Organosilicon polymer-derived mesoporous 3D silicon carbide, carbonitride and nitride structures as platinum supports for hydrogen generation by hydrolysis of sodium borohydride

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Abstract
Herein, mesoporous 3D silicon carbide (SiC), carbonitride (Si–C–N) and nitride (Si3N4) structures have been synthesized by nanocasting and pyrolysis using commercial organosilicon polymers as precursors of the different compositions. Detailed characterizations by BET and XRD allowed us to fix the most appropriate parameters to design mesoporous 3D structures with high specific surface areas and high pore volume. Then, the series of 3D structures has been used as supports to grow platinum nanoparticles (Pt NPs) by wet impregnation followed by reduction in hydrogen/argon flow. The Pt-supported mesoporous 3D supports kept the mesoporosity of the virgin supports to be used for catalytic hydrolysis of sodium borohydride (NaBH4). A hydrogen generation rate of 24.2 L min⁻¹ g⁻¹Pt is measured for the Pt-supported mesoporous 3D Si3N4 structure, which is notably higher than the catalytic hydrolysis using Pt-supported mesoporous 3D SiC and Si–C–N structures. HRTEM investigations demonstrated the homogeneous distribution of Pt NPs over the Si3N4 support.

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Introduction

Liquid organic and inorganic chemical hydrides like methanol, formic acid, ammonia borane and sodium borohydride are attractive for fuel cell applications, owing to some advantageous features [1]: they are in liquid state (especially in aqueous solution) and can be easily handled; they may store and produce hydrogen on-demand; they are relatively stable in ambient conditions during long periods of storage without usage; they are non-flammable and non-toxic; they are hydrogen-rich, i.e. with high gravimetric energy densities. A typical and widely-investigated example of those is the alkaline aqueous solution of sodium borohydride NaBH4, knowing that the hydride carries 10.8 wt% of hydrogen [2,3].

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By hydrolysis, molecular hydrogen is spontaneously released by reaction of one hydric hydrogen ($\text{H}^+\text{H}$) of $\text{NaBH}_4$ with one protic hydrogen ($\text{H}^+$) of $\text{H}_2\text{O}$, which thus provides half of the $\text{H}_2$ generated. The by-product, sodium tetrahydroxyborate, may be recycled back into $\text{NaBH}_4$ via a complex process which may offer a continuous delivery of hydrogen to engine or fuel cell [4]. To achieve high effective gravimetric hydrogen storage capacities, hydrolysis has however to be accelerated by a metal-based catalyst [5–7]. For example, Kojima et al. reported an effective capacity of 9 wt% owing to the presence of a supported catalyst [7]. Furthermore, such attractive performances imply harsh operating conditions according to the fact that the reaction is exothermic and the by-product sodium tetrahydroxyborate is a strong base which significantly increases the pH of the solution. Within this context, both the catalyst and the support have to be designed with the objective to withstand these harsh operating conditions.

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 [8], the support is expected to be prepared with tunable pore morphologies and accessible porosity [9]. In particular, the high specific surface area (SSA) of mesopores provides selectivity and active sites to be effectively accessed for catalysis. We therefore focused our study on the preparation of mesoporous components.

Metal oxide-type supports form one of the most important classes of supports of active nanocatalysts [9,10]. Even though these materials display excellent properties, their efficiency is limited to reactions where the conditions are not harsh. In reactions involving high temperatures, reducing media (highly alkaline) and/or fast reaction rates, these supports exhibit stability issues (thermal, chemical and mechanical). For such reactions, non-oxide ceramics represent better alternative supports.

In the category of non-oxide ceramics, silicon or transition metal carbides, carbonitrides and nitrides display attractive properties (high thermal and chemical stability, oxidation and corrosion resistance, low bulk density, high thermal conductivity, mechanical reliability) to be used in harsh environment [11,12]. However, the preparation of non-oxide ceramics with tailored mesoporosity is a great challenge difficult to reach using conventional ceramic process. 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. A precursor route is the way to reach this goal.

