol dimethacrylate was used with nitrogen as carrier gas at 4.65 Psi pressure. Each analysis was carried out with the same conditions: a flow rate of 3 ml/min, an isotherm at 150°C, and a detector sets with a data rate of 5 Hz and a minimum peak width of 0.04 min.

- **Infrared spectra** were recorded on a Nicolet 6700 FT-IR spectrometer by using an infrared cell equipped with CaF₂ windows, allowing in situ monitoring under controlled atmosphere. Typically 4 scans were accumulated for each spectrum (resolution, 16 cm\(^{-1}\)).

- **Surface elemental analyses** were performed at Mikroanalytisches Labor Pascher (Germany) and handled under inert gas.

- **NMR spectroscopy:** One-dimensional ^1\text{H} MAS and ^13\text{C} CP/MAS solid-state NMR spectra were recorded at 600 and 150 MHz resonance frequencies respectively, with a conventional double-resonance 4 mm CPMAS probe, NMR chemical shifts are reported with respect to TMS as an external reference.

The ^15\text{N} CP/MAS NMR spectra were recorded at 40.5 MHz frequencies with a conventional double-resonance 7 mm CPMAS probe with an external reference of L-Alanine for NMR chemical shift.
The samples were introduced under argon into zirconia rotors, which were then tightly closed. The spinning frequency was set to 15, 10, and 5 kHz for $^1$H, $^{13}$C, and $^{15}$N spectra, respectively.

For CP/MAS $^{13}$C and $^{15}$N NMR, the following sequence was used: 90° pulse on the proton (pulse length 2.4 μs), then a cross-polarization step with a contact time of typically 5 ms, and finally acquisition of the $^{13}$C and $^{15}$N signals under high-power proton decoupling.

The delay between the scans was set to 5 s, to allow the complete relaxation of the $^1$H nuclei, and the number of scans was 5 000 for carbon and nitrogen, and 32 for proton. An apodization function (exponential) corresponding to a line broadening of 80 Hz was applied prior to Fourier transformation.

Two-dimensional double-quantum and triple-quantum experiments were recorded with a conventional double-resonance 3.2 mm CPMAS probe, according to the following general scheme: excitation of DQ coherences, $t_1$ evolution, $z$-filter and detection.

The spectra were recorded in a rotor-synchronized fashion in $t_1$; that is, the $t_1$ increment was set equal to one rotor period (4.545 μs). One cycle of the standard back-to-back re-coupling sequence was used for the excitation and reconversion period.

Quadrature detection in $\omega_1$ was achieved using the States-TPPI method. A spinning frequency of 22 kHz was used. The 90° proton pulse length was 2.5 μs, while a recycle delay of 5 s was used. A total of 32 $t_1$ increments with 32 scans each were recorded.

The 2D $^1$H-$^{13}$C and $^1$H-$^{15}$N heteronuclear correlation (HETCOR) solid-state NMR spectroscopy experiments were conducted using a 4 mm MAS probe.

The experiments were performed according to the following scheme: 90° proton pulse, $t_1$ evolution period, cross-polarization (CP) to carbon and nitrogen spins, and detection of carbon and nitrogen magnetization under TPPM decoupling.

For the cross-polarization step, a ramped radio frequency (rf) field centered at 75 kHz was applied to protons, while the carbon and nitrogen rf field were matched to obtain optimal signals.

A total of 64 $t_1$ increments with 5 000 scans each were collected. The sample spinning frequency was 8.5 kHz, and the contact time for the cross-polarization step was set to 0.4 ms, allowing for the selective observation of C-H and N-H nuclei that are spatially very close.

During acquisition, the proton decoupling field strength was also set to 75 kHz. Quadrature detection in $\omega_1$ was achieved using the TPPI method.
The small-angles X-ray powder diffraction (XRD) data were acquired on a Bruker D8 advance diffractometer using Cu Ka monochromatic radiation (λ = 1.054184 Å) to confirm the hexagonal ordered structure of the sample.

Nitrogen adsorption–desorption isotherms at 77 K were measured using a Micromeritics ASAP 2024 physisorption analyzer. Before any measurements, the sample was degassed at 150°C at 10°C/min for 4 hours.

The specific surface area was calculated following typical Brunauer-Emmett-Teller (BET) procedures and was evaluated in the P/P₀ range 0.01-1. The pore volume was taken at the P/P₀ = 0.970 single point.

The pore size distribution curve was obtained using Barrett-Joyner-Halenda (BJH) pore analysis applied to the desorption branch of the nitrogen adsorption / desorption isotherm.

Elemental mapping was carried out by technique of Energy-Filtered Transmission Electron Microscopy (EFTEM) and the EFTEM experiments were performed with a post-column energy filter of model GIF Tridiem™ from Gatan, Inc. attached below the column of a Titan G2 80-300 TEM from FEI Company.

All elements present in the material were mapped but only the results from Silicon (Si) and Zirconium (Zr) were presented. Si was mapped by using its L23-edge at an energy-loss of 99 eV, oxygen (O) was mapped by using its K-edge at an energy-loss of 532 eV and Zr was mapped by using its M45-Edge at an energy-loss of 180 eV. For each element, the elemental map was obtained by using 3-window method[17].

2. Preparation of surface oxide

a) Synthesis of hexagonal ordered mesoporous silica

The silica-based support was prepared according to reported procedure to yield SBA-15 with expected textural parameters[9].

An amphiphilic triblock copolymers P123 (8.03 g, 1.40 mmol) is added to a solution of HCl (250 mL, 1.9 N). After complete dissolution (generally 2.5 hours), the solution is heated at 40 °C. Then, TEOS (17 g, 81.6 mmol) is added drop by drop. After 5 min a white precipitate is formed. The reaction is maintained at 40°C for 24 hours. The obtained suspension is transferred in a 500 mL autoclave and aged for 24 hours at 100°C.
The white solid is filtered off and washed several times with deionized water until being free from foam. The removal of organic template is achieved by two calcinations at 500°C and 650°C (1°C/min) (see appendix 2). About 4.5g of white fine powder SBA-15 is obtained.

Scheme 6: Formation of mesoporous materials by structure-directing agent (SDA)

b) Dehydroxylation of SBA-15: Generation of single silanols and strained siloxane bridges

Dehydroxylation of calcinated SBA-15 occurs at 1000 °C under dynamic vacuum (10^{-5} mbar) to generate SBA-15_{1000} (see appendix 2). The temperature program includes two rises at 1°C /min and two plateaus at 130°C and 1000°C for 3h and 16h respectively.

The first step is used to take any water molecules away from the SBA-15 surface (dehydration).
The second step, called as dehydroxylation, generates strained siloxane bridge (≡SiOSi≡) whom the number increases with the temperature, contrary to the number of silanol groups \[1,3,5b,18\].

The silicon atom of the strained siloxane bridge is electron deficient, thereby acting as a Lewis acid center.

After dehydroxylation the silica need to be handled under inert atmosphere in order to avoid any contamination with air and/or water.

3. Chemisorption of ammonia

a) Reaction of $^{14}$NH$_3$ on SBA-15$_{1000}$

Bendjeriou et al. have shown that the conversion of silanol into silylamine is improved by using a flow reactor: 80 % versus 28 % under static conditions$^{191}$ (see appendix 3).

