Mesoporous materials with zeolite framework: remarkable effect of the hierarchical structure for retardation of catalyst deactivation†

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Received (in Cambridge, UK) 22nd August 2006, Accepted 19th September 2006
First published as an Advance Article on the web 29th September 2006
DOI: 10.1039/b612116k

Hierarchical MFI zeolite was synthesized following a synthesis route using organic–inorganic hybrid surfactants; the resultant zeolite with mesoporous/microporous hierarchical structure exhibited remarkably high resistance to deactivation in catalytic activity of various reactions such as isomerization of 1,2,4-trimethylbenzene, cumene cracking, and esterification of benzyl alcohol with hexanoic acid, as compared with conventional MFI and mesoporous aluminosilicate MCM-41.

Zeolites are crystalline microporous aluminosilicates, widely used as catalysts in a variety of chemical reactions in the petrochemical industry.[1] The success of zeolite catalysis is attributed to the presence of strong acid sites on the frameworks with well-defined microporous structures that are responsible for the shape-selectivity (pore diameter < 15 Å). For instance, zeolite-based cracking processes correspond to an added value of 40 billion US dollars/year.[2] However, in catalytic reaction of bulky molecules, the sole presence of micropores inhibits facile mass transfer to and from the active sites, often limiting the catalytic applications. The last decade has witnessed the development of ordered mesoporous aluminosilicate materials such as M41S and SBA.[3] However, despite their large pores, the mesoporous materials with a noncrystalline framework were low in acidity and hydrothermal stability, thus limiting their practical applications.

In recent years, various strategies have been developed in order to enhance the pore accessibility of zeolites: synthesis of zeolite nanoparticles,[4] synthesis of ordered mesoporous materials using zeolite seeds,[5] and generation of mesopores inside zeolite particles through steaming[6] or other chemical etching routes.[7] Mesoporous zeolites have also been successfully synthesized by using nanosized carbon templates.[8] Very recently, we developed a new synthesis strategy for the direct, hydrothermal crystallization of zeolites having a mesoporous/microporous hierarchical structure.[9] The mesopores were disordered, but the pore diameters could be uniformly tailored. The zeolite frameworks were highly crystalline and exhibited strong acidity. The hierarchical zeolites showed remarkably enhanced catalytic activity for bulky molecular transformation.[9]

In the present communication, we report our finding of another favourable effect of such hierarchical zeolite structures. That is, the hierarchical MFI zeolite exhibited remarkably high resistance to deactivation in catalytic activity of various reactions, such as gas phase isomerization of 1,2,4-trimethylbenzene and cumene cracking, and liquid phase esterification of benzyl alcohol with hexanoic acid. Improvement in catalytic activity using mesoporous materials composed of zeolite frameworks was anticipated[10] and recently reported.[9,11] However, to the best of our knowledge, such retardation of catalyst deactivation for zeolite with mesoporous/microporous hierarchical structures is reported here for the first time.

The hierarchical MFI zeolite was prepared according to a procedure in which 3-[(trimethoxysilyl)propyl]hexadecyl-dimethylammonium chloride ($[(CH_3O)_3SiC_3H_6N(CH_3)_2C_{16}H_{33}]Cl$, TPHAC) was added into an initial synthesis composition for ordinary MFI zeolite. Tetraethyl orthosilicate (TEOS) was used as the silica source. Tetrapropylammonium bromide (TPABr) was used as the MFI structure director. The initial gel composition was 1.0 Al_2O_3/4.0 TPABr/10.0 Na_2O/41.8 SiO_2/2.2 TPHAC/7200 H_2O. Conventional hydrothermal reaction was employed for the crystallization during 2 d at 170 °C. Inductively coupled plasma analysis of the zeolite product gave Si/Al = 20. For comparative purposes, other aluminosilicate catalysts such as conventional MFI zeolite and mesoporous MCM-41 (Al-MCM-41) with Si/Al = 20 were prepared according to the reported procedures.[9] Scanning electron micrographs (SEM) (Fig. 1) and N_2 adsorption isotherms

