Fabrication of Hierarchically Structured Monolithic Silicalite-1 through Steam-assisted Conversion of Macroporous Silica Gel

Qian Lei,[1] Tianbo Zhao,*[1] Fengyan Li,[2] Yue Wang,[2] and Mingfang Zheng[1]
[1]*The Institute for Chemical Physics, Beijing Institute of Technology, Beijing 100081, P. R. China*
[2]*Department of Applied Chemistry, Beijing Institute of Petrochemical Technology, Beijing 102617, P. R. China*

(Received February 6, 2006; CL-060155; E-mail: zhaotb@bit.edu.cn)

The hierarchically structured monolithic silicalite-1 was synthesized by transforming the skeleton of the macroporous silica gel into silicalite-1 crystals through steam-assisted conversion method. It was found that the higher steam amount obviously promotes the crystallization.

Zeolites are crystalline aluminosilicates containing pores and cavities of molecular dimensions. They have been widely used in industry as catalysts, adsorbents, ion exchangers, etc.[1,2] However, the sole presence of micropores often limits the performance in the industrial applications because they cause diffusion limitations on the reaction rate. Hierarchical zeolites, which combine different levels of porosity into a single and highly ramified network, have been found to minimize diffusion limitations.[1,3] The previous preparation approach relied on removable "template," such as latex sphere beads,[4] carbon fiber,[5] mesoporous silica spheres,[6] and carbon aerogel,[7] to prepare hierarchical zeolite. An alternative possibility is in situ grow zeolite crystals on the porous substrate (e.g., diatom skeletons,[8] ceramic foams,[9] wood cell,[10] polyurethane foams,[11] cellulose acetate[12]).

Nakanishi et al.[13] prepared the macroporous silica gel with hierarchically pore structured by inducing phase separation parallel to the sol–gel transition in the presence of organic polymer and have been applied as monolithic column for high-performance liquid chromatography (HPLC). Takahashi et al.[14,15] have reported the preparation of silica–alumina catalysts with bimodal pore. The results clearly indicated that the continuous macropores provided pathways for rapid molecular transportation and the mesopores served large area of active surface. Recently, Shikata et al.[16] have reported that the silicalite-1 was formed on the inner surface of the macroporous silica gel produced by hydrothermal method. However, the morphology of macroporous silica was lost with the overgrown zeolite crystals during the zeolitization process, and the silica skeleton was dissolved, caused by the highly alkaline hydrothermal synthesis conditions. A new synthetic method for zeolite in which aluminosilicate gel crystallized to zeolite phase in steam environment has been developed and named as steam-assisted conversion method (SAC).[17–19] Takahashi et al.[20] have synthesized a porous material which had fully controlled macropores and zeolite skeleton using the SAC. However, the strength of this porous material was too low for several practical applications because of both high alkalinity in the precursor solution and long steam treatment time.

In this work, we synthesized the hierarchically structured monolithic silicalite-1 which retained adequate mechanical strength by the SAC. Additionally, the effect of the role of the steam during the present synthesis process was also investigated. The preparation of the macroporous silica gel used in this work was according to the literature method.[21] The monolithic zeolites were synthesized at 423 K for 24 h using TPAOH as structure-directing agents (SDA) with different amounts of water at the bottom of an autoclave which influences the steam amount in it. In the "lower steam amount" case, no water was introduced at the bottom of the autoclave. In the "higher steam amount" case, 15-mL water was introduced to the bottom of the autoclave. The precursor solution was prepared by mixing sodium hydroxide, distilled water, and SDA following the molar composition: $2Na_2O:1266.7H_2O:6SDA$.

Figure 1 presents the effect of steam in crystallization process. Crystallization of MFI occurs both in the LS-TPA and the HS-TPA. It shows that the silicalite-1 peaks of the LS-TPA are superimposed on the high scattering background from the amorphous silica-gel phase, while no amorphous phase is observed in the XRD pattern of the HS-TPA. This result indicates that the higher steam amount obviously encourages the crystallization of MFI. At the same time, the shape of the LS-TPA and the HS-TPA shows monolithic pole, 20 mm in length and 7 mm in diameter.

