Catalytic cracking of large molecules over hierarchical zeolites

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A hierarchical zeolite catalyst was synthesized by transforming the skeletons of a bimodal pore silica gel into a zeolite through a steam-assisted conversion method, and shows high catalytic activity and a long catalyst lifetime for catalytic cracking of large molecules.

Nowadays, hierarchically structured zeolites are considered to have potential impact in heterogeneous catalysis, adsorption and separation, so hierarchical zeolites have become the subject of intense research for such applications.[1,2] As compared with conventional zeolites, these hierarchical zeolites could overcome the limitations of the pore size, possessing the capability of cracking large molecules. The general synthetic approach to hierarchical zeolites previously relied on an endotemplating or exotemplating route,[3] such as molecular, supramolecular, colloidal crystal template, latex spheres beads,[4] carbon fiber,[5] mesoporous silica spheres,[6] ceramic foams,[7] and wood cell.[8] However, they suffered from restricted mechanical stability and controlled morphology. Recently, Nakanishi *et al.* reported the preparation of a novel template with macropores and mesopores based on phase separation, in the presence of organic polymer, in a silicon alkoxide sol–gel process. Meanwhile, macroporous silica had been applied in high-performance liquid chromatography (HPLC) columns, which showed superior separation properties in analysis compared with conventional packed columns.[9,10] Takahashi *et al.*[11,12] have reported the preparation of silica–alumina catalysts with continuous macropores and mesopores. They showed higher catalytic activity than commercial silica–alumina catalysts in cracking of cumene[11] and dehydration of 2-propanol.[12] The results clearly show that macropores with interconnected structure work effectively as pathways for rapid diffusion and improve the reaction kinetics.[12]

In this study, we synthesized novel catalysts with hierarchically structured zeolites by transforming the skeletons of a bimodal pore silica gel into a zeolite through a steam-assisted conversion method (SAC).[13] Firstly, the macroporous silica used in this experiment was prepared, following published procedures.[14] Tetramethoxysilane (TMOS) was hydrolyzed under acidic conditions in the presence of various additives such as water soluble polymers that induced a phase separation during the polymerization stage. Then, the macroporous silica gel was immersed in the precursor solution and subjected to steam-assisted conversion at 423 K for 24 h. The precursor solution was prepared by mixing aluminium isopropoxide, sodium hydroxide, distilled water and tetrapropylammonium hydroxide (TPAOH) following the molar composition: 1 Al_2O_3 : 1 Na_2O : 1266.7 H_2O : 6 TPAOH. Thereafter, the samples were dried at 373 K for more than 24 h and calcined at 873 K for 6 h. Finally, the protonated form of the sample was obtained by ion-exchange with NH_4Cl, followed by calcination at 823 K for 6 h.

The scanning electron microscopy (SEM) images (Fig. 1) clearly show the morphology of the original macroporous silica and the hierarchical zeolite catalyst. The morphology of the macroporous silica gel shows the 'interconnected structure' (Fig. 1a), where both the silica skeletons and the macropores (about 3 to 8 μm in diameter) are continuous. The interconnected macroporous morphology is formed when transitional structures of spinodal decomposition are frozen-in by the sol–gel transition of silica.[15] It is clear that the morphology of the hierarchical zeolite catalyst (Fig. 1b) is quite similar to that of the macroporous silica gel.

Fig. 2 shows the X-ray diffraction (XRD) patterns of the original macroporous silica gel, the hierarchical zeolite catalyst and microporous ZSM-5. The hierarchical zeolite catalyst showed a pattern typical of ZSM-5 as well as the amorphous silica,

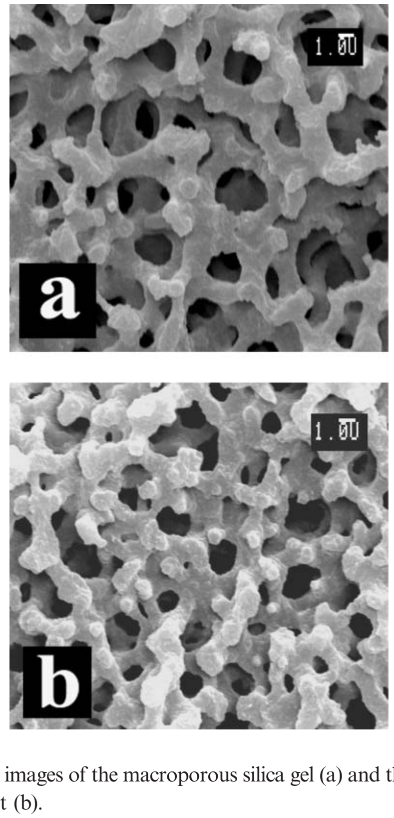

Fig. 1 SEM images of the macroporous silica gel (a) and the hierarchical zeolite catalyst (b).