Preceramic polymers in which uniform chemical composition is established at molecular scale are making an increasingly important contribution to the research development and manufacture of carbide, carbonitride and nitride components as single-phase, multi-phase, solid solution and nanocomposite structures by pyrolysis in inert or reactive atmosphere [13–16]. This concept called Polymer-Derived Ceramics (PDCs) route combines molecular chemistry, processing, engineering and chemistry of materials to control over elemental composition, nanostructural organization and shape of the final materials. This inherently allows proposing a large range of properties which is difficult to find in materials prepared by conventional synthesis routes. The possibility to develop materials bearing tailored mesoporosity can be envisioned by coupling the PDCs route with a templating approach [17–22]. 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 [23,24]. 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 with particular mesoporosity with a preceramic polymer solution, (ii) performing the subsequent pyrolysis to achieve the precursor-to-ceramic conversion, then (iii) removing the mold while generating a monolith with tailored mesoporosity. To our knowledge, this strategy has never been applied to generate fully mesoporous PDCs as monoliths.

Herein, we use three different commercial organosilicon polymers to form mesoporous 3D structures of silicon carbide (SiC), carbonitride (Si–C–N) and nitride (Si3N4). Monolithic activated carbon specimens are used as templates. As-obtained high surface area 3D Si-based carbide, carbonitride and nitride materials are used as platform to grow catalytically-active platinum nanoparticles (NPs). To assess the catalytic activity of the Pt/SiC, Pt/Si–C–N and Pt/Si3N4 materials, these systems are tested for hydrolysis of NaBH4 to generate hydrogen in aqueous medium; the performances are finally compared. A hydrogen release of $24.2 \text{ L min}^{-1} \text{ gPt}^{-1}$ is measured for Pt/Si3N4. This material has been investigated by HRTEM before and after Pt NP growth. The overall flow chart of the process is shown in Fig. 1.

**Experimental**

**Materials**

The preceramic polymers, namely allylhydrodipolycarboxilane (AHPCS, SMP-10 provided by Starfire Systems, USA), HTT1800 (provided by Clariant Advanced Chemicals) and perhydropolysilazane (PHPS, AQUAMICA NN-310 provided by Mitsuya Boeki Ltd., Japan) available in xylene (20 wt%), are unstable in air. All manipulations are carried out under inert conditions. In particular, all chemical products are handled in an argon-filled glove box (MBraun MB200B; O2 and H2O concentrations kept at <0.1 ppm). Argon (>99.995%) is purified by passing through successive columns of phosphorus pentoxide, siccapent™, and BTS catalysts. Schlenk tubes are dried at 120 °C overnight before pumping under vacuum and filling them with argon for synthesis. Toluene (99.85%, Extra Dry over Molecular Sieve, AcroSeal(R)) is purchased from Acros Organics. Activated carbon (Norit RX3® Extra) is provided by Cabot Corporation and its textural and structural parameters are as follows: monolith/rod type;
specific surface area of 953 m$^2$ g$^{-1}$ and 2.1 nm of pore size. For the preparation of the Pt supported samples and for the hydrogen generation experiments, chloroplatinic acid hexahydrate (H$_2$PtCl$_6$·6H$_2$O, Sigma–Aldrich), sodium borohydride (NaBH$_4$, Acros Organics), sodium hydroxide (NaOH, Carlo Erba) and deionized ultra-pure water (Milli-Q grade; resistivity $>$ 18 M$\Omega$ cm) are used.