The results of FTIR also confirm that higher steam amount promotes the crystallization during SAC process. For the LS-TPA and the HS-TPA, the absorption of the five-member rings in MFI zeolite structure at 550 cm^{-1} and the absorption of Si–OH at 960 cm^{-1} are observed. In addition, the peak intensity at 550 cm^{-1} becomes stronger when the sample was treated in the higher steam.[24] After SAC crystallization, it is also found that the intensity of the absorption at 800 cm^{-1} become stronger, which is assigned to the asymmetric stretching of the Si–O–Si bond in silicates.[22]

Although an excess of water is not essential for the zeolite synthesis, the higher steam amount greatly enhances the rate of crystallization in this experimentation. Jung et al. reported the synthesis of ZSM-5 films on quartz surface using SAC method and considered that crystallization mechanism in the SAC method was same as it has been proposed for hydrothermal sys-

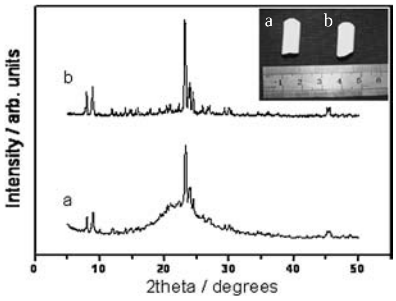

Figure 1. XRD patterns of the LS-TPA (a) and the HS-TPA (b). The inset is a photograph of the LS-TPA (a) and the HS-TPA (b).

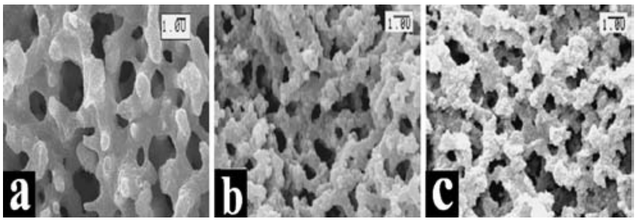

Figure 2. SEM images of the original macroporous silica gel (a), the LS-TPA (b) and the HS-TPA (c).

tems,[18] By performing vapor-phase transport (VPT) crystallization of zeolite from sol–gel precursor, Thoma et al.[19] estimated that the role of the water in the VPT solvent mixture was likely rehydration of surface siloxane groups to create hydroxy groups that could act as adsorption sites for the SDA and to facilitate bond breakage required for molecular rearrangement to construct the crystalline cage of zeolite. The present results are consistent with the conclusion by Thoma et al.[19] Increasing the amount of the steam led to the more molecular rearrangement and higher crystalline product. However, the direct conversion to zeolite in the steaming step is a complicated process. The mechanisms of crystallization in SAC are still open questions.

Figure 2 shows scanning electron microscopy (SEM) images of the LS-TPA and the HS-TPA. The zeolitized skeletons and the macropore of the LS-TPA and HS-TPA are cocontinuous. It is clearly seen that HS-TPA shows extensive crystallization of silicalite-1. When the skeleton surface was treated in the alkaline precursor solution, active sites (TPA$^+$–O–Si≡) could be formed on the skeleton surface.[18] As a result, the crystallization started from the active site.

The macroporous silica gel exhibits type IV adsorption–desorption isotherms characteristic with H1 hysteresis loop.[24] However, the adsorption isotherms after SAC become Type I isotherms, which is usually considered to be indicative adsorption in the micropores material. In addition, the shape of the hysteresis loops turns from H1 to H4 of IUPAC classification. The type H4 hysteresis may merely arise from the presence of large mesopores embedded in a matrix with pores of much smaller size.[23] The pore size distribution for LS-TPA and HS-TPA by BJH method also showed the presence of larger and smaller size mesopores. It can be found that the pore size distribution of the HS-TPA is narrow, with main pores centering at 1.92 nm, while a broad pore size distribution is observed in the LS-TPA.

As shown in Table 1, the BET specific surface area of the macroporous silica gel is higher than that of the LS-TPA and the HS-TPA, and the pore volume decreases upon zeolite formation. It was evident that the micropore surface area and micropore volume of macropores silica gel were zero, and the LS-TPA exhibited negligible micropority ($0.00643\,cm^3\,g^{-1}$). While the HS-TPA has reasonable micropore volume ($0.0715\,cm^3\,g^{-1}$), indicating that most the skeleton of the macroporous silica gel has transformed into the large amount of silicalite-1. This is additional proof that the higher steam amount promotes the crystallization during SAC process.

Table 1. Pore structural parameter of silicalite-1 monoliths and macroporous silica gel[a]

sample	S_{BET} /m^2 g^{-1}	S_{mic} /m^2 g^{-1}	V_{mic} cm^3 g^{-1}	V_{tot} /cm^3 g^{-1}
Macroporous silica gel	492	—	—	0.908
LS-TPA	170	18.6	0.00643	0.661
HS-TPA	292	91.3	0.0715	0.343

[a] S_{BET}: specific surface area; S_{mic}: micropore surface area, V_{mic}: micropore volume; V_{tot}: single point total pore volume.

This study has demonstrated that the hierarchical pore structure material can be synthesized by transforming the skeleton of porous silica into silicalite-1 crystals through steam-assisted conversion method. In this way, the micropores were formed by the silicalite-1, and the mesopore and macropore were formed within macroporous silica gel. Although the higher steam amount was not essential for the zeolite synthesis, it obviously promotes the crystallization. It is believed that the hierarchical structured zeolite monoliths will be extensively used as catalysts, ion exchangers, and adsorbents in industries.

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