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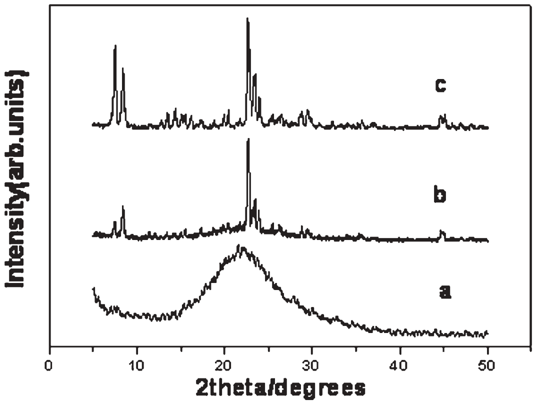

Fig. 2 XRD patterns of the macroporous silica gel (a), the hierarchical zeolite catalyst (b) and microporous ZSM-5 (c).

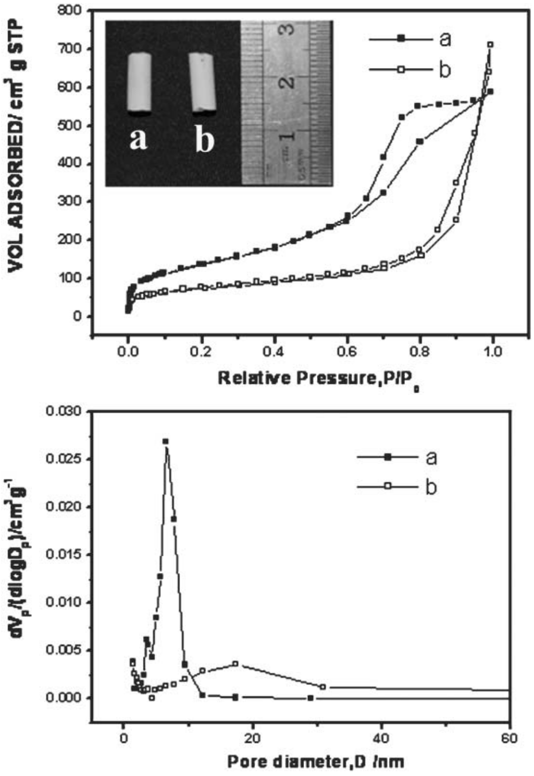

Fig. 3 Nitrogen adsorption–desorption isotherms and pore size distributions of the macroporous silica gel (a) and the hierarchical zeolite catalyst (b). The inset is a photograph of the macroporous silica gel and the hierarchical zeolite catalyst.

indicating that the skeletons of the macroporous silica gel were incompletely converted into the MFI zeolite structure. Actually, when this hierarchically structured zeolite monolith is used as a catalyst, not all the skeletons need to be completely converted into a zeolite structure. By reducing the alkalinity of the precursor solution and the steam treatment time, most of the interconnected skeletons were preserved as shown in Fig. 1b, and some silica skeletons dissolved and were subsequently transformed into zeolite crystals. Therefore, we consider that the macroporous silica gel provides both a template and a silica source.

As shown in the inset in Fig. 3, the hierarchical zeolite catalyst exhibits a monolithic shape of 10 mm in length and 5 mm in diameter. Additionally, the retained mechanical strength of the hierarchical zeolite catalyst was adequate for practical applications.

The adsorption–desorption isotherm of the macroporous silica gel is a type-IV isotherm and shows little increase until P_0, indicating the presence of both mesopores and macropores.[16] But the adsorption–desorption isotherm of the hierarchical zeolite catalyst is a type II isotherm as shown in Fig. 3, which is usually considered to be indicative of adsorption in the macroporous material. It is interesting to note that for the hierarchical zeolite catalyst the hysteresis loops turn to type H3, indicating the presence of extra mesoporosity.[17] The corresponding pore size distribution of the macroporous silica shows a narrow peak centered at 6.6 nm, while the hierarchical zeolite catalyst shows a broad pore-size distribution range from 10 nm to 30 nm. The BET specific surface area of the macroporous silica gel (492 m^2/g) is higher than that of the hierarchical zeolite catalyst (253 m^2/g). The micropore surface area and micropore volume were calculated by the *t*-plot method. The macroporous silica gel shows negligible micropores, while the hierarchical zeolite catalyst has a reasonable micropore volume (0.0233 cm^3/g) and micropore surface area (51.7 cm^2/g). Ammonia temperature-programmed desorption (NH_3-TPD) analysis gave acidity values of 0.266 H^+ mmol/g for the hierarchical zeolite catalyst.