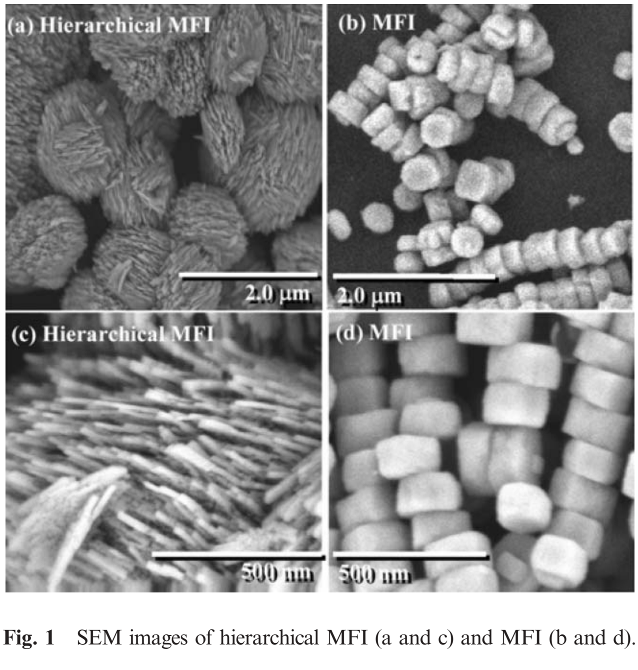

Fig. 1 SEM images of hierarchical MFI (a and c) and MFI (b and d).

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† Electronic supplementary information (ESI) available: TEM image of hierarchical MFI, XRD profiles for hierarchical MFI and MFI, experimental procedure for the catalytic activity measurements. See DOI: 10.1039/b612116k

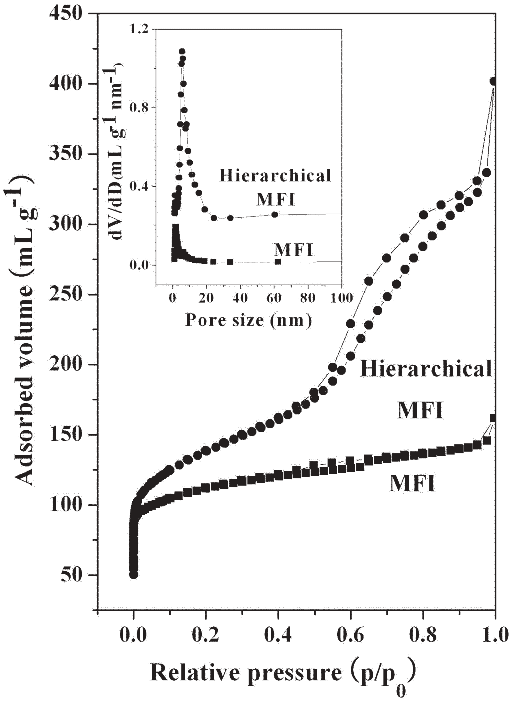

Fig. 2 N_2 adsorption/desorption isotherms of MFI and hierarchical MFI materials (inset shows their pore size distributions).

(Fig. 2) were obtained and analyzed in the same way as in our previous work.[9] The N_2 adsorption isotherms and SEM images of the hierarchical zeolite prepared in the present work are similar to those reported in our previous work, except for the slight variation of mesopore diameters depending on details of synthesis conditions (Table 1).

