Partial Transformation of MCM-41 Material into Zeolites: Formation of Nanosized MFI Type Crystallites

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Received July 12, 2000. Revised Manuscript Received November 9, 2000

A new potentially catalytic material has been developed by partial recrystallization of the porewall of MCM-41. Recrystallization is induced by impregnation of MCM-41 with tetrapropylammonium hydroxide followed by a hydrothermal treatment. This procedure resulted in the formation of small particles of approximately 3 nm, which can be observed with TEM. The fact that the formation of these particles resembles the first stages of ZSM-5 formation and the fact that a templating material is used, which is also frequently applied in the synthesis of ZSM-5, suggest that the 3 nm particles have a ZSM-5 structure. Furthermore, ^{13}C NMR on recrystallized MCM-41 shows a split-up of the methyl signal of TPA, which is also known to be present in as-synthesized ZSM-5. After calcination of the recrystallized material the small crystallites could no longer be observed, although IR measurements show still some ZSM-5-like acidity to be present. Other, milder calcination routes should be developed in order to preserve the ZSM-5 crystallites. Another stability problem encountered concerns the stability of the MCM-41 since the hydrothermal treatment severely damaged the framework. It was found that the use of a template molecule, hexadecylamine, to support the framework during the recrystallization was beneficial.

Introduction

Due to environmental concern, the interest in solid acid catalysts as replacements of liquid acids is growing.[1] The problems associated with the currently used catalysts such as mineral acids or metal halide Lewis acid catalysts are their toxicity, corrosivity, and effluent disposal. Furthermore, a complete separation of the product and the catalyst is sometimes difficult. Zeolites possess several catalytically desirable properties: a high surface area; adjustable pore size; hydrophilicity; acidity; high thermal and chemical stability. Therefore, they are gaining importance in the quest for cleaner processes. Industrial examples[2,3] include aromatic alkylation,[4] the synthesis of *tert*-butylamine from ammonia and isobutene over zeolite MFI,[5] the conversion of methanol and ammonia to mono-and dimethylamine over modified mordenites[6] or zeolite Rho,[7] and the hydration of cyclohexene to cyclohexanol over ZSM-5. Furthermore, zeolites have found widespread applications in oil refining processes.[8,9] A disadvantage of zeolite catalysts is their limited pore size (up to 1.0 nm), which renders them useless as catalysts in the conversion of larger sized reactants.

The discovery of the mesoporous material MCM-41[10−12] has greatly enlarged the window of porous materials applicable as catalyst for organic reactions. Unfortunately, the acid strength of MCM-41 resembles that of the amorphous silica aluminas rather than that of the more strongly acidic zeolites.[13] Although the material is valuable for many organic conversions,[14,15] enhancement of its acidity is desirable for extension of its applicability.

Several approaches aimed at increasing the acid strength of the material. Kozhevnikov et al. showed that heteropoly acids (HPA) supported on MCM-41 are excellent catalysts in several reactions.[16−19] However,

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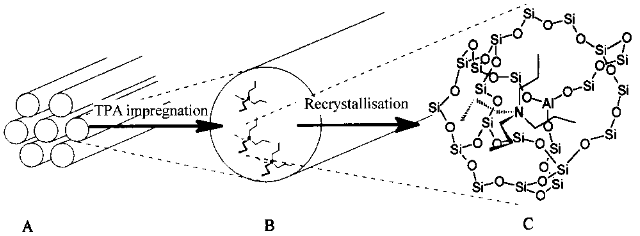

Figure 1. Schematical representation of the partial recrystallization of the MCM-41 pore wall.

the lack of stability of this catalyst system in case polar reactants or products are involved, concerning mainly the dispersion of the HPA[20] and leaching of the HPA from the support, prevents its introduction in industrial applications. Another possibility is the use of sulfonic acid groups covalently attached to the MCM-41 pore wall via an organic spacer.[21,22] In this case, leaching does not seem to be a problem, but the organic spacer limits the thermal stability of the system and, consequently, the possibilities of thermal reactivation of the catalyst. Another approach is the simultaneous synthesis of a micro- and mesoporous composite material using in situ formation of MFI and MCM-41 material.[23] Complex aggregates of MCM-41 and MFI were obtained of which the relative amounts of MCM-41 and MFI can be tuned by varying the synthesis conditions. However, it is not quite clear whether these materials offer more possibilities than a physical mixture of both phases would.

The present paper deals with the partial recrystallization of the MCM-41 pore wall to ZSM-5 crystallites, a concept illustrated in Figure 1.