As a result, the ammonia treatment of SBA-15$_{1000}$ has been carried out by using the same experimental conditions (scheme 7).
SBA-15$_{1000}$ (0.8 g) is introduced in a glass tube equipped by a fritte. At constant NH$_3$ flow (200 mL/min) the temperature is increased to 500°C in 1 hour and is maintained at this temperature for 3 hours (see appendix 4).

Then, the glass tube is cooled down to room temperature under N$_2$ flow. Ammoniated samples obtained from SBA-15$_{1000}$ are designated as NSBA-15$_{1000}$.

Scheme 7: Dynamic ammonia set-up

b) Reaction of $^{15}$NH$_3$ on SBA-15$_{1000}$

To confirm the chemisorption of ammonia but also to obtain additional information on the different species present on the SBA-15$_{1000}$ surface, a $^{15}$N NMR study has been conducted.

A “pseudo-dynamic” set up, different from the previous one, is used (see appendix 5). Indeed, given the cost of $^{15}$NH$_3$, this set up allows a recycling of ammonia through a pump. The pressure inside the system is monitored by a capacitance manometer.

A U-like reactor containing SBA-15$_{1000}$ (100 mg) is placed under vacuum. A flow of ammonia is sent to the system until a pressure of 800 mbar. The U-like reactor is heated up till 500°C. After 15 minutes, the system is put under vacuum again in order to remove all water molecules release during the process.$^{[20]}$

These operations are repeated 3 times in order to attain an optimal ammonia treatment. Indeed, by removing all water molecules formed during the process, the conversion from silanol groups to silylamine groups is more favorable and more efficient. This avoids any reaction between silylamine groups (Si-$^{15}$NH$_2$) and the water after each cycle/loop.
4. Reactivity of ZrNp₄ on NSBA-15₁₀₀₀: impregnation method

Tetraneopentyl zirconium Zr(CH₂C(CH₃)₃)₄ (denoted ZrNp₄ in the following) was first synthesized according to reported procedure[21].

A mixture of SBA-15₁₀₀₀ (350 mg) and ZrNp₄ (380 mg, 1.5eq) in pentane (20 mL) was stirred at 25°C for 8h. After filtration, the solid was washed several times with pentane. The resulting brown powder was dried under vacuum (10⁻⁵ mbar) to yield 315 mg.

V. Results and Discussions

1. Characterizations of surface species formed by reaction of ammonia on SBA-15₁₀₀₀

a) Infrared transmission characterizations

The IR spectrum of highly dehydroxylated SBA-15₁₀₀₀ presents a characteristic stretching vibration band $\nu_s$(OH), of single silanol groups at 3748 cm⁻¹ [2c]. After treatment of SBA-15₁₀₀₀ at 500 °C with either $^{14}$NH₃ or $^{15}$NH₃, three new bands appear at 3536, 3452 and 1550 cm⁻¹ corresponding respectively to either $\nu_{as}(^{14}$NH₂), $\nu_s(^{14}$NH₂) and $\delta(^{14}$NH₂) or $\nu_{as}(^{15}$NH₂), $\nu_s(^{15}$NH₂) and $\delta(^{15}$NH₂)[2a] (figure 2, 3 and 4). Indeed, the vibrational frequency of the isotopic shift comes from square root of reduced mass ratio. $^{15}$N-H/$^{14}$N-H ratio only gives 1.004, so no difference is observed (table 3).

These results are the first proof of chemisorption of ammonia. Characteristic IR bands of physisorbed ammonia do not appear at 3380, 3290 and 1608 cm⁻¹ corresponding to the vibration and deformation bands of N-H bond.

Moreover, after ammonia chemisorption, the free silanol stretching band exhibit a shift to lower wavelength from 3748 to 3741 cm⁻¹. It has been already shown that this shift is a result of opening siloxane bridges by ammonia treatment[2b]. Besides, the intensity is slightly decreased but certainly not significantly as it would have been expected if the silanols were fully transformed into Si-NH₂.

Furthermore, in comparison with the previous literature data, IR suggests that the chemisorptions of ammonia on the SBA-15₁₀₀₀ surface occurs without formation of silazane bridges $\equiv$Si-$\mu$(NH)-Si$\equiv$, the ($\nu_{as}$(NH) band would be expected at 3386 cm⁻¹)[22].

25
Table 3: Infrared assignments after ammonia treatment

<table>
<thead>
<tr>
<th>Assignments</th>
<th>IR bands (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ν₃(OH)</td>
<td>3741</td>
</tr>
<tr>
<td>ν₃(NH₂)</td>
<td>3536</td>
</tr>
<tr>
<td>ν₆(NH₂)</td>
<td>3452</td>
</tr>
<tr>
<td>δ(NH₂)</td>
<td>1550</td>
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</tbody>
</table>

Lattice combination of SBA-15

<table>
<thead>
<tr>
<th>Assignments</th>
<th>IR bands (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice combination</td>
<td>1973</td>
</tr>
<tr>
<td>vibration of SBA-15</td>
<td>1864</td>
</tr>
<tr>
<td></td>
<td>1639</td>
</tr>
</tbody>
</table>

Figure 2: IR spectra (A) SBA-15₁₀₀₀; (B) after addition of $^{14}$NH₃ at 500 °C by using a dynamic set-up
Figure 3: IR spectra (A) SBA-15_{1000}; (B) after addition of $^{15}\text{NH}_3$ at 500 °C by using a pseudo dynamic set-up

Figure 4: Comparison between IR spectra (A) SBA-15_{1000} after addition of $^{15}\text{NH}_3$ at 500 °C by using a dynamic set-up; (B) SBA-15_{1000} after addition of $^{14}\text{NH}_3$ at 500 °C by using a pseudo dynamic set-up

Therefore, chemisorption of ammonia seems to occur through two distinctive pathways (scheme 8):
- By reaction of the remaining isolated silanols with formation of Si-NH₂
- By opening siloxane bridges which generates both silanol and silylamine groups. In this case the IR bands of silanol groups increase. Establishment of electrostatic interactions between both functionalities explains the wavelength shift.
- By substitution of all single silanols resulting from siloxane opening bridges, in excess of ammonia.

Given that SBA-15₁₀₀₀ generates an important amount of strained siloxane bridges and a small amount of single silanol, ammonia treatment leads to much more strained siloxane bridges opening.

**Scheme 6: Proposed reactions for the ammonia treatment**

In order to identify the different species present on the SBA-15₁₀₀₀ surface and understand the mechanism of ammonia chemisorption, solid state NMR studies have been conducted.

**b) Solid-state NMR spectroscopies**

Surface species (=Si-NH₂) were characterized by solid-state NMR.

The reaction of ammonia on SBA-15₁₀₀₀ yields a solid, NSBA-15₁₀₀₀, which presents two resonances in ¹H MAS spectroscopy.
A strong signal at 0.63 ppm is likely due to silylamine groups (≡SiNH₂) and a minor signal at 1.6 ppm, due to residual silanol groups (figure 5).

Figure 5: ¹H MAS solid-state NMR spectrum of NSBA-15₁₀₀₀

Recent developments in 2D ¹H-¹H double quantum allow the access to more accurate characterizations of the surface modification [²³].

The 2D multiple-quantum (MQ) proton spectrum under magic angle spinning confirms the presence of at least two protons on the grafted nitrogen. Indeed, the 2D MQ spectrum exhibits two correlations, both on the diagonal (figure 6):

- One centred at around 0.55 ppm in F2 and 1.1 ppm in F1 and attributed to the ≡SiNH₂ moiety.
- Another one centred at around 1.8 ppm in F2 and 3.8 ppm in F1 and assigned to the residual geminal silanol [≡Si(OH)₂].