Gas phase isomerization and disproportionation reaction of 1,2,4-trimethylbenzene [1,2,4-TMB][12] was performed in order to investigate the catalytic activity of these catalyst samples. Details of the experimental proceedures are given in the ESI.† Isomerization of 1,2,4-TMB led to the simultaneous formation of 1,2,3-TMB and 1,3,5-TMB. The disproportionation produced all isomers of xylene and tetramethylbenzene [TeMB] (Fig. 3(a), ESI). During the initial reaction period, conventional MFI exhibited slightly higher activity than the hierarchical MFI zeolite. The 1,2,4-TMB conversion was 30 and 25% for MFI and hierarchical MFI, respectively. Al-MCM-41 exhibited somewhat lower activity (1,2,4-TMB conversion = 11%). The selectivity for TMB and TeMB was higher in the case of hierarchical MFI (96%) and Al-MCM-41(95%) than for conventional MFI (74%). The selectivity difference can be ascribed to the improved mass transport of TMB and TeMB in hierarchical zeolite. In the hierarchical zeolite catalyst, it is reasonable that the diffusion path would be significantly shorter than that in the conventional zeolite catalyst. The low selectivity of xylenes (3%) can be attributed to the short diffusion path, which would prevent further disproportionation reactions. If only the disproportionation reaction took place, the molar ratio between xylenes and TeMB should be one. However, in the case of conventional MFI, a surplus of xylenes was observed. This result indicates that TeMB could be trapped in the micropores of MFI as a precursor to cokes. Indeed, the formation of cokes was identified by the black colour of the catalyst recovered after reaction.

Table 1 Textural properties of various catalysts used in the present study

Catalysts	$^{a}S_{\mathrm{BET}}$ (m^2 g^{-1})	$^{b}V_{\mathrm{total}}$ (ml g^{-1})	$^{b}V_{\mathrm{meso}}$ (ml g^{-1})	^{c}d (nm)
MFI	350	0.22	0.08	—
Hierarchical MFI	590	0.50	0.38	5.2
Al-MCM-41	930	0.69	0.61	2.6

[a] S_{BET} is surface area calculated using the Brunauer–Emmett–Teller equation. [b] V_{total} is total pore volume and V_{meso} is mesopore volume. [c] d is mesopore diameter calculated using the BJH method with adsorption branch.

The three catalyst samples exhibited remarkably different behaviours for deactivation. Slow deactivation was observed for hierarchical MFI, whereas conventional MFI was deactivated very rapidly, and Al-MCM-41 was about in the middle. The stability of the hierarchical MFI against deactivation, as compared with conventional MFI, may be attributed to the facile diffusion of reactants and products through mesopores. It is well known that catalyst deactivation in zeolites can occur due to coke formation at the pore mouths, which is produced *via* secondary reactions. The large surface area of the mesoporous structure would allow facile molecular diffusion into and out of the micropores in the zeolite frameworks. The micropore blockage would occur very slowly because of the large number of pore mouths at the surface of the mesopore walls. Similar slow deactivation has also been reported with nanocrystalline zeolites that have much higher external surface area than bulk zeolites.[13]

Cumene cracking was also tested with the three catalyst samples mentioned above. This reaction is a well-established test reaction for hydrocarbon cracking activity that requires strong acidity.[14] Benzene and propylene were found to be the major products in the present investigation (ESI). C_4–C_6 hydrocarbons, ethylbenzene, toluene and dipropylbenzene were minor products. The C_4–C_6 hydrocarbons can be attributed to the transformation of propylene produced in the course of cumene cracking. Alkylation of cumene with propylene leads to dipropylbenzene.[11] The catalytic activity of Al-MCM-41 was found to be very low (cumene conversion = 14%), due to its low acidity, whereas both conventional and hierarchical zeolites exhibited high activities (cumene conversion = 97 and 94% respectively). The two MFI zeolite samples showed similar activities during the initial reaction period (Fig. 3(b)). With prolonged reaction time on stream, the two zeolite samples showed a remarkable difference in their deactivation behaviour. That is, catalytic activity of the conventional MFI decreased very rapidly with time whereas no significant deactivation was detected in the case of hierarchical MFI zeolite. Al-MCM-41 catalyst showed low initial activity, and further, the catalyst was rapidly deactivated with time on stream.