**Preparation of mesoporous silicon-based non-oxide ceramic supports**

The mesoporous supports are prepared by polymer nanocasting route. The activated carbon monoliths we label ACM are first treated at 600°C under vacuum (5 · 10$^{-1}$ mbar) for 10 h to remove presence of any trace oxygen, moisture or dangling groups (–OH, –COOH, etc) without structure modification. Then, heat-treated ACM are stored inside the glove box. A specific weight of ACM is taken from the glove box in a Schlenk-type flask to be put under vacuum before impregnation of the preceramic polymers. ACM are infiltrated at reduced pressure by the selected preceramic polymer (AHPCS, HTT1800 or PHPS) according to an optimum mass ratio between the polymer and ACM. Then, the composites are allowed to age for 24 h under static vacuum with continuous ultrasonicication. Vacuum is required for the complete absorption of the polymers in the porosity of ACM. After aging for 24 h, a filtration step is performed and the composites are washed with toluene under argon flow. Excess of liquid is removed using a syringe and then the solvent is evaporated at low pressure (5 · 10$^{-1}$ mbar) at 30°C for 2 h to generate the impregnated monoliths labeled AHPCS/ACM, HTT1800/ACM and PHPS/ACM. The samples AHPCS/ACM and HTT1800/ACM are transferred into a silica tube inserted in a horizontal tube furnace (Thermoconcept® OS50/450/12) in an argon flow. The tube is pumped under vacuum for 30 min and refilled with argon (AHPCS/ACM) and nitrogen (HTT1800/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 SiC/ACM (obtained from AHPCS/ACM) and Si–C–N/ACM (obtained from HTT1800/ACM). We should keep in mind that excess of free carbon is present in such compositions. 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 (SiC/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 labeled mSiCX and mSi-C-NX (X being the two first numbers of the final temperature, e.g., 12 for 1200). For PHPS/ACM, the procedure is different: 3 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 Si$_3$N$_4$–Si/ACM. After the polymer-to-ceramic conversion process, the samples Si$_3$N$_4$–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 Si$_3$N$_4$ monoliths labeled mSi$_3$N$_4$1010. In a second strategy, the tube is filled with ammonia to be subjected to a cycle of ramping at 1°C min$^{-1}$ to 1000°C, dwelling there for 2 h. Cooling to RT is carried out at 2°C min$^{-1}$ generating samples Si$_3$N$_4$–Si/ACM. After the pyrolysis and conversion process, the samples Si$_3$N$_4$–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 Si$_3$N$_4$ monoliths labeled mSi$_3$N$_4$1010.
there for 5 h. Cooling directly produces the mesoporous Si$_3$N$_4$ monoliths labeled mSi$_3$N$_4$10. In a third strategy, the tube is filled with nitrogen to be subjected to a cycle of ramping at 1 °C min$^{-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$_3$N$_4$ monoliths labeled mSi$_3$N$_4$410. The sample mSi$_3$N$_4$410 undergoes heat-treatment at higher temperature using a graphitic furnace (Cero Model HTK 8) to follow the evolution of its porosity as a function of the pyrolysis temperature. The furnace is pumped out for 30 min then refilled with nitrogen (200 mL min$^{-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 mSi$_3$N$_4$41X (X being the second number of the temperature, e.g., 2 for 1200 °C).

**Platinum deposition/impregnation on the ceramic support**

The platinum nanoparticles (Pt NPs) synthesized from the precursor H$_2$PtCl$_6$·6H$_2$O are supported over the Si-based non-oxide ceramic monoliths with the highest SSA in each system by wet impregnation followed by heat-treatment under a hydrogen/argon flow. A low platinum loading is targeted (1 wt %). The palatinate is dissolved in 1 mL distilled water (obtained from Millipore systems) and ultra-sonicated for 30 min generating a yellowish solution. The mesoporous Si-based non-oxide ceramic monoliths are suspended in 2.5 mL of distilled water and the platinate solution is added to this. The mixtures are allowed aging under ultrasonication for 24 h. The mixtures are 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 labeled Pt/mSi$_3$N$_4$X, Pt/mSiCX, and Pt/mSi-C-NX. For comparison, Pt/ACM has been prepared following the same experimental procedure.