Firstly, these results show that isolated surface silanol groups on SBA-15₁₀₀₀ are converted into silylamine species.

Secondly, the remaining gem di-silanol groups are unreactive toward ammonia. The surprising lack of reactivity of gem di-silanol groups is consistent with the difference in acidity (the pKa of these latter is 8.2 whereas it is 2 for isolated silanols) [²⁴].
Chemisorption of 100% labeled ammonia on SBA-15$_{1000}$ has been also investigated by $^{15}$N solid-state NMR spectroscopy. The $^{15}$N CP-MAS NMR spectrum shows only one resonance at -396 ppm (figure 7). Furthermore, no resonance indicating the presence of labeled physisorbed ammonia, is observed at -385 ppm$^{[25]}$. 

![Figure 6: 2D DQ 1H MAS NMR spectrum of NSBA-15$_{1000}$](image)

![Figure 7: MAS NMR spectrum of fully $^{15}$N-labelled NSBA-15$_{1000}$](image)
The assignment of this resonance was also performed through a two-dimensional $^1$H-$^{15}$N HETCOR spectroscopy (figure 8). The 2D HETCOR spectrum, which yields correlations between spatially close $^1$H and $^{15}$N spins, displays only one clear correlation. This latter is centered at around -396 ppm and confirms the presence of silylamine groups.

![2D HETCOR solid-state NMR spectrum of fully $^{15}$N-labelled NSBA-151000](image)

**Figure 8: 2D HETCOR solid-state NMR spectrum of fully $^{15}$N-labelled NSBA-151000**

<table>
<thead>
<tr>
<th>Species</th>
<th>$^1$H NMR, $\delta$ ppm</th>
<th>$^{15}$N NMR, $\delta$ ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>=Si(OH)$_2$</td>
<td>1.8</td>
<td>-</td>
</tr>
<tr>
<td>=SiNH$_2$</td>
<td>0.6</td>
<td>-396</td>
</tr>
<tr>
<td>Physisorbed NH$_3$</td>
<td>2.4</td>
<td>-385</td>
</tr>
</tbody>
</table>

Table 4: $^1$H and $^{15}$N NMR chemical shifts of NSBA-151000
c) Analytical data

To determine the nitrogen loading of the material, two methods of quantification have been carried out: elemental analysis and gas phase analysis (table 5).

Table 5: Elemental Analysis and Gas released upon interaction of the material with MeLi

<table>
<thead>
<tr>
<th></th>
<th>Wt. %&lt;sup&gt;a&lt;/sup&gt;</th>
<th>mmol/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>2.90</td>
<td>2.07&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>H&lt;sup&gt;c&lt;/sup&gt;</td>
<td>-</td>
<td>2.24&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Nitrogen loading determined by elemental analysis
<sup>b</sup> Obtained by : \( \frac{W_{\text{N}}}{W_{\text{H}} \times 100} \)
<sup>c</sup> Total amount of proton determined by gas phase analysis: MeLi reacts with protons of remaining silanol and silylamine groups on NSBA-15 surface. It releases one molecule of methane for each SiOH group, and two molecules of methane for each NH<sub>2</sub> group.

d) Conclusion

Ammonia treatment allows the generation of two kinds of species, as shown in the scheme 9:

- Single silylamine groups arising from the direct substitution of single silanol.
- Silylamine pairs derived from:
  - First, an opening siloxane bridges which generates both silylamine and silanol pairs.
  - Second, a substitution of the formed silanol.
The gem-silanols do not react with ammonia but they are completely passivated by HMDS to yield a surface whose most reactive moieties are silylamine groups plus $=$Si(OSiMe$_3$)$_2$.

2. Characterizations of the surface species formed by passivation on NSBA-15$_{1000}$

The aim of this step is to obtain a surface displaying only silylamine groups. For this purpose, a protecting reagent is used and two conditions are necessary:

- The protecting reagent needs to be selective toward silanol. Usually, trimethylchlorosilane or hexamethyldisilazane can be considered as passivation reagent of silanol surface groups [26].
- The by-product needs to be unreactive toward the silylamine surface groups.

As described in the scheme 10, TMSCl and HMDS release respectively HCl and NH$_3$. In consequence, this latter is retained in order to avoid any protonation of silylamine groups.
Passivated samples obtained from NSBA-15\textsubscript{1000} are designated as P-NSBA-15\textsubscript{1000}.

![Scheme 8: Passivation reagents](image)

**a) Infrared transmission characterizations**

The results of IR spectroscopy after treatment of NSBA-15\textsubscript{1000} by HMDS at RT are shown in table 6 and figure 9.

All silanol groups are consumed as indicated by the complete disappearance of the band at 3741 cm\textsuperscript{-1} while intense CH stretching peaks are detected between 3000 and 2800 cm\textsuperscript{-1} and CH bending modes below 1400 cm\textsuperscript{-1}\cite{27}.

No differences in the Si-O-Si combination and overtone bands (1639, 1864, 1973 cm\textsuperscript{-1}, respectively) are detectable after reaction and SiNH\textsubscript{2} bands remain intact as well.

Due to the high dehydroxylation at 1000°C most of silylamine groups result from strained siloxane bridges opening. However, a few isolated silylamine groups are still present (resulting from the direct substitution of silanol groups into NH\textsubscript{2}).

Moreover, a broad band at about 3600 cm\textsuperscript{-1} corresponds to the inaccessible silanol groups situated inside the microporosity of the support.

As a result, a surface displaying only SiNH\textsubscript{2} and =Si(OSiMe\textsubscript{3})\textsubscript{2} is obtained (scheme 11).
Table 6: Infrared assignments after HMDS treatment of NSBA-15

<table>
<thead>
<tr>
<th>Assignments</th>
<th>IR bands (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu$(OH)</td>
<td>3741</td>
</tr>
<tr>
<td>$\nu_{as}$(NH$_2$)</td>
<td>3536</td>
</tr>
<tr>
<td>$\nu_{s}$(NH$_2$)</td>
<td>3452</td>
</tr>
<tr>
<td>$\nu$(CH$_3$)</td>
<td>2970</td>
</tr>
<tr>
<td>$\nu_{as}$(CH$_3$)</td>
<td>2873</td>
</tr>
<tr>
<td>$\delta_{as}$(CH$_3$)</td>
<td>1461</td>
</tr>
<tr>
<td>$\delta$(NH$_2$)</td>
<td>1550</td>
</tr>
<tr>
<td>Lattice combination vibration of SBA-15</td>
<td>1973, 1864, 1639</td>
</tr>
</tbody>
</table>

Figure 9: IR spectra (A) SBA-15$_{1000}$ after addition of NH$_3$; (B) NSBA-15$_{1000}$ after passivation by HMDS
Scheme 11: Passivation reaction

\[
\text{NH}_2 \quad \text{Si} \quad \text{O} \quad \text{O} \quad \text{OH} \quad + \quad \text{HMDS, Pentane} \quad \text{RT, overnight} \quad \rightarrow \quad \text{Me}_3\text{Si} \quad \text{Si} \quad \text{O} \quad \text{O} \quad \text{Me}_3\text{Si} \\
\text{NSBA-15}_{1000} \quad \text{P-NSBA-15}_{1000}
\]

b) Analytical data

To determine the nitrogen loading of the material, two kinds of quantification have been done: elemental analysis and gas phase analysis (table 7).

