Mesoporous material containing framework tectosilicate by pore–wall recrystallization

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Partial recrystallization of the interporous aluminosilicate surface of MCM-41 and HMS by ion-exchanged tetrapropylammonium template results in a mesoporous material with surface-tectosilicate structures giving enhanced acidity and catalytic cracking activity.

The development of the mesoporous molecular sieve MCM-41 by the workers of Mobil[1,2] has stimulated much research efforts in the field of acid[3,4] and base[5] catalysis. The strength of the acid sites of MCM-41 as well as of the related HMS material[6,7] is, however, rather weak compared to zeolites[8,9] owing to the amorphous character of the framework of both materials.[2,6–9] Here we report that upon increasing locally the crystallinity of the amorphous framework of MCM-41 and HMS, the acidity and catalytic activity improves substantially. The design of these catalysts is based on positioning tetrapropylammonium (TPA) cations at the interporous surface of MCM-41 and HMS which induces partial recrystallization of the pore wall *via* heterogeneous nucleation during thermal processing. Owing to short-range aluminosilicate–template interactions non-porous framework tectosilicate[10] is formed of the ZSM-5 precursor type.

Our approach to design a composite consisting of a mesoporous molecular sieve with interporous tectosilicate, denoted as porous nanocrystalline aluminosilicate (PNA) is based on the idea to recrystallize partially the amorphous framework of MCM-41 and HMS. By attachment of TPA cations, the template for ZSM-5,[11] onto the mesopore walls *via* an ion-exchange procedure a high dispersion of the TPA in the mesoporous material is achieved. This should result in a nucleation of ZSM-5 species and controlled conversion of MCM-41 and HMS. When the pre-positioning of TPA is omitted and a homogeneous aqueous mixture of TPAOH and MCM-41 is heated we observed that the MCM-41 is recrystallized overnight into aggregates of ZSM-5.[12] This process went even faster when purely siliceous MCM-41 was used, resulting in silicalite-1, which is however not useful in catalytic processes. Thus the need to pre-position TPA at the Al sites is a prerequisite to induce the recrystallization at the Al sites and suppress the diffusivity of TPA.

Considering partial recrystallization of MCM-41 and HMS, the ZSM-5 stoichiometry in the starting materials has to be optimized. It is well known that in as-synthesized ZSM-5 each TPA is surrounded by 24 tetrahedrally coordinated Si and/or Al atoms.[13] The Si/Al ratio (30) of the parent MCM-41 and HMS materials was chosen to be close to the above value. Here thirty one T-atoms (T = SiO_4 and/or AlO_4^- tetrahedra) are neighbouring one TPA cation in TPA ion-exchanged MCM-41 (TPA-MCM-41). This ZSM-5 precursor-type situation is, according to Ostwald's rule of successive transformations,[10] expected to induce ZSM-5 crystallization Glycerol was selected as the solvent in the recrystallization, because it appeared to have unusual advantages in ZSM-5 synthesis. The high viscosity of glycerol will moderate zeolite growth and moreover glycerol can act as a stabilizing guest molecule.[14,15] It was proposed that various silicate structures are formed during aging due to the interaction of glycerol with silicate species.[15]

Calcined MCM-41 (1.0 g; Si/Al = 30; HNa-form)[5] was converted to TPA-MCM-41 by ion-exchange with a 50% excess of aqueous TPAOH (2×10^{-3} M solution) for 20 h, followed by washing and drying at 80 °C under vacuum. The Na/Al ratio decreased from 0.8 to 0.1 indicating a 90% substitution of Na^+ for TPA cations. TPA-MCM-41 with a tenfold excess mass of glycerol was loaded in a Teflon-lined autoclave and stirred for 2 h at room temp. and subsequently allowed to react at 120 °C statically for 24 h. Finally the material was collected by filtration, washed with demineralized water, dried at 100 °C and calcined at 500 °C for 5 h to remove the organics from the composite material (coded as PNA-1). Aluminosilicate HMS (Si/Al = 30; H-form)[16] was subjected to the same procedure resulting in the material PNA-2.

The substantial improvement of the catalytic activity, and thus the acidity, of the PNAs compared to the parent materials is demonstrated by the cracking of cumene (Table 1). The catalytic reactions were performed at 300 °C in a down-flow reactor (id = 7 mm) using 1 g of catalyst pellets (diameter 0.7–1.0 mm) and a N_2 flow of 25 ml min^{-1} containing 14.4 μmol min^{-1} of cumene. The parent MCM-41 and HMS materials in the H^+-form produce only benzene and propene with traces of α-methylstyrene. The enhanced cumene conversion over the PNAs is exclusively the result of a higher cracking activity.[17] The improved activity is therefore assigned to enhanced Brønsted acidity which is also reflected by the initial *n*-hexane cracking activity of the PNAs which is about four times higher than that of the MCM-41 and HMS materials. The PNAs showed no significant deactivation during 3 h on stream in the cumene reaction and showed similar activities after regeneration at high temperature indicating that the framework does not collapse and that the acid sites are still accessible. It may be mentioned that the cumene conversions over the four mesoporous aluminosilicates were not diffusion limited. This was, however, not the case for the cumene cracking over the microporous ZSM-5.

