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Synthesis of Zeolite Monoliths for Flow Continuous Processes. The Case of Sodalite as a Basic Catalyst

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Microreactors offer attractive opportunities for their use in pharmaceutical and fine chemical syntheses. This is particularly true in the field of heterogeneous catalysis in relation with process intensification, heat and mass transfer enhancement, and continuous flow operations.[1] Among many other configurations, some nonexhaustive examples can be given: micrometer-sized open tubes with catalytic moieties grafted on the walls,[2] packed-bed reactors,[3] and monolithic reactors.[4−8] In this last family there is special interest for those featuring highly interconnected flow-through macropores in the range of 2 to 20 μm and mesopores from 5 to 15 nm. Their skeleton can be composed of a polymer[6] or an inorganic oxide.[7,8] The first reports with regard to the use of monolithic silica as a continuous flow reactor dealt with biocatalysis with immobilized enzymes (see ref 9 for a review). A recent report addressed the use of hierarchical silica monoliths grafted with acid and basic moieties as continuous flow reactors for catalysis.[8] In two model reactions, Knoevenagel condensation and transesterification, the monolithic microreactor proved to be 2 to 10 times more productive than packed-bed or batch-mode reactors, respectively. Moreover, this kind of monolith demonstrated high mechanical strength with elasticity limit $\sigma \sim 3$ MPa and elastic Young modulus $E \sim 0.5$ GPa.[10] A new challenge is given by modification of the nature of the inorganic skeleton of the monolith by means of pseudomorphic transformation leading to new structural properties to broaden the nature of the active sites.

Though the catalytic potential of zeolites has been demonstrated for a long time in the synthesis of fine chemicals,[11] their application in real processes remains scarce.[12] The main drawback is the sole presence of micropores, which imposes diffusion limitations on the reaction rate leading to clogging and sites inhibition. To overcome these limitations, there have been several approaches to either minimize the size of the zeolite crystals or to increase the pore size of zeolites. During the past decade, many efforts have been focused on the fabrication of materials combining multiscale meso- and microporosity. In a very general way, they can be obtained by embedding zeolite crystals in appropriate matrices, by growing zeolites on macro- or mesoporous substrates, or by controlled packing of zeolite nanocrystals.[13] A hierarchical micro/mesoporous catalyst can be achieved by the transformation of the silica walls of substrates into zeolite after the addition of the appropriate template[13a,e−g] or by seeding the solution with zeolite nuclei and stopping the particle growth by adding organosilanes.[14,15] In the latter case, a mesoporous sodalite has been successfully synthesized showing 10 times larger surface area as compared with sodalite with solely microporous structure.[13] Aluminosilicate sodalite (SOD) has never been extensively used as catalysts due to the size of its pores, too small to receive organic molecules (flexible aperture between 0.20 to 0.28 nm depending on the environnment[16]). However, SOD has been suggested as a catalyst for reactions in which a fast product removal is needed.[17] Hierarchical micro/mesoporous SOD was shown to exhibit higher basicity, higher catalytic activity, and higher stability than CsNaX or KAlMCM-41 for small and bulky substrates.[14]

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Our goal is to design a monolithic catalytic microreactor with a skeleton formed of SOD to develop a stable and highly basic catalyst for process intensification. In addition, for performing catalysis under flow conditions, the challenge is to obtain a crack-free monolith with interconnected and uniform flow-through macropores. Some attempts were made previously to transform the amorphous silica skeleton of the above-mentioned monolith into a nanocrystalline zeolite system. A monolithic beta zeolite with hierarchical porosity was prepared by using a complicated protective transitional carbon casting of the silica monolith.[18] A beta zeolite was also fabricated by steam-assisted conversion of the amorphous silica skeleton into zeolite nanocrystals but not tested in catalysis.[19] The same approach was followed to prepare a ZSM-5 monolith,[20] which exhibited a higher performance in the cracking of large molecules than classical microporous ZSM-5. However, these ZSM-5 micro/macroporous catalysts were not evaluated as monolith microreactors but as powders in packed-bed reactors.

In this communication, we report a method for the preparation of sodalite monolith (MonoSil-SOD) for basic catalytic reactions under flow. For this we have developed a pseudomorphic transformation of a Nakanishi type silica monolith[7] into the zeolite counterpart (as we previously succeed for MCM-41 monoliths[21]), while maintaining its complete crack-free morphology allowing its use as a flow-through microreactor.