Table 7: Elemental analysis and Gas released upon interaction of the material with MeLi

<table>
<thead>
<tr>
<th></th>
<th>Wt. %&lt;sup&gt;a&lt;/sup&gt;</th>
<th>mmol/g</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SBA-15 after ammonia treatment</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>2.90</td>
<td>2.07</td>
</tr>
<tr>
<td>H</td>
<td>-</td>
<td>2.24</td>
</tr>
<tr>
<td><strong>NSBA-15 after passivation</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>2.73</td>
<td>1.95&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>H&lt;sup&gt;c&lt;/sup&gt;</td>
<td>-</td>
<td>1.66&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>Nitrogen loading determined by elemental analysis
<sup>b</sup>Obtained by: \( \frac{W_x*100}{(M_x+100)} \)
<sup>c</sup>Total amount of proton determined by gas phase analysis: MeLi does not react with Si-O-Si(Me)<sub>3</sub> but only with silylamine groups. Hence, two molecules of methane are released for each NH<sub>2</sub> group.
c) Conclusion

After ammonia treatment SBA-15\textsubscript{1000} contains free Si-NH\textsubscript{2} and SiOH whereas NSBA-15\textsubscript{1000}, after passivation, displays just Si-NH\textsubscript{2} given that HMDS reacts just with Si-OH (scheme 12).

Scheme 12: Final surface species after passivation

![Scheme 12](image)

Compare to the elemental analysis before passivation, the carbon and hydrogen mass percent are increased given that one hydrogen is substituted with one trimethylsilyl group (9H and 3C more).

3. Characterizations of the surface species formed by reaction of ZrNp\textsubscript{4} on P-NSBA-15\textsubscript{1000}

a) Infrared transmission characterizations

The results of IR spectroscopy after reaction of ZrNp\textsubscript{4} on P-NSBA-15\textsubscript{1000} by impregnation method are shown in table 8 and figure 10.

The reaction with Zr(Np)\textsubscript{4} results in a decrease of the 3536, 3452 and 1550 cm\textsuperscript{-1} bands, characteristic of the (NH\textsubscript{2}) vibrations.

New bands in the range 1465 cm\textsuperscript{-1} and 1365 cm\textsuperscript{-1} appear and are assigned to the symmetric and asymmetric deformation vibrations of CH\textsubscript{2} respectively, from the neopentyl group (Np).

Two bands characteristic of the passivation (2970 cm\textsuperscript{-1} and 2873 cm\textsuperscript{-1}) are not seen. The most simple explanation is that they are still present but hidden by the two large and intense bands at 2954 cm\textsuperscript{-1} and 2869 cm\textsuperscript{-1} assigned to \(v_{as}(\text{CH}_2)\) and \(v_s(\text{CH}_2)\) of the Np ligand.
Finally three bands at 3502, 3425 and 3332 cm\(^{-1}\) appear and belong to the stretching vibration of \(\nu(\text{Zr-NH})\).

Table 8: Infrared assignments after grafting of Zr\(\text{Np}_4\) on NSBA-15 after passivation

<table>
<thead>
<tr>
<th>Assignments</th>
<th>(\text{IR bands (cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\nu(\text{OH}))</td>
<td>3741</td>
</tr>
<tr>
<td>(\nu(\text{Zr-NH}))</td>
<td>3502 (\quad) 3425 (\quad) 3332</td>
</tr>
<tr>
<td>(\nu(\text{CH}_3))</td>
<td>2970</td>
</tr>
<tr>
<td>(\nu_{as}(\text{CH}_3))</td>
<td>2873</td>
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<td>(\nu_{as}(\text{CH}_2))</td>
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<td>(\nu(\text{CH}_2))</td>
<td>2869</td>
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<td>(\delta_{as}(\text{CH}_2))</td>
<td>1465</td>
</tr>
<tr>
<td>(\delta(\text{CH}_2))</td>
<td>1365</td>
</tr>
<tr>
<td>Lattice combination vibration of SBA-15</td>
<td>1973 (\quad) 1864 (\quad) 1639</td>
</tr>
</tbody>
</table>

Figure 10: IR spectra (A) NSBA-15\(_{1000}\) after passivation; (B) P-NSBA-15\(_{1000}\) after complexation
b) Solid state NMR spectroscopies

Figure 11 representing the $^1$H MAS solid-state NMR of SBA-15$_{1000}$ after ammonia treatment, passivation by HMDS and grafting by ZrNp$_4$ displays three resonances.

The peak at 0.21 ppm is attributed to the protons of the trimethylsilyl groups, obtained after reaction of remaining silanols with HMDS.

The intense resonance observed at 1.11 ppm corresponds to the two groups of protons of the neopentyl moieties $(CH_3)_3C-CH_2-Zr$.

The weak resonance at 4.42 ppm corresponds to the proton of the $\equiv$Si-NH-Zr$^{[28]}$, confirming the reaction between silylamine groups and the organometallic complex.

2D DQ $^1$H MAS NMR spectrum presents three correlations, all of them on the diagonal (figure 12):
- One centered at around 0.2 ppm is attributed to the protons of the trimethylsilyl groups.
- The second correlation at around 1.1 ppm is assigned to the protons of the secondary carbon of the neopentyl ligands.
- The third correlation at around 4.5 ppm corresponds to the nitrogen proton and validates the existence of two neighbors NH groups.

![Figure 12: 2D DQ \(^1\)H MAS solid state NMR](image)

\((CH_3)_3C-\text{CH}_2-\text{Zr}\)

Si-NH-Zr

1.1 ppm

4.5 ppm

\(=\text{SiOSi(CH}_3)_3\)

0.2 ppm

Proton single-quantum frequency (ppm) - F2

Proton single-quantum frequency (ppm) - F1

\(^{13}\)C CPMAS Solid State NMR spectroscopy proves the presence of neopentyl groups bonded to zirconium (figure 13). A sharp peak at approximately 33.4 ppm is attributed to methyl groups of the neopentyl ligand and the signal at 96.8 ppm is attributed to the Zr\(\text{CH}_2\) carbon.
The quaternary carbon atom, expected to give a signal at approximately 25 ppm, is not observed, given that it is not directly bound to protons.

In the literature, the organometallic complex \( \equiv \text{Si–O–Zr(CH}_2\text{C(CH}_3\text{)}_3\) was synthesized on the surface of silica dehydroxylated at 500\(^\circ\)C\[^{[5a]}\].

The \(^{13}\)C CP-MAS NMR spectrum of the resulting material is quite similar to \( \equiv \text{Si–(NH)}_2\text{–Zr(Np)}_2\).

Indeed, the carbon peak of CH\(_3\) is shifted from 33.9 to 33.4 ppm as well as the CH\(_2\) peak from 95.5 to 96.8 ppm likely due to the two amine groups NH which especially shift downfield further the secondary carbon (J^2 coupling).

---

Figure 13: \(^{13}\)C CPMAS solid state NMR
2D DQ \(^1\)H/\(^{13}\)C MAS NMR spectroscopy is in relation with all precedent results (figure 14). Unlike CH\(_2\)/CH\(_3\) groups of Zr(Np)\(_2\), NH cannot correlate with the secondary carbon of the neopentyl ligand given than the distance between them is supposed to be too long (\(J^3\) coupling) and are separated by one zirconium.