Recrystallization is induced by introducing the template for ZSM-5 crystallization, tetrapropylammonium (TPA), by impregnation or ion exchange. An increase of the local crystallinity around the aluminum atoms is expected to give MCM-41 a more zeolite comparable acid strength. Oswald's rule of successive transformations states that a metastable silicate phase will successively transform to more stable (denser) phases until it reaches the most stable phase (quartz).[24] This implies that, in principle, recrystallization of MCM-41 to ZSM-5 is possible. It should be noted that if an amorphous phase exists between MCM-41 and ZSM-5, this may be formed first, after which ZSM-5 will be formed. Attempts to reproduce a former procedure[25] resulted in amorphized MCM-41 before the formation of any ZSM-5.

It will be shown that the formation of nanosized particles, resembling ZSM-5, homogeneously dispersed over the MCM-41 framework, is possible.

Experimental Section

MCM-41 material with a Si/Al ratio of 32 was synthesized by following the procedure of Beck et al.[12] Silica sources used were Cab-osil M-5 (fumed silica, Fluka) and sodium silicate solution (Aldrich). Cetyltrimethylammonium bromide and tetramethylammonium hydroxide (TMA) as well as aluminum isopropoxide were obtained from Aldrich. MCM-41 was synthesized by heating the synthesis gel (molar composition: 1 SiO_2, 63.3 H_2O, 0.04 $(TMA)_2O$, 0.016 $(C_{16}NMe_3)_2O$, 0.016 Al_2O_3) in a polypropylene bottle at 100 °C for 2 days. The resulting solid was filtered out, washed with deionized water, and dried in a vacuum oven at 50 °C/0.3 mmHg. The template was removed by calcination at 540 °C for 10 h in air, yielding H-MCM-41 with a Si/Al ratio of 30.

Recrystallization experiments were carried out in four ways.

Procedure 1. MCM-41 was ion-exchanged to TPA-MCM-41 by shaking a suspension of 2.00 g of H-MCM-41 in 1.22 g of 25 wt % TPA-OH solution in 1 L of water overnight at room temperature. The solid was recovered by centrifugation, washed with 100 mL of water, redispersed into 30 mL of water, and subjected to a hydrothermal treatment at 170 °C in a 15 mL Teflon-lined autoclave using different synthesis times. The recrystallized MCM-41 was recovered by centrifugation, washed with deionized water, centrifuged again, and subsequently dried in a vacuum oven at 60 °C. The TPA template was removed by calcination in air at 500 °C for 6 h.

The other three methods used MCM-41 in its Na form as the starting compound. Na-MCM-41 was obtained by 3-fold ion exchange in 1 M aqueous NaCl at room temperature.

Procedure 2. Impregnation with TPA-OH was performed by suspending Na-MCM-41 in a solution containing the appropriate amount of TPA-OH (Al to TPA ratio = 1, 1 g of MCM-41/50 mL). The suspension was then shaken for 2 h at room temperature, followed by evaporation of the water in a rotary evaporator. The recrystallization synthesis mixture was obtained by suspending TPA/MCM-41 in water (1 g/10 mL), which was aged overnight prior to recrystallization at 170 °C. Workup was as described above.

Procedure 3. The impregnation of MCM-41 with TPA-Br was similar to that with TPA-OH. For the actual recrystallization the TPA/MCM-41 was suspended in water (1 g of MCM-41/10 mL) after which the pH was adjusted to 9 using an 0.1 M NaOH solution. Again the same hydrothermal treatment and workup were applied.

Procedure 4. This was performed as procedure 2 with the exception that, prior to the hydrothermal treatment, hexadecylamine was added in order to support the MCM-41 structure during the recrystallization. Impregnation with hexadecylamine was achieved by dissolution of 3.41 g (14 mmol) of hexadecylamine in 60 mL of ethanol followed by addition of 3 g of TPA-Na/MCM-41. This suspension was shaken overnight at room temperature followed by evaporation of the ethanol. The hydrothermal treatment is the same as that of the other procedures.

X-ray diffractograms were recorded on a Philips PW 1840 diffractometer using Cu Kα radiation. Transmission electron microscopy (TEM) was performed using a Philips CM30ST or a CM30T electron microscope operated at 300 kV. Samples were prepared for TEM by placing droplets of a suspension of the sample in ethanol on a polymer microgrid supported on a Cu grid. CP-MAS ^{13}C NMR spectra were recorded on a Varian VXR-400S spectrometer, equipped with a 5 mm Doty probe. Contact times of 2 ms and sine-bell resolution enhancement were applied. N_2 adsorption isotherms were measured on a Quantachrome Autosorp-6B at 77 K. The samples were pretreated in a vacuum at 350 °C for 16 h. Infrared spectra of acidic OD groups in calcined materials were obtained by selective deuteration of calcined samples at 323 K with deuteriobenzene, in a standard infrared setup (Biorad FTS-

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175 and vacuum cell), after activation at 673 K in vacuo. Details of the procedure are described elsewhere.[26] The hydroisomerization tests were carried out in a fixed bed reactor at a total pressure of 30 bar. The feed consisted of *n*-heptane and hydrogen in a 1:4 molar ratio. The temperature at which a conversion of 40% was reached was used as an indication of the acidity of the catalytic material.