**Hydrolysis of NaBH$_4$**

Catalytic activity is probed using hydrolysis of NaBH$_4$ at 80 °C in a highly alkaline medium (pH > 10). Typically, the specimens (16 mg) are put in 1 mL solution of NaBH$_4$ (120 mg in 2% NaOH) into a reactor (glass tube) that is sealed with a silicon septum and Parafilm (NaOH) into a reactor (glass tube) that is sealed with a silicon septum and Parafilm and then heat treated under diluted H$_2$ flow (5% H$_2$ and 95% Ar) 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 mSi$_3$N$_4$41X (X being the second number of the temperature, e.g., 2 for 1200 °C).

**Characterization**

Thermogravimetric analyses (TGA) of the polymer-to-ceramic conversion are recorded on a Setaram TGA 92 16.18. Experiments are performed using silica crucibles (sample weight of ~40 mg for AHPCS and HTT1800 and 161 mg of the PHPS in xylene) at ambient atmospheric pressure. The vertical tube is pumped under vacuum for 30 min (AHPCS and HTT1800) and then refilled with argon (AHPCS), nitrogen (HTT1800) or ammonia (PHPS) to be subjected to a cycle of ramping at 5 °C min$^{-1}$ to 1000 °C, dwelling there for 10 min. Then cooling to RT is carried out at 5 °C min$^{-1}$. The powder X-ray diffraction patterns (XRD) are recorded using a Philips FW 3040/60 X’Pert PRO X-ray diffraction system operating at 20 mA and 40 kV, and between 20° and 80° (20 angle) with a step size of 0.033° to identify the global structure of the Si$_3$N$_4$ phase. The specimens are observed by SEM (Hitachi S4800) equipped with energy-dispersive spectroscopy analysis (EDXS). The Brunauer–Emmett–Teller (BET) method was used to calculate the specific surface area of the samples before and after platinum deposition as well as after hydrolysis. The pore-size distribution is derived from the desorption branches of the isotherms using the 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. TEM analysis was performed using TECHNAI 20G [2], FEI instruments, USA using an accelerating voltage of 200 kV & JEOL 3010 (Japan) instrument at an accelerating voltage of 300 kV. The samples were powdered using mortar and pestle, diluted in ethanol and ultrasonicated for 10 min. The samples were then transferred onto a copper grid and analysis was done.

**Results and discussion**

**Preparation of mesoporous 3D structures**

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

AHPCS has a nominal structure of [Si(CH$_2$=CH$_2$)$_2$]$_n$·[SiH$_2$CH$_2$]$_m$·[SiH]$_m$ (Fig. 1) [25,26]. 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 (Fig. S1 in Supporting Information). The polyacrylsilazane HTT1800 is a copolymer containing 20% of methyl/vinyl and 80% of methyl/hydride substituted silazane units (Fig. 1) [27]. HTT1800 can be cross-linked 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% (Fig. S1 in Supporting Information) corresponding to a ceramic yield of 68%. PHPS (Fig. 1) is a highly reactive preceramic polymer containing two Si–H and one N–H functions in its structure [2,28]. 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
the same ratio using AHPCS and HTT1800 as SiC and Si materials. Based on the results obtained with PHPS, we apply volume without altering the mechanical robustness of the material which can generate a large porosity and in turn a large pore size. 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 Si₃N₄ structure after pyrolysis of PHPS/ACM and the template removal step. Table S1 in supporting information shows the effect of the mass ratio for the sample mSi₃N₄_10. 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.

For AHPCS/ACM and 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 AHPCS/ACM and 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 h. 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.

For PHPS/ACM, the template is removed under ammonia during the PHPS-to-Si₃N₄ conversion within one step based on two procedures or during a second step when the PHPS-to-Si₃N₄ conversion is achieved under nitrogen in a first step. Once the most appropriate has been selected, the temperature of pyrolysis is then increased above 1000 °C under nitrogen to follow the evolution of the SSA and microstructure as a function of the pyrolysis temperature.

In the following sections, 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.