![Figure 14: 2D DQ \(^1\)H/\(^{13}\)C MAS solid state NMR](image)

**c) Analytical data**

To determine the nitrogen loading of the material, two methods of quantification have been achieved: elemental analysis and gas phase analysis (table 9).
Table 9: Elemental analysis and Gas released during the grafting of ZrNp₄

<table>
<thead>
<tr>
<th></th>
<th>Wt. %ᵃ</th>
<th>mmol/g</th>
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<tbody>
<tr>
<td>SBA-15 after ammonia</td>
<td>2.90</td>
<td>2.07</td>
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<tr>
<td>treatment</td>
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<tr>
<td>NSBA-15 after passivation</td>
<td>2.73</td>
<td>1.95</td>
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<tr>
<td>PNSAB-15 after reaction</td>
<td>2.36</td>
<td>1.68ᵇ</td>
</tr>
<tr>
<td>with ZrNp₄</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>6.75</td>
<td>0.74ᵇ</td>
</tr>
</tbody>
</table>

ᵃ Nitrogen loading determined by elemental analysis
ᵇ Obtained by: \( \frac{W/c\%}{M/100} \)
ᶜ The same total amount of zirconium (0.74mmol/g) has been determined by gas phase analysis: for each complex formed with Zr(Np)₄, two NH₂ groups react and two NpH molecules are released. Thus, for each NH₂ pair two NpH are lost.

NB: Neopentane (NpH) is evolved probing that a reaction occurred between the support and the organometallic complex.

d) Conclusion

The trimethylsilyl groups remain untouched whereas the silylamine groups react with the organometallic complex to give mainly a bi-podal zirconium bis-neopentyl complex (scheme 13).

Therefore, a new well-defined silica surface displaying bi-podal zirconium complexes is formed after reaction with Zr(Np)₄ (see appendix 7).

Scheme 13: Main surface species after grafting of the Zirconium Tetraneopentyl complex
The mass percentage of Zr, C and H increases due to the replacement of two H by one Zr(C\textsubscript{10}H\textsubscript{22}) whereas the number of nitrogen remains the same.

4. **Structural characterization**

a) **XRD and BET**

To explore the structural behavior of SBA-15\textsubscript{1000} after each step, XRD and BET analysis have been performed.

The XRD pattern (figure 15) shows the presence of reflections at 2\(\theta\) angle of 0.9\(^{\circ}\)-1.7\(^{\circ}\) and 1.9\(^{\circ}\), corresponding to planes (100), (110) and (200). Bragg reflections confirm the hexagonal symmetry of the material.

Higher intensity of peaks in the XRD pattern of SBA-15\textsubscript{1000} than P-NSBA-15\textsubscript{1000} after complexation, indicate a decrease in the long-range order of pores by the addition of the organometallic.

The decrease in intensity of XRD peaks at 1.7\(^{\circ}\) and 1.9\(^{\circ}\) are due to the incorporation of the zirconium complex. However, it does not significantly change the hexagonal ordering of SBA-15 framework as seen from the BJH isotherms below.

Furthermore, the ammonia treatment, passivation and organometallic reaction do not destroy the mesoscopically ordered structure. The mesostructure of SBA-15\textsubscript{1000} is conserved for each step.
Figure 14: XRD pattern

SBA-15 dehydroxylated at 1000 degree C
NSBA-15
Complexation of P-NSBA-15

$\text{Intensity}$

$2\theta$ (degree)

$d_{100} = 85.31$

$d_{100} = 85.37$

$d_{100} = 84.32$

Figure 15: XRD pattern
BET analysis (figure 16) shows that capillary condensation and multilayer adsorption take place at high and lower pressures respectively.

Thus, SBA-15\textsubscript{1000} samples display a type IV isotherm with H1 hysteresis and a sharp increase in volume adsorbed at $P/P_0 \approx 0.76$, characteristic of highly ordered mesoporous materials.

![N\textsubscript{2} adsorption–desorption isotherms of SBA-15\textsubscript{1000} at 77K](image)

The estimated textural parameters of SBA-15\textsubscript{1000} such as BET surface area, total pore volume, pore size and wall thickness for each step are shown in the table 10.

The BET surface area, pore size and pore volume of SBA-15\textsubscript{1000} are 679 m\textsuperscript{2}.g\textsuperscript{-1}, 5.8 nm and 0.90 cm\textsuperscript{3}.g\textsuperscript{-1} respectively.
After ammonia treatment these values decrease lightly. After complexation the BET surface area, pore size and pore volume diminish much more and have for values 511 m$^2$.g$^{-1}$, 5.2 nm and 0.59 cm$^3$.g$^{-1}$ respectively.

These results are coherent since the substitution of OH by NH$_2$ (ammonia treatment) then the complexation of Zr(Np)$_4$ on the surface of NSBA-15$_{1000}$ increase the size of the substituent after each step and so decrease the pore volume and surface area.

In another word, this decrease is due first to surface hydroxyl groups of the support “consumed” by reaction with NH$_3$ to give NH$_2$ (slightly bigger).

Therefore, the material appears to retain its original physical properties (i.e. porosity, surface area and mesoscopic order) after ammonia treatment.

Then, NH$_2$ reacts with Zr(Np)$_4$ to give a bi-podal zirconium bis-neopentyl complex (much bigger). Hence, surface reactions caused the decrease of the available surface area of the support.

Table 10: Textural parameters of SBA-15 support

<table>
<thead>
<tr>
<th>SBA-15 support</th>
<th>d$_{100}^a$ (Å)</th>
<th>a$_0^b$ (Å)</th>
<th>Wall thickness$^c$ (Å)</th>
<th>V$_p^d$ (cm$^3$.g$^{-1}$)</th>
<th>D$_p^e$ (Å)</th>
<th>S$_{BET}^e$ (m$^2$.g$^{-1}$)</th>
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<tbody>
<tr>
<td>SBA-15$_{1000}$</td>
<td>85.37</td>
<td>98.58</td>
<td>40.88</td>
<td>0.902</td>
<td>57.7</td>
<td>679</td>
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<td>NSBA-15$_{1000}$</td>
<td>84.32</td>
<td>97.36</td>
<td>41.56</td>
<td>0.840</td>
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<td>638</td>
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<td>Complexation P-NSBA-15$_{1000}$</td>
<td>85.31</td>
<td>98.51</td>
<td>47.01</td>
<td>0.590</td>
<td>51.5</td>
<td>511</td>
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</table>

$^a$ d(100) spacing.

$^b$ a$_0 = 2d(100)\sqrt{3}$, hexagonal lattice parameter calculated from XRD.

$^c$ Calculated by a$_0$ – pore size.

$^d$ Total pore volume at P/P$_0 = 0.970$.

$^e$ Pore size from desorption branch applying the BJH pore analysis.

b) High Resolution Transmission Electron Microscopy

Mesoporous SBA-15$_{1000}$ profile shows a well ordered material, featuring a wall and channels diameter of 2.98 nm and 5.59 nm respectively. Channels are large enough to allow the grafting of the zirconium complex.
The blue line in the micrograph shows the place that was used to get a line-profile for determining the width of walls and channels in the mesoporous silica.

c) Elemental mapping by Energy Filtered Transmission Electron Microscopy (EFTEM)

The addition of the EFTEM of Silicium (white dots) with the EFTEM of zirconium (black dots) result to a map, showed below, representing the distribution of the zirconium complex on the surface of SBA-15\textsubscript{1000}.
This map shows a homogeneous distribution of Zr complexes inside the channels of the material. Zirconium is exclusively located in these channels which fit very well with its size.