As shown in Fig. 1, the X-ray powder diffraction patterns of the parent MCM-41 and HMS materials and the corresponding PNAs do not differ significantly. The characteristic hexagonal features of MCM-41, which are reflected by the common d_{100} diffraction peak and the 110, 200 and the much weaker 210 reflections in the 2θ range 4.0–7.0° are retained though with less

Table 1 Conversion of cumene at 300 °C over PNAs and related parent materials

	Cumene conversion (%) at time on stream	
Sample	10 min	3 h
MCM-41[a]	14.7	13.6
PNA-1	41.3	37.5
HMS[a]	24.8	26.8
PNA-2	47.6	42.4
ZSM-5[b]	95.1	93.7

[a] MCM-41 and HMS in the H^+-form. [b] H-ZSM-5 with Si/Al = 78.

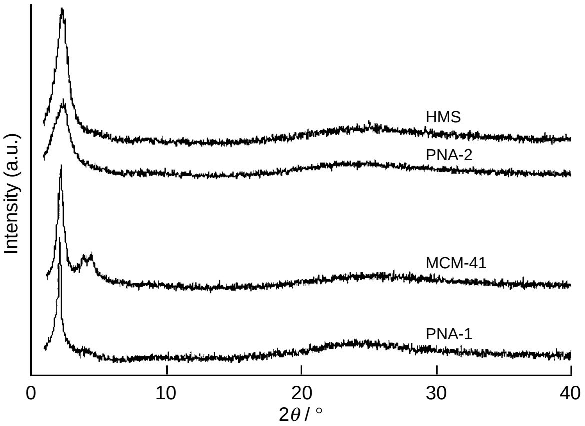

Fig. 1 X-Ray powder diffraction patterns of the composite materials PNA-1 and PNA-2 together with the parent MCM-41 and HMS materials, respectively

intensity in PNA-1. The absence of high-order Bragg reflections in HMS, indicating small crystallite domains,[6,7] is also preserved in PNA-2. The intensity of the d_{100} diffraction peak had decreased drastically when, instead of glycerol, water was used as the solvent. As indicated by the X-ray powder diffraction patterns the PNAs still possess mesoporous features and a large specific surface area measured by N_2 adsorption (1267 and 796 m^2 g^{-1} BET area and a pore size of 27 and 23 Å for HMS and PNA-2, respectively). TEM measurements showed that exclusively one solid phase was present.

FTIR spectroscopy reveals only for the PNA samples a distinct vibration at 550–560 cm^{-1} (Fig. 2). Several researchers have assigned the 550 cm^{-1} band to the asymmetric stretching mode of the five-membered ring present in ZSM-5 which should therefore be an indication of the presence of embryonal ZSM-5 structures.[18–22] The parent MCM-41 and HMS which have both an amorphous framework do not absorb at this wavenumber and therefore the 550 cm^{-1} vibration is a good probe for detecting the degree of crystallinity of a siliceous MFI-type material even at this initial stage of ZSM-5 formation giving very small tectosilicate structures.[18,22]

Interestingly, ^{27}Al MAS NMR measurements show a transformation of strongly anisotropic Al into a quasi-isotropic tetrahedral environment going from HMS to PNA-2.

We conclude that thermally-treated TPA-MCM-41 and TPA-HMS recrystallize, assisted by glycerol, the amorphous aluminosilicate framework partly to such an extent that the framework Al environment is made more highly symmetric. Owing to the attachment of the TPA cations at the interporous framework in combination with the short TPA–aluminosilicate distance[23,24] the recrystallization process is forced to nucleate heterogeneously. The advantage of this process is the formation of embryonal ZSM-5 in a controlled way.

The importance of the TPA/T-atom ratio when partly recrystallizing MCM-41 and HMS materials is reflected by the production of only X-ray amorphous material when TPA/Al = 1 and Si/Al = 15 instead of 30. The higher amount of framework Al and therefore the increase of interattached TPA causes disturbance of the recrystallization of the framework. However, when the same mesoporous aluminosilicate is ion-exchanged at a TPA/Al ratio of 0.5 and subsequently thermally processed, the X-ray diffraction pattern was retained much better and an IR band at 550 cm^{-1} was observed. The small size of the tectosilicate nanostructures makes detection of the 1220 cm^{-1} band impossible.[22] Attempted preparation of PNA by interrupting the ZSM-5 crystallization using water as the medium appeared to be very difficult and not reproducible.[12]

In conclusion, the present approach to position the appropriate amount of template molecules inside a mesoporous aluminosilicate can lead to controlled partial reacrystallization and provide new interesting catalytic materials. Thus, upgrading of the catalytic properties of MCM-41 and related materials might lead to a more valuable component in commercial cracking catalysts used in oil refining of heavy feedstocks.[25]

We thank NIOK, the Dutch School of Catalysis, for financial support.

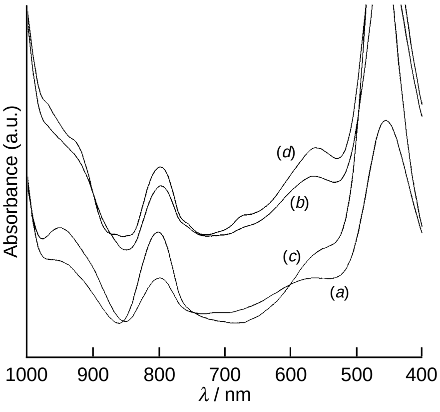

Fig. 2 FTIR absorption spectra of MCM-41 (*a*), PNA-1 (*b*), HMS (*c*) and PNA-2 (*d*)

Footnote and References

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Received in Cambridge, UK, 5th August 1997; 7/05681H