First meso/macroporous silica monolith rods (7.8 cm length, 6.14 mm diameter) were synthesized as described previously[8,21] by mixing 10 g of TEOS, 12.3 g of H_2O, 1.22 g of HNO_3 (68%), and 1.27 g of PEO (20 kDa). The resulting silica monoliths featured 6 μm macropores, 3 μm skeleton thickness, 1.75 mL/g macroporous volume, 750 m^2/g surface area, 7 nm mesopores, and a mesoporous volume of 0.96 mL/g resulting from a basic treatment at 40 °C and a calcination at 550 °C for 8 h. Second, the silica monolith (0.63 g) was impregnated with a solution prepared by dissolving NaOH (0.06 g), $NaAlO_2$ (2.16 g), and TPAOH (0.046 g, 20 wt % in H_2O) in deionized H_2O (6.02 g), to achieve a molar composition of 1 SiO_2/0.15 NaOH/2.6 $NaAlO_2$/33 H_2O/0.004 TPAOH. The impregnation is carried out in a Teflon-lined stainless steel autoclave, followed by hydrothermal treatment at 150 °C for 18 h. The monolith was then washed with water, dried at 40 °C, and calcined at 550 °C for 8 h. The monolith after pseudomorphic transformation has maintained its shape and has increased its mass from 80 mg to 100 mg per cm length, evidencing the incorporation of the aluminum. The MonoSil-SOD was cut in 1 cm pieces and cladded with a heat-shrinkable DERAY-PTFE clad for 2 h at 280 °C ended by two glass tubes to ensure the connections to the pump for flow continuous processes (Figure 1).

Figure 1. Photograph of the cladded MonoSil-SOD.

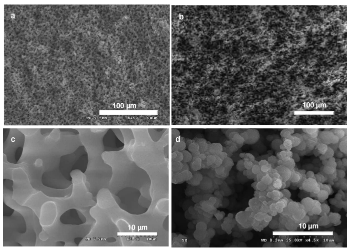

Figure 2. SEM images of (a) and (c) original monolith and (b) and (d) its pseudomorphic transformation into MonoSil-SOD.

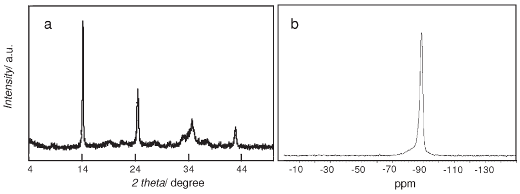

Figure 3. XRD patterns (a) and ^{29}Si MAS NMR (b) of MonoSil-SOD.

Figure 2 shows a scanning electron micrograph (SEM) of the original monolith and its pseudomorphic transformation into MonoSil-SOD. Figure 2a,b indicates the preservation of the original macroporous network, with a uniform size between 2 and 5 μm. The amorphous silica of the skeleton of the original monolith has been transformed into crystals of the size of approximately 0.5−1.5 μm, which the X-ray powder diffraction pattern of Figure 3 shows to be formed of sodalite. This crystal size corresponds to the best compromise of catalytic activity and stability for hierarchical micro/mesoporous SOD described by Shanbagh et al.[14] The small amount of TPA^+ used in the present synthesis prevents the SOD crystals from growing (as TMA^+ does for LTA and FAU crystals and as an excess of TPA^+ does for silicalite crystallization[22]), but more crucially contributes to the good stability of the monolith which remains in one piece after pseudomorphic transformation probably by controlling the distribution of crystal size inside the monolith.

The complete transformation of the amorphous silica skeleton into SOD is deduced from the absence of any bump at $2\Theta = 20°$, characteristic of amorphous silica in the XRD pattern and from the ^{29}Si MAS NMR spectra (Figure 3) featuring only a sharp peak at −91 ppm, characteristic of SOD with Si/Al ratio 1, without the broad peaks at −100 and −110 ppm of the original amorphous silica phase. ^{27}Al MAS NMR (not shown) reveals a major peak (~82%) at 59 ppm ($Al(OSi)_4$ units) indicating that the majority of Al atoms are located inside the zeolite framework. Additional small peaks at 10 ppm (~12%) assigned to octahedral Al and at 77 ppm (~4%) suggest the presence of

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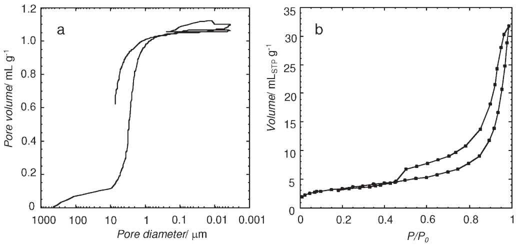

Figure 4. Mercury porosimetry (a) and nitrogen adsorption−desorption isotherm at 77 K (b) of K-MonoSil-SOD.

extraframework alumina or framework Al species located at defect sites. A small thin peak (~3%) at 81 ppm is the result of some residual salt of $Na^+[Al(OH)_4]^-$ trapped in SOD cages as sometimes obtained for zeolites synthesis at high alkalinity (LTA, LSX).