Indeed, the mesoporous Cp₂Zr(NH)₂-SBA-15₁₀₀₀ profile reveals an average thickness of Zr complex diameter of 5.25 nm, smaller than the channel diameter 5.59 nm.

Furthermore, due to the synthesis method requiring the formation of micelles arranged with their functional (hydrophilic) groups outwards and their hydrophobic segments inside, the ammonia treatment followed by the passivation and the organometallic reaction give an exceptional material, with a grafting only located inside its channels.

Besides, these results point out a very good repartition and diffusion of the organometallic complex, without any obstruction of pores.
Prospective and Applications

This groundbreaking discovery could play a major role for incoming researches. Indeed this first bi-podal organometallic complex grafted on well-defined SBA-15\textsubscript{1000} surface displaying silylamine pairs has been generated and fully characterized for the first time.

With this new surface organometallic, new materials could emerge by using different transition metals (Ruthenium, Palladium) for instance, in order to obtain diverse other properties thanks to this unique surface organometallic complex grafted via two different nitrogen-metal bonds. Assess their performances for various catalysis transformations is the next step in order to find, perhaps, a new breakthrough which will lead to another type of catalysts featuring a better Turn Over Number (TON), a better stability or/and a better selectivity.

In addition, the control of the ammonia treatment could allow us to graft two different organometallic complexes on the surface. Indeed, the surface displaying two distinctive chemical groups (alcohol and amine) could selectively react with two different catalysts. Unfortunately, this is not straightforward and further investigations remain to do in order to find two catalysts which do not compete and react each other.

1. Industrial and environmental potential

A catalyst enhances the efficiency of a reaction, reduces waste production by increasing the selectivity of the chemical reaction, reduces the energy demand of the process, and enables the use of new resource. Catalysts are essential nowadays, and are present everywhere in all chemical and oil companies, either for the synthesis of polymers or chemical compounds such as ethanol, acetic acid....

In industry, 75 \% of all processes are catalytic and catalysis in chemical industry represents 80 \% of all added values. Most of the time, these synthesis need several steps and so different kinds of catalysts in order to obtain the final product.

Unfortunately, these steps involve the change of solvent and catalyst, the transfer of the solution in another reactor and the re-heating of this solution. All these actions are a waste of time, energy and money.

Which benefits would be obtained if a reaction could be carried out in only one step, with no intermediate steps in between? If each catalyst could be processed at a higher Turnover Number (TON)?
The first suggestion could be achieved by a perfect control of the support’s surface in order to graft two types of catalytic sites into one single, with the aim of achieving a bi-functional catalyst.

Indeed, on the same compound, one catalyst can carry out the first reaction’s step and the second one the next reaction. These two different catalysts will be able to team up and work together in order to obtain the wanted product. This complementary whole will avoid the time and energy losses associated with a several steps mechanism, mostly requiring the isolation of the intermediary. In this work, the SBA-15 surface has been fully controlled and understood and so, could be a step forward in the achievement of this future bi-functional catalyst.

The second suggestion could be possible by changing the metal of this new bipodal Zirconium bis-neopentyl or/and by reacting this latter with hydrogen in order to form an innovative Zirconium hydride complex grafted via two silylamine on the surface. This specificity could lead to new properties, never suspected before and open the door to a new kind of catalytic reaction more efficient and more environmental friendly.

Therefore, these groundbreakings catalysts could improve the manufacturing process and save the company dozen millions of dollar per annum. Rethinking and changing our current manufacturing process is the milestone to consume less, produce more and save our environment. A new chemical catalyst is the key to reduce our energy, a catalyst as well, for global economic growth and prosperity.

Economic progress, especially in developing countries, will drive global energy demand higher, despite substantial efficiency gains. Significantly improving CO₂ emissions requires global participation, step changes in energy efficiency, technology gains and massive investment. All these issues imply massive use of catalyst technology.

Each new discovery, like this one previously presented, bring us closer of this ideality: Consume less to produce more and to save our valuable environment for our next generation....
Conclusion

A new surface species has been synthesized by reaction of Zr(Np)\textsubscript{4} on a SBA-15\textsubscript{1000} surface previously treated by ammonia followed by a passivation. These different steps have led to the formation of a bi-podal zirconium bis-neopentyl complex grafted by two distinct nitrogen-metal bonds. These unique new surface organometallic bonds have been understood and fully characterized. The use of NMR analysis allows unambiguous determination of this well-defined grafted organometallic complex.

Moreover, the elemental and gases analysis allow to clarify the concentration of each species present and find out what is going on during and after each step. All results validate that Zr(Np)\textsubscript{4} reacts mostly with two next by silylamine groups, releasing two neopentane molecules.

Beside this achievement, the elemental mapping of SBA-15\textsubscript{1000}, displaying the zirconium bis-neopentyl complex, shows a perfect dispersion and diffusion of this latter inside its channels. This is due to the rapport organometallic’s size to channel’s size, inferior to one. Further studies can be made to have a better understanding of this phenomenon with the purpose of having a high loading and repartition of catalyst.

XRD and BET analysis show that the effect of Zr(Np)\textsubscript{2} is noteworthy in that it causes a significant decrease in surface area and pore volume. Patterns of all steps are similar to SBA-15\textsubscript{1000}, indicating that each material: NSBA-15\textsubscript{1000} and P-NSBA-15\textsubscript{1000} after complexation contain well-ordered hexagonal arrays of one-dimensional channel structure. The hexagonal structure of SBA-15\textsubscript{1000} was observed for all steps via the small angle XRD pattern consisting of two weak peaks at 2\(\theta\) around 1.6˚ and 1.8˚.

Hence, the ammonia treatment, the passivation and the organometallic reaction do not destroy the mesoscopically ordered structure and allow a perfect homogenization of the diamine zirconium bis-neopentyl complexes in the SBA-15\textsubscript{1000} channels.

This new surface organometallic disposition has been successfully characterized, understood and improved. This material, made for the first time at King Abdullah University of Science and Technology, could play a potential role as a new ligand in Surface Organometallic Chemistry (SOMC) and could impact future area of research such as catalysis and offers fascinating new possibilities and applications.

Surface Organometallic Chemistry has proved, once again, to be a valuable method for the synthesis of well-defined organometallic fragments grafted on surfaces.

As Elina Karlsson said: “Scientist and artists are all explorers, fascinated by the complexities of the world around them, constantly questioning what is known, and seeking to understand what is unknown”.

52
REFERENCES

Publications


**Posters Presentation for the 100th KCC Publication**

## Appendix 1: Main chemical compounds used

<table>
<thead>
<tr>
<th></th>
<th>TEOS</th>
<th>P123</th>
<th>HCL 35%</th>
<th>Pentane</th>
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<td><strong>Name</strong></td>
<td>Tetraethyl orthosilicate</td>
<td>Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)</td>
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<td>Pentane</td>
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<td><strong>Formula</strong></td>
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<td>(C₃H₆O.C₂H₄O)ₓ</td>
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<td>C₅H₁₂</td>
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<td><img src="image3.png" alt="HCL Chemical Structure" /></td>
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<td><strong>Molecular weight</strong></td>
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<td>0.626 g/cm³ at 25 °C</td>
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<td>liquid</td>
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<td>Flammable liquids (Category 2)</td>
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<table>
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<tr>
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<th>168 °C</th>
<th>56 - 61 °C (melting point)</th>
<th>&gt; 100 °C</th>
<th>35 - 36 °C</th>
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<td><strong>Flash Point</strong></td>
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<td>-</td>
<td>-</td>
<td>-49,0 °C</td>
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<td>closed cup</td>
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<td>closed cup</td>
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<td>23 % (V)</td>
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<td>-</td>
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<td>1.4 % (V)</td>
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<td>LD50 Dermal – rabbit - 5.878 mg/kg</td>
<td>LD50 Dermal – rabbit - 20.000 mg/kg</td>
<td>LD50 Dermal – rabbit - 3.000 mg/kg</td>
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Appendix 2: Calcination and dehydroxylation program of SBA-15

Calcination is the final step to remove the template and obtain SBA-15

Dehydroxylation temperature plays a major role in the ratio silanol/siloxane bridge to give SBA-15$^{1000/700}$
Appendix 3: Static versus Dynamic ammonia treatment at 500°C

Influence of the ammonia treatment condition on SBA-15

IR spectra strengthen the notion that all SiOH groups are almost consumed and any silazane bridges are formed.