The SAC requires an appropriate amount of water in the bottom of the autoclave to maintain the saturated vapor pressure, and a higher amount of steam greatly enhances the rate of crystallization. Thoma *et al.*[18] estimated that the role of the water in the VPT solvent mixture was likely rehydration of surface siloxane groups to create hydroxyl groups that could act as adsorption sites for the structure-directing agents (SDA), and to facilitate bond cleavage required for molecular rearrangement to construct the crystalline cage of the zeolite. Serrano and van Grieken[19] took the direct conversion from gel to zeolite as evidence for the solid–solid transformation in their recent review article. However, the direct conversion to zeolite in the steaming step is a complicated process. The mechanisms of crystallization in SAC are still open questions.

The catalytic cracking performances of the hierarchical zeolite catalyst and the microporous HZSM-5 were tested in a fixed-type reactor for catalytic cracking of 1,3,5-triisopropylbenzene (TIPB) at 623 K. The feed rate of TIPB was 0.07 ml/min and the catalyst

Table 1 Initial catalytic activity of the microporous ZSM-5 and the hierarchical zeolite catalyst for the cracking of 1,3,5-triisopropylbenzene

		Selectivity (%)[a]				
Catalyst	Conversion (%)	Benzene	IPB	MIPB	PIPB	others
Microporous ZSM-5	14.3	—	—	66.8	—	33.2
Hierarchical zeolite catalyst	97.8	13.1	33.9	22.7	5.1	25.2

[a] IPB, MIPB and PIPB denote isopropylbenzene, *m*-diisopropylbenzene and *p*-diisopropylbenzene respectively.

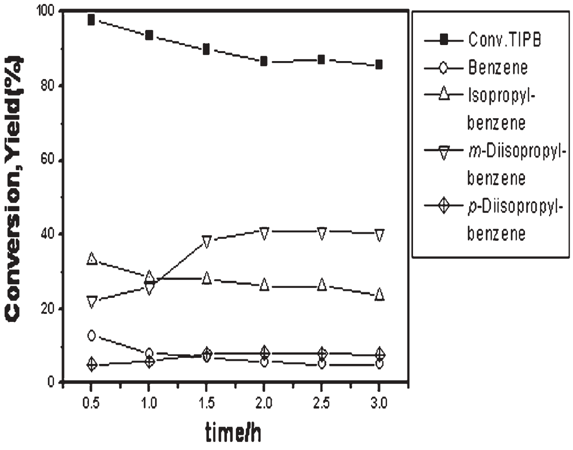

Fig. 4 TIPB cracking activity of the hierarchical zeolite catalyst.

volume was 3.9 g. The microporous ZSM-5 afforded an initially low TIPB conversion of 14.3%, as shown in Table 1. The microporous ZSM-5 has 10-ring pores with diameter no larger than 0.56 nm, while TIPB has a dynamic diameter of 0.94 nm and cannot diffuse through the inner pores of ZSM-5. Therefore, catalytic reaction can only occur on the external surface of ZSM-5 crystals.[20] However, the hierarchical zeolite catalyst showed an initially high catalytic activity corresponding to 98% conversion. After 3 h TIPB conversion was still 85% . Fig. 4 shows that isopropylbenzene and *m*-diisopropylbenzene were the major products. The yield of *m*- and *p*-diisopropylbenzene increased with prolongation of reaction time, while the yield of isopropylbenzene and benzene decreased. It is interesting that the conversion and product distributions are basically stable when the reaction time is longer than 1.5 h. The remarkable catalytic reactivity of large molecules is attributed to the presence of the hierarchical zeolite structure. The continuous macropores provide pathways for transportation of larger molecules and the microporous HZSM-5 provides acidic sites for catalytic activity. These results suggest that this hierarchical zeolite catalyst may lead to improvements in the catalytic cracking of large molecules.

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