Characterizations of SiC and Si–C–N 3D structures

The pore architecture of samples mSiCX (from AHPCS/ACM) and mSiC-NX (from HTT1800/ACM) (X being the two first numbers of the final temperature, e.g., 12 for 1200) is assessed at the mesoscopic length scale by nitrogen gas adsorption–desorption measurements at 77 K (Fig. 2 for mSiCX) and Fig. 3 (for mSi-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 samples mSiCX. The samples mSiC10 and mSiC12 show two similar IV type-curves in which the adsorption and desorption curves do not coincide over the region of relative pressure P/P₀ = 0.4–0.99 indicative of H₂ hysteresis loops for these samples. The IV-type isotherms suggest that the samples have uniform mesoporous channels while H₂ hysteresis loops are generally found in disordered porous materials or in ordered mesoporous material with 3-D cage-like pores and interconnected pores [31]. Based on the structure of ACM, we can consider that mSiC10 and mSiC12 are mesoporous materials bearing interconnected porosity. The specific BET surface area is 396.5 m² g⁻¹ for the sample mSiC10 and 581.4 m² g⁻¹ for the sample mSiC12. The SSA of the sample mSiC12 is close to that one reported by Zhao et al. on ordered mesoporous PCS-derived SiC powders for a temperature of pyrolysis of 1200 °C [32]. The micropore area for mSiC10 is 244.2 m² g⁻¹, whereas there are no micropores in the sample mSiC12. The total pore volume determined from the amount of nitrogen adsorbed at P/P₀ = 0.97 for mSiC10 is 0.34 cm³ g⁻¹ and it increases to 0.76 cm³ g⁻¹ for the fully mesoporous mSiC12. The pore size distribution (PSD) calculated from desorption branch by means of the Barrett-Joyner-Halenda method gives an average pore diameter of 5.26 nm (mSiC12, see Fig. S2 in supporting information). It should be mentioned that the SiC composition of the sample mSiC10 cannot be retained under the air-treatment to remove ACM. Silica is generated. A treatment at 1200 °C before template removal is therefore required to enhance the thermal stability during the subsequent air-treatment.

Fig. 2 shows that the profiles of isotherms significantly change for the samples mSiC14 and mSiC16 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 m² g⁻¹ to 83 m² g⁻¹ which significantly decrease in comparison to mSiC10 and mSiC12. The total pore volume determined from the amount of nitrogen adsorbed at P/P₀ = 0.97 decreases to 0.36 cm³ g⁻¹ and 0.24 cm³ g⁻¹ for mSiC14 and mSiC16, 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-
Fig. 2 – Evolution of BET adsorption isotherms for mSiCX (X being the two first number of the final temperature, e.g., 12 for 1200).

Fig. 3 – Evolution of BET adsorption isotherms for mSi-C-NX (X being the two first number of the final temperature, e.g., 12 for 1200).
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 (see Fig. S3 in supporting information). 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 $\beta$-SiC phase ($\{111\}$ at 35.6°, $\{220\}$ at 59.9° and $\{311\}$ at 71.7°) as well as of $\beta$-SiC and $\alpha$-SiC through the two poorly intense peaks at 41.5° and 76°.

A similar behavior is observed with the samples $\text{mSi-C-N}_{X}$ in the nitrogen adsorption desorption isotherms (Fig. 3).

The isotherms of $\text{mSi-C-N}_{10}$ and $\text{mSi-C-N}_{12}$ show IV type-curves in which the adsorption and desorption curves do not coincide over the region of relative pressure $P/Po = 0.4$–0.99. The adsorption hysteresis represents a $H_2$-type for both samples. Therefore, we suggest that the samples $\text{mSi-C-N}_{10}$ and $\text{mSi-C-N}_{12}$ are mesoporous materials with interconnected pores similarly to $\text{mSiC}_{10}$ and $\text{mSiC}_{12}$. A specific BET surface area as high as 623.7 m$^2$ g$^{-1}$ is measured for the sample $\text{mSiC}_{12}$ 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 [33]. The total pore volume determined from the amount of nitrogen adsorbed at $P/Po = 0.97$ is 0.77 cm$^3$ g$^{-1}$. The pore size distribution (PSD) is calculated from the desorption branch by means of the Barrett-Joyner-Halenda method. A uniform diameter of 4.9 nm is found (see Fig. S4 in supporting information).