The use of a dynamic ammonia treatment leads to a much better conversion of silanol than a static ammonia treatment. This improvement, estimated at 300%, is mainly due to the flowing of gaseous NH₃ which removes the water formed during the ammonia treatment\(^\text{[20]}\) and so, the equilibrium is shifted to the side that favors the formation of silylamine groups (Le Chatelier's principle).

Furthermore, this technic offers several advantages over the static assembly: a larger amount of powder silica can be treated (typically 500 mg) and an increase of the ammonia can be applied.

**NB:** For each study, any modifications of the lattice are observed.

<table>
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<tr>
<th>Assignments</th>
<th>IR bands (cm(^{-1}))</th>
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<tr>
<td>(\nu_s) (OH)</td>
<td>3745</td>
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<tr>
<td>(\nu_{as}(NH_2))</td>
<td>3536</td>
</tr>
<tr>
<td>(\nu_s) (NH₂)</td>
<td>3452</td>
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<tr>
<td>(\nu_{as}(NH))</td>
<td>3386</td>
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</table>
Appendix 4: Optimal ammonia treatment temperature

Influence of the ammonia treatment temperature on SBA-15

Isolated silanols groups (≡Si-OH) are selectively, but only partially, converted to silylamine (≡Si-NH₂) at different temperatures.

At 500°C, there is a partial substitution of OH by NH₂, estimate to around 70% conversion. The rest are geminal silanol groups that didn’t react with NH₃. These results reinforce the elemental analysis which reveals that SBA-15₀₀₀ is made up 30% and 70% of geminal and isolated silanol groups respectively.

### Assignments IR bands (cm⁻¹)

<table>
<thead>
<tr>
<th>Assignments</th>
<th>IR bands (cm⁻¹)</th>
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<tbody>
<tr>
<td>νₛ(OH)</td>
<td>3745</td>
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<tr>
<td>νₐs(NH₂)</td>
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<td>νₐs(NH)</td>
<td>3386</td>
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<tr>
<td>δ(NH₂)</td>
<td>1552</td>
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</table>

NB: Ammonia treatment is realized with a ramp temperature of 1 °C/min and a plateau at 500 °C for 2 hours.
Above 500°C SiOH groups still remain and even increase due to the formation of silazane bridges:

Therefore, the optimal temperature of the ammonia treatment for a maximal conversion is about 500°C.

Indeed, above this temperature the amount of silanol groups increase due to silazane bridges and below, the temperature is not sufficient enough to lead to a good conversion of silanol to silylamine groups.
Appendix 5: Ammonia treatment set up for $^{15}\text{NH}_3$

Total Volume in the system: 246.18 ml
Appendix 6: SBA-15\textsubscript{1000} Gas Analysis

Preparation

- Silica and methyl lithium (MeLi) are separately introduced in a double Schlenk tube under Argon. Then, MeLi is dried under vacuum until obtaining a white powder.

![Diagram of vacuum and MeLi drying]

- Pentane is added to the MeLi under HVL by using a T tube for the connection double Schlenk/vacuum/solvent (pentane degassed).

- The transfer is made by cooling down the tube containing the methyl lithium, with liquid nitrogen.

- Once the solvent amount is sufficient (about twice the silica volume), the double Schlenk is removed and the solution is decanted to the other tube, containing the silica, by cooling down this latter with liquid nitrogen as well.

![Diagram of liquid nitrogen]

- Then, the solution is stirred at room temperature overnight in the fume hood.
Transfer

- The following day, a T tube is used on the HVL for the connection double Schlenk/vacuum/big flask (6000 ml) previously desorbed under HVL overnight.

- Then, gases contained in the double Schlenk are transferred in the big flask by putting a diwar on the tank of this latter (condense gases).
  
  NB: All the system is at 10⁻⁵mmHg.

- After 20 minutes the big flask’s tap is closed and the liquid nitrogen removed.

- The big flask is left as it is at room temperature over night to allow a good homogenization.

- A T tube is used for the connection big flask/vacuum/rotaflow and put under vacuum.

- A known amount of gas (as internal standard) is injected in the rotaflow only.

- Next, the connection is put under vacuum again, until 10⁻⁵ mmHg, in order to eliminate the gas in the junction.

- After that, the known amount of gas contained in the rotaflow is transferred to the big flask by cooling this latter down with liquid nitrogen (re-condense gases contained in the big flask)

Injection

- The day after, a T-shape connector (with septum) is placed between the HVL and the big flask.

- The connection is put under vacuum, until 10⁻⁵mmHg and then filled up with gas contains in the big flask.

- Then, the junction is put to 1 bar (by putting and removing a syringe without the piston) and left 10 minutes in order to mix gases.

- 10 microliters are injected in a GC-FID for analysis.

The amount of gas evolved is determined by the peak area ratio between the analyte and the internal standard. Knowing the volume, pressure and temperature of the internal standard transferred in the big flask and using the ideal gas law equation: PV=nRT it is easy to determine the concentration of this latter and so, to determine the concentration of gas released during the reaction between SBA-15₁₀₀₀ and CH₃Li for instance.
### Results

**Gas Chromatography**
- Agilent Tech 6890
- HP Plot U
- Isotherm 150°C

**Method**
- Gas evolved

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<th>Air of the internal standard</th>
<th>Air of CH₄</th>
<th>Air of CH₄ normalised</th>
<th>Number of moles of CH₄</th>
<th>Moles of CH₄ per gram of SBA</th>
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**Average**: 2.24 mmol/g

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<th>Air of CH₄</th>
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<td>2</td>
<td>40.3</td>
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<td>2.24E-04</td>
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<td>3</td>
<td>37.6</td>
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**Average**: 2.24 mmol/g

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<thead>
<tr>
<th>m P-SBA-15 Passivation</th>
<th>Internal standard</th>
<th>Injection</th>
<th>Air of the internal standard</th>
<th>Air of CH₄</th>
<th>Air of CH₄ normalised</th>
<th>Number of moles of CH₄</th>
<th>Moles of CH₄ per gram of SBA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>23.1</td>
<td>27.00</td>
<td>1.73E-04</td>
<td>2.14E-05</td>
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<td>2</td>
<td>32.4</td>
<td>25.80</td>
<td>1.18E-04</td>
<td>1.45E-05</td>
<td>0.58 mmol/g</td>
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<td>3</td>
<td>32.2</td>
<td>26.00</td>
<td>1.18E-04</td>
<td>1.45E-05</td>
<td>0.58 mmol/g</td>
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<tr>
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<td>4</td>
<td>28.6</td>
<td>23.60</td>
<td>1.45E-04</td>
<td>1.84E-05</td>
<td>0.44 mmol/g</td>
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<td>5</td>
<td>28.6</td>
<td>23.60</td>
<td>1.30E-04</td>
<td>1.46E-05</td>
<td>0.42 mmol/g</td>
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</tbody>
</table>