Interestingly, the hierarchical zeolite also indicated very slow deactivation in the liquid phase esterification reaction between benzyl alcohol and hexanoic acid (Fig. 3(c)), compared with the other catalysts. In this reaction, the ester was produced as a major product while dibenzyl ether was obtained as a by-product due to a dehydrative condensation between two alcohol molecules. During the first run, the hierarchical MFI, conventional MFI and Al-MCM-41 samples gave 92, 23 and 83% conversion of benzyl alcohol, respectively. The ester selectivity was 75.2, 98.2 and 67.0%, respectively. Notably, both the conventional MFI and

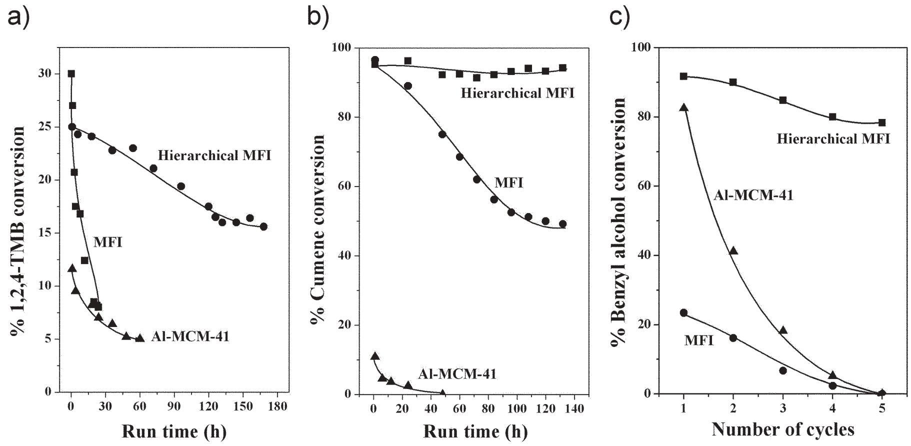

Fig. 3 Deactivation behaviour of hierarchical MFI, MFI and Al-MCM-41: (a) 1,2,4-TMB isomerization, (b) cumene cracking, and (c) esterification of benzyl alcohol and hexanoic acid.

Al-MCM-41 catalysts lost catalytic activity completely in five recycling experiments. However, the hierarchical MFI still exhibited 78% benzyl alcohol conversion even after five recycling experiments.

The facile diffusion through mesopores can explain the data in Fig. 3(a) and 3(b), where the deactivation of hierarchical MFI was comparable to that of Al-MCM-41 and much slower than that of conventional MFI. However, it is noteworthy that hierarchical MFI is much more stable than Al-MCM-41, in the case of esterification of benzyl alcohol. The esterification reaction involves large molecular species, hence takes place mainly at the surface of mesopore walls (compared with the small molecular reactions shown in Fig. 3(a) and Fig. 3(b)). We attribute the difference between hierarchical MFI and Al-MCM-41 in Fig. 3(c) to their differences in acid strength and Al concentration at the mesopore walls. It is reasonable that all Al sites in Al-MCM-41 are concentrated exclusively at the mesopore-wall surface because of the post-synthesis incorporation.[9] Despite a similar Al content, the hierarchical MFI zeolite can have Al locations inside the mesopore walls (zeolite framework) as well as at the wall surface. That is, Al sites are much more highly concentrated in Al-MCM-41. The short distance between adjacent Al sites in the Al-MCM-41 surface seems to be favourable for the formation of polymeric coke species that can deactivate the catalyst.

In summary, the MFI zeolite with mesoporous/microporous hierarchical structure exhibited very slow deactivation in the three cases of catalytic applications shown above, as compared with MFI without mesoporosity. Further work would be necessary for the generalization of the slow deactivation phenomena into other catalytic reactions. Nevertheless, through the present reactions, it is proposed that the generalization would be highly probable. It is reasonable that facile diffusion through mesopores can improve access of reactant molecules to the strong acid sites and also minimize the diffusion length of coke precursors out of the micropore. This effect can lead to a significant change in the product selectivity, increase the catalytic activity, and increase the catalysts' lifetime. The increasing lifetime will give a remarkable advantage in many catalytic processes, particularly in continuous flow processes, because of the cost-down effect due to less frequent interruption for catalyst regeneration or replacement. Further studies are in progress in our laboratory.

This work is supported by the Ministry of Science and Technology through the Creative Research Initiative Program.

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