In contrast, the sample $\text{mSi-C-N}_{14}$ presents II-type isotherms suggesting the formation of macroporous or non-porous samples. The specific BET surface area decreases to 111.4 m$^2$ g$^{-1}$ in line with the total pore volume decreasing to 0.36 cm$^3$ g$^{-1}$. These results confirm the behavior observed with the samples $\text{mSiC}_{14}$. However, in contrast to $\text{mSiC}_{14}$, the sample $\text{mSi-C-N}_{14}$ is X-ray amorphous as shown on the corresponding X-ray diffraction patterns (see Fig. S5 in supporting information). This confirms that the decrease of the SSA in the samples $\text{mSiC}_{14}$ and $\text{mSi-C-N}_{14}$ is mainly due to the high temperature heat-treatment which probably involves framework shrinkage. Surprisingly, the sample $\text{mSi-C-N}_{16}$ 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 ($P/Po$) from 0.4 to 0.99 indicative of $H_2$ hysteresis loop. The sample displays a SSA of 490.7 m$^2$ g$^{-1}$ and a pore volume of 0.74 cm$^3$ g$^{-1}$; the reason of this behavior may be understood through the XRD patterns. Like the samples $\text{mSiC}_{X}$, the heat-treatment of the samples $\text{mSi-C-N}_{10}$, $\text{mSi-C-N}_{12}$ and $\text{mSi-C-N}_{14}$ are X-ray amorphous whereas $\text{mSi-C-N}_{16}$ shows the main diffraction peaks of $\beta$-SiC and small peaks of mixture of $\beta$-$\text{Si}_3\text{N}_4$ and $\alpha$-$\text{Si}_3\text{N}_4$ phases. $\beta$-SiC is formed through the carbo-reduction of $\text{Si}_3\text{N}_4$ in the sample $\text{mSi-C-N}_{14}$ [3]. 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 $\text{mSi-C-N}_{16}$ to increase its SSA and pore volume. The main disadvantage is the lack of control over total mesoporosity.

### Characterization of $\text{Si}_3\text{N}_4$ 3D structures

As described in the experimental part, three strategies are investigated to prepare mesoporous $\text{Si}_3\text{N}_4$ 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 [18]. The first strategy consists to pyrolyze PHPS/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 conversion of PHPS into $\text{Si}_3\text{N}_4$ 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 (653.8 m$^2$ g$^{-1}$) and structural integrity. Furthermore, it allows to fully remove the template while free silicon is converted into silicon nitride. Such a SSA value is close to the values we got for ordered mesoporous PHPS-derived $\text{Si}_3\text{N}_4$ powders using CMK3 as a template [2].

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 $\text{mSi}_3\text{N}_4\text{C}_{10}$ by $N_2$ sorption (micropores and mesopores scale) is discussed below based on the BET isotherms reported in Fig. 4.

The sample $\text{mSi}_3\text{N}_4\text{C}_{10}$ demonstrates mesoporosity according to the nitrogen sorption isotherms (Fig. 4). 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 ($P/Po$) from 0.4 to 0.9 indicative of $H_2$ hysteresis loops.

It is observed that the sample $\text{mSi}_3\text{N}_4\text{C}_{10}$, which is X-ray amorphous (see Fig. S6 in supporting information) 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 $\text{Si}_3\text{N}_4$ nanowires in the porosity starting from 1200 °C (Fig. 5) while crystallization of $\alpha$-$\text{Si}_3\text{N}_4$ occurs (see Fig. S6 in supporting information).

The formation of nanowires at these temperatures for silicon nitride made via polymer derived ceramic route has been well documented [23]. Hence for $\text{Si}_3\text{N}_4$ supports, the optimum
specific surface area of 653.8 m² g⁻¹ was obtained for the sample mSi₃N₄410.