**Average**: 1.46 mmol/g

**Gas Chromatography**
- Agilent Tech 6890
- HP Plot U
- Isotherm 150°C

**Method**
- Gas evolved

<table>
<thead>
<tr>
<th>m Complexation - P-SBA-15 Passivation</th>
<th>Internal standard</th>
<th>Injection</th>
<th>Air of the internal standard</th>
<th>Air of NpH</th>
<th>Air of NpH normalised</th>
<th>Number of moles of NpH</th>
<th>Moles of NpH per gram of SBA</th>
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</thead>
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<tr>
<td></td>
<td></td>
<td>1</td>
<td>373.9</td>
<td>20.1</td>
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<td></td>
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<td>350.1</td>
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<tr>
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<td></td>
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<td>328.7</td>
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<td>4</td>
<td>311.6</td>
<td>17.1</td>
<td>136.88</td>
<td>2.01E-05</td>
<td>1.01E-03</td>
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</tbody>
</table>

**Average**: 1.04 mmol/g
Appendix 7: Zirconium Neopentyl Grafting

Preparation

- Silica and ZrNp$_4$ are separately introduced in a double Schlenk tube under glove box, as showed below:

  ![Diagram of double Schlenk tube](image)

- Pentane is added to the organometallic complex under HVL by using a T tube for the connection double Schlenk/vacuum/solvent (pentane degassed).

- The transfer is made by cooling down the tube containing ZrNp$_4$, with liquid nitrogen.

Connection (under vacuum) to pentane

Liquid Nitrogen
➢ Once the solvent amount is sufficient (about twice the silica volume), the double Schlenk is removed and the solution is decanted to the other tube, containing the silica, by cooling down this latter with liquid nitrogen as well.

![Diagram of liquid nitrogen](image.png)

Liquid Nitrogen

➢ Then, the solution is stirred at room temperature overnight in the fume hood.

➢ The following day, the decanting is repeated to remove the solvent and Zr(Np)₄ in excess.

➢ The solvent is removed from the double Schlenk tube under HVL and the silica is dried for 5 hours.
Briefly summarize for each step

Highly dehydroxylated SBA-15 at 1000°C

Controlled ammonolysis as function temperature (+ NH₃)
followed by a passivation (+ HMDS)

Generation of single silylamine and silylamine pairs

New well-defined silica surface displaying mainly bipodal zirconium complexes
### Main IR bands characteristics

<table>
<thead>
<tr>
<th>Species</th>
<th>IR bands (cm⁻¹)</th>
<th>Assignments</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Image" /></td>
<td>3748</td>
<td>(\nu(\text{OH}))</td>
<td>Dehydroxylation at 1000 °C, 24h</td>
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<tr>
<td><img src="image2.png" alt="Image" /></td>
<td>1973, 1864, 1639</td>
<td>Lattice combination vibration of SBA-15</td>
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<tr>
<td><img src="image3.png" alt="Image" /></td>
<td>3748</td>
<td>(\nu(\text{OH}))</td>
<td>Ammonia treatment at 500 °C, 3h</td>
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<tr>
<td><img src="image4.png" alt="Image" /></td>
<td>3536, 3452, 1550</td>
<td>(\nu_{\text{as}}(\text{NH}<em>2), \nu</em>{\text{s}}(\text{NH}_2), \delta(\text{NH}_2))</td>
<td>Passivation HMDS/pentane, overnight</td>
</tr>
<tr>
<td><img src="image5.png" alt="Image" /></td>
<td>2970, 2873</td>
<td>(\nu_{\text{s}}(\text{CH}<em>2), \nu</em>{\text{as}}(\text{CH}_3))</td>
<td></td>
</tr>
<tr>
<td><img src="image6.png" alt="Image" /></td>
<td>3502, 3425, 3332</td>
<td>(\nu(\text{NH}))</td>
<td></td>
</tr>
<tr>
<td><img src="image7.png" alt="Image" /></td>
<td>2954, 2869, 1465, 1365</td>
<td>(\nu_{\text{as}}(\text{CH}<em>3), \nu</em>{\text{s}}(\text{CH}<em>2), \delta</em>{\text{as}}(\text{CH}<em>3), \delta</em>{\text{s}}(\text{CH}_3))</td>
<td>Complexation at RT, Zr(Np)₄</td>
</tr>
<tr>
<td><img src="image8.png" alt="Image" /></td>
<td>3536, 3452, 1550</td>
<td>(\nu_{\text{as}}(\text{NH}<em>2), \nu</em>{\text{s}}(\text{NH}_2), \delta(\text{NH}_2))</td>
<td></td>
</tr>
</tbody>
</table>
Each step of the grafting can clearly be followed by IR spectroscopy given that each reaction involved the formation of a new surface species and so, the appearance and disappearance of new peaks characteristic of:

- The ammonia treatment

New bands at 1550, 3452 and 3536 cm\(^{-1}\) due to SiNH\(_2\)

- The passivation

Intense peaks between 3000 and 2800 cm\(^{-1}\) and below 1400 cm\(^{-1}\) due to CH

- The organometallic grafting

New bands at 1465 and 1365 cm\(^{-1}\) as well as 2869 cm\(^{-1}\) and 2954 cm\(^{-1}\) due to CH\(_2\) in the neopentyl (Np) groups.
Personal Feeling

I had the great opportunity to study in KAUST and pursue my Thesis in the Kaust Catalysis Center during about 12 months. KAUST has for goal to create knowledge for the benefit of human kind and to educate the scientists of tomorrow, what it is doing perfectly.

KCC is becoming a pioneer in the catalysis field, especially by triggering a paradigm shift towards catalyst discovery by design. This center has a lot of potential and will promise a great future and international reputation.

My objectives for this thesis were to learn as much as possible in order to become knowledgeable in catalysis. But also to lead an important and very interesting research project as well as to contribute time and expertise to do as much breakthroughs as possible.

I completed these goals by first becoming familiar with the usage and functions of many different instruments found in KCC. I largely worked under glove box and High Vacuum Line. I also characterize my samples with a lot of different analytical and characterization techniques such as BET, XRD, NMR, IR, CCM and GC and learnt to handle all of them.

I have been autonomous in my research thanks to the trust given to me by my supervisor Mr. Jean-Marie Basset and my wonderful tutor Dr. Anissa Bendjeriousedjerari. I organized my objectives, my tasks and my experiments day after day. Get his own results is something very exciting and rewarding (sometime).

Therefore, I have been exposed to (almost) all functions of the heterogeneous laboratory and I have learnt to manage my results and move my research further, which, and I take pride in it, will most likely allow me to make a publication in JACS as well as a revue.

Hence, I fully applied and expanded all the theoretical knowledge and practical skills I have acquired during my studies. There is no doubt these academic years were a really great experience. I have learned a lot in catalysis, analytical instruments and scientific research. I find it captivating and inspiring to use our knowledge and technical skills to resolve scientific problems and improve our future and the life around the world.

I am confident that KAUST will excel in creativity and innovation in order to support global development and national economy. KCC will be a world-leading node for the establishment of a multi-disciplinary approach to “catalysis by design.”