To induce strong basic sites in the MonoSil-SOD microreactor, Na^+ cations present in as-synthesized MonoSil-SOD were exchanged in flow (0.2 mL min^{-1}) for 14 h at 80 °C by K^+ cations (solution 0.5 M KCl). The resulting K-MonoSil-SOD was washed with water until no Cl^- anions were detected by $AgNO_3$ test and dried at 80 °C for 1 day before performing catalytic tests. K-MonoSil-SOD has the following molar composition: 35.4 Si/34.9 Al/3.1 Na/26.6 K evidencing the successful exchange of Na^+ by K^+ with 90% exchange capacity. A slight lack of cation (cation/Al = 0.82) confirms the presence of a small amount of extraframework alumina as suggested by ^{27}Al NMR.

The porosity of the MonoSil-SOD was examined by mercury porosimetry and nitrogen sorption (Figure 4). MonoSil-SOD exhibits a macroporous network of uniform size around 3 μm with a macroporous volume of 1.00 mL g^{-1} or 0.34 mL per cm^3 of monolith in comparison to 0.47 mL cm^{-3} for the parent MonoSil. The slightly smaller macroporosity results from the growth of the SOD crystals. Large secondary pores between 4 to 100 nm are identified by the upper volume uptake in mercury porosimetry (0.07 mL g^{-1}) and by the vertical hysteresis loop above 0.8 p/p_0 in nitrogen isotherm followed by the horizontal hysteresis loop revealing intercrystalline porosity between crystals and embedded inside the SOD crystals, respectively, probably corresponding to cracks opened up by thermal stresses during calcination.[23] The small aperture of SOD (~0.28 nm) does not allow N_2 (0.354 nm) to penetrate into the pores. Nitrogen adsorption on MonoSil-SOD occurs therefore only at the external surface of the SOD crystals. A surface of 12 m^2 g^{-1} suggests an aggregation of crystals size of 200 nm, confirmed by SEM pictures. This hierarchical pore system significantly contributes to the surface area accessible to the substrates. K-MonoSil-SOD was tested in Knoevenagel reaction, a C−C bond forming reaction, in liquid phase involving bulky substrates. Knoevenagel condensation is a key step in the preparation of several pharmaceutics including the antimalaria drug lumefantrine[24] and coumarins,[25] which are valuable products for pharmaceuticals and flavor industries. The activity of K-MonoSil-SOD is attributed to the basic sites located in the external surface of the crystals connected through large mesopores allowing diffusion and to micrometer size macropores ensuring flow through mass transfer with a low drop pressure (< 4 bar). Before catalytic reaction K-MonoSil-SOD was activated for 2 h at 140 °C under reduced pressure. Knoevenagel condensation was performed between 4-isopropylbenzaldehyde (4-IPB) and ethylcyanoacetate (ECA) to give 4-isopropylstyrylethyl-cyanoacetate as product and water, using 100 mg of K-MonoSil-SOD microreactor of 1 cm length (Figure 1). A solution containing 4-IPB (4.74 g, 32 mmol) and ECA (3.07 g, 27.2 mmol) in 40 mL of DMSO was fed at 80 °C and 0.05 mL min^{-1} flow rate (2 min contact time). The steady state conversion (65%) was reached after 5 min. No loss of activity was observed during at least 200 h in flow, proving the high mechanical and chemical stabilties K-MonoSil-SOD. The interesting parameter for process intensification is the productivity of microreactor, which reaches 18 mmol h^{-1} g^{-1} without any deactivation. Near full conversion (> 98%) was achieved for a 5 min contact time. In blank experiments, MonoSil impregnated with KCl solution exhibits 3−4% conversion in similar conditions. On K-exchanged micro/mesoporous SOD of 180 m^2 g^{-1}, Shanbagh et al.[14] reported a productivity of 156 mmol h^{-1} g^{-1}. Compared on a per m^2 basis, the productivity of K-MonoSil-SOD is 1.7 times larger. We may expect that only a partial transformation of silica into SOD would be beneficial for activity by generating nanosized SOD crystals and higher surface area. The same monolith crushed as 50−100 μm particles was 2 times less productive when tested in packed-bed reactors.

In summary, a synthetic method has been established for the fabrication of zeolite monoliths with a hierarchical pore system by pseudomorphic transformation of a meso-/macroporous silica monolith. The preservation of the crack-free body of the monolith as well as the homogeneous macroporous network account for a successful use as a basic catalyst for reactions in liquid phase under flow conditions. Sodalite monoliths could replace catalysts that are damaged during catalysis, especially for those where water is formed. The pseudomorphic transformation of monoliths should be easily extended to other zeolites with high alumina content such as LTA and LSX and would contribute to the development of flow processes not only in catalysis but also for different processes like ion-exchange, trapping of radioactive elements (Cs, Sr) or ultrarapid pressure swing adsorption for air-separation processes.

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