Based on the previous results and discussion, the samples mSiC₁₂, mSi-C-N₁₂, mSi₃N₄⁴¹₀ 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.

**Platinum nanoparticle impregnation**

Pt NPs are deposited on mSiC₁₂, mSi-C-N₁₂ and mSi₃N₄⁴¹₀ using hexahydrated chloroplatinic acid as Pt precursor by wet impregnation followed by chemical reduction in hydrogen/argon flow. This generates nanocatalysts labeled Pt/mSiC₁₂, Pt/mSi-C-N₁₂ and Pt/mSi₃N₄⁴¹₀. These materials are used to catalytically activate the hydrolysis of NaBH₄. The successful loading of Pt on the supports has been verified by BET (Fig. 6) and EDXS.

It should be mentioned that 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 mSiC₁₂, mSi-C-N₁₂ and mSi₃N₄⁴¹₀, 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 [34]. 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 Fig. 6 and Table 1. After Pt growth, the shape of the isotherms and the hysteresis loop of the samples Pt/mSiC₁₂, Pt/mSi-C-N₁₂ and Pt/mSi₃N₄⁴¹₀ are similar to the isotherms of the parent mSiC₁₂, mSi-C-N₁₂ and mSi₃N₄⁴¹₀. 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 1. 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 samples mSiC₁₂, mSi-C-N₁₂ and mSi₃N₄⁴¹₀ hinder the agglomeration or migration of the nanoparticles. This is also fundamental to allow diffusion of borates through the porosity during hydrolysis of NaBH₄.

**Hydrolysis of sodium borohydride**

The activity of Pt/mSiC₁₂, Pt/mSi-C-N₁₂ and Pt/mSi₃N₄⁴¹₀ 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 NaBH₄ for 17.5 mol H₂O; water excess of 438%). These conditions are considered as being harsh for any catalyst support (cf. Sub-section Hydrolysis of NaBH₄). The hydrogen generation results are presented in Fig. 7. It should be mentioned that we synthesized a Pt-supported activated carbon monolith labeled Pt/ACM through the same process we applied to prepare Pt/mSiC₁₂, Pt/mSi-C-N₁₂ and Pt/mSi₃N₄₁₀.

Fig. 7 demonstrated the highest performance obtained with the sample Pt/mSi₃N₄₁₀. A hydrogen generation rate (slope of the curves at a conversion < 50%) of 4.3 mL min⁻¹/C₀ was measured. Expressed per gram of Pt, the rate is as high as 24.2 L min⁻¹/C₀/gPt, which is the maximum value reported in the literature [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 samples Pt/mSiC₁₂ and Pt/mSi-C-N₁₂ but the hydrogen evolution rate is significantly lower: at 50% conversion, 2.016 mL min⁻¹/C₀ (8.18 L min⁻¹/C₀/gPt) and 0.68 mL min⁻¹/C₀ (2.38 L min⁻¹/C₀/gPt) are measured for the samples Pt/mSiC₁₂ and Pt/mSi-C-N₁₂, respectively. The results obtained with the sample Pt/ACM (4.21 L min⁻¹/C₀/gPt) are comparable to those obtained with the samples Pt/mSiC₁₂ and Pt/mSi-C-N₁₂. 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 BH₄⁻ and B(OH)₄⁻.

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Table 1 — SSA values of samples Pt/mSiC₁₂, Pt/mSi-C-N₁₂ and Pt/mSi₃N₄₁₀.

<table>
<thead>
<tr>
<th>Samples</th>
<th>SSA (m²/g⁻¹) Before impregnation</th>
<th>SSA (m²/g⁻¹) After impregnation</th>
</tr>
</thead>
<tbody>
<tr>
<td>mSiC₁₂</td>
<td>581.4</td>
<td>378.2</td>
</tr>
<tr>
<td>mSi-C-N₁₂</td>
<td>623.7</td>
<td>347.8</td>
</tr>
<tr>
<td>mSi₃N₄₁₀</td>
<td>653.8</td>
<td>357.7</td>
</tr>
</tbody>
</table>

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Fig. 6 — Evolution of BET adsorption isotherms for Pt/mSiC₁₂, Pt/mSi-C-N₁₂ and Pt/mSi₃N₄₁₀.
Whereas the SSA of the samples Pt/mSiC12, Pt/mSi-C-N12 and Pt/mSi3N410 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 and the catalytic properties of nitrides.

The primary catalytic interest in nitrides has centred around two general themes: (i) the well documented ability of some transition metal nitrides to exhibit catalytic properties which are similar to platinum group metals [35–37], and (ii) the acid-base properties of nitrides and oxynitrides. Within the literature, catalytic studies of silicon nitride are restricted to a few papers. As an illustration, D. Hullmann prepared amorphous silicon nitride for the Knoevenagel condensation of benzaldehyde and malonitrile [38]. However, the catalytic behavior is largely unknown. Theoretical and computational investigations should make tremendous advances in the understanding of the interest to use silicon nitride as catalytic supports. Within this context, 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 sample Pt/mSi3N410 has been analysed by elemental mapping and TEM (Fig. 8a–b), EDXS and elemental mapping (Fig. 8c–f).

The sample mSi3N410 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 (Fig. 8a), HRTEM investigation allows observing Pt NPs with a spherical shape and we clearly observe their homogeneous distribution on the surface of the sample mSi3N410 forming the sample Pt/mSi3N410. We observe spots belonging to Pt, which crystallizes in the fcc system (Fig. 8a). Fig. 8b shows that a few tens 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 (Fig. S7, See Supporting Information). Elemental mapping (Fig. 8c–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 Si1.6O0.8N4.1. The relatively low O content level is mainly associated with physisorbed/chemisorbed water from the internal and external surface of the samples. 0.12 at% of Pt are measured. However, we should point to the fact the hydrogen production under the reaction conditions we imposed was very vigorous. The sample Pt/mSi3N410 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 samples Pt/mSiC12 and Pt/mSi-C-N12 (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 sample Pt/mSi3N410 formed a suspension with stirring and was stable for a long time even after the stirring was stopped.

**Conclusion**

Mesoporous 3D structures of silicon carbide (SiC), carbonitride (Si–C–N) and nitride (Si3N4) have been prepared by polymer
nanocasting using activated carbon as hard template and allylhydridopolycarbosilane as SiC precursor, a copolysilazane containing 20% of methyl/vinyl and 80% of methyl/hydride substituted silazane units as Si–C–N precursor and perhydropolysilazane as Si3N4 precursor. The solution infiltration-ceramic conversion-template removal cycle based on different procedures results in the formation of mesoporous amorphous 3D silicon carbide (SiC), carbonitride (Si–C–N) and nitride (Si3N4) structures with high surface areas and pore volumes and a low pore size distribution. These materials have been used as supports to grow platinum nanoparticles leading to nanocatalysts to be successfully assessed for hydrogenolysis of an alkaline aqueous solution of sodium borohydride (NaBH4) at 80 °C. High H2 rate has been measured for the platinum-supported silicon nitride (24.2 L min⁻¹ g⁻¹). The performance is significantly superior to platinum-supported silicon carbide and carbonitride. However, all materials collapse after hydrolysis tests. Further works are under investigations to keep the structural integrity of the mesoporous structures after hydrolysis. However, some other perspectives are clear.

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, the use of PDCs is still a formative stage and the role of most of the reported polymer-derived nitrides as catalytic supports is largely unknown, with most studies focusing on the various preparative procedures rather than their development as catalyst supports. It is clear that nanostructuration is an important aspect. Furthermore, surface area considerations play a key role. Finally, the design of nanocomposites displaying synergetic effects with the metal catalyst is one of the best strategies to optimize the catalytic properties of polymer-derived nitrides. These opportunities are now being addressed. It is anticipated that this will lead to host of functional applications for a new generation of materials.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.ijhydene.2016.06.186.

References