Results

The ion exchange of MCM-41 to TPA-MCM-41 (procedure 1) was performed in a diluted TPA-OH solution at room temperature. Nevertheless, TEM showed the MCM-41 framework to be significantly damaged by this procedure. XRD showed a strong decrease of the intensity of the d_{100} signal and an almost complete disappearance of the long range ordering. At very low angle (0.62° in 2θ) a new signal appeared. Though speculative, this signal might be ascribed to the formation of larger pores due to the partial collapse of the MCM-41 framework. N_2 adsorption experiments show macropores to be present, though these N_2 condensations could be caused by interparticle void spaces as well. The hydrothermal treatment caused a further decrease in crystallinity up to a point where no MCM-41 was present anymore. Neither XRD nor TEM showed indications of ZSM-5 formation.

In the second recrystallization method, TPA was offered by means of impregnation instead of ion exchange. Once again the alkaline character of TPA-OH caused severe damage to the MCM-41 structure, as witnessed by the XRD pattern. Na-MCM-41 impregnated with TPA-OH showed a sharp decrease of the d_{100} signal in the XRD pattern of MCM-41 and a complete disappearance of all higher order signals. During the hydrothermal treatment, the d_{100} signal decreased further until no crystallinity could be detected. N_2 adsorption shows a dramatic collapse of the MCM-41 structure. After 1 h of hydrothermal treatment the MCM-41 structure was found to be severely damaged and the surface area dropped from 855 m^2/g for the parent material to 74 m^2/g. Upon hydrothermal treatment, a very small XRD signal, at $2\theta = 23°$, became visible. The nature of this reflection is uncertain, but it is possibly caused by either very small ZSM-5 crystals or crystalline areas in general. TEM confirms the MCM-41 framework to be increasingly damaged upon longer recrystallization times, up to a point where practically no MCM-41 is present anymore. Already after 1 h of hydrothermal treatment some dark spots, caused by a denser phase, become visible. Both the amount and the size of these spots appeared to be independent of the recrystallization time. These dark spots were 3 nm in size and were homogeneously distributed over the sample (see Figure 2). A blank experiment in the absence of TPA did not show these spots.

Support for the formation of ZSM-5 structures was obtained from ^{13}C NMR. TPA confined in ZSM-5 shows a characteristic splitting of the methyl ^{13}C NMR signal at 10 ppm. This is ascribed to the different surroundings of the propyl chains extending in the two different channels of the ZSM-5 crystallite. ^{13}C NMR performed on as-synthesized recrystallized MCM-41 showed a small splitting of the signal at 10 ppm as well. In MCM-41 impregnated with TPA (before hydrothermal treatment) this splitting of the methyl signals is absent. After removal of the TPA by calcination neither the dark spots in TEM nor the signal at 23° in 2θ in the XRD spectrum could be detected any longer. IR measurements (see Figure 3) on the calcined material show a weak signal of ZSM-5-like acid sites suggesting that some of the crystallites are still present. Figure 3 shows infrared spectra of calcined, selectively deuterated MCM-41, of MCM-41/ZSM-5 materials, and of a ZSM-5 material for comparison. The spectrum of acidic deuterioxyl (or hydroxyl) groups in MCM-41 is not fully understood.[26] It displays two peaks at 2738 and 2625 cm^{-1} (corresponding OH stretching mode frequencies are 3710 and

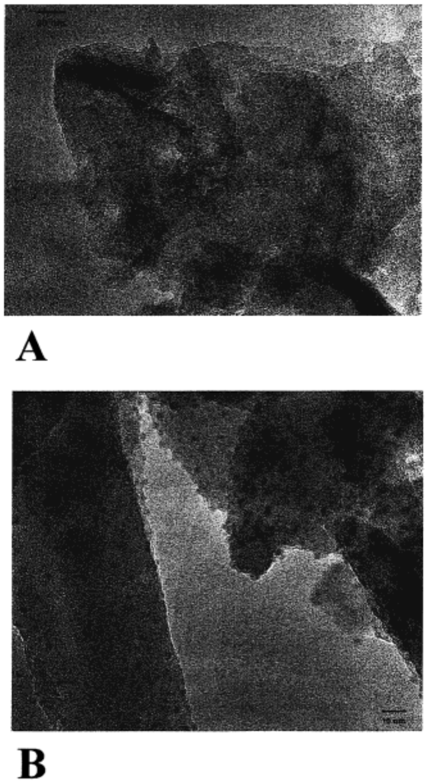

Figure 2. TEM images with different magnification of recrystallized material (procedure 2): A, magnification of 4.0 × 10^5; B, magnification of 1.3 × 10^6. The dark spots are small crystalline areas probably with a ZSM-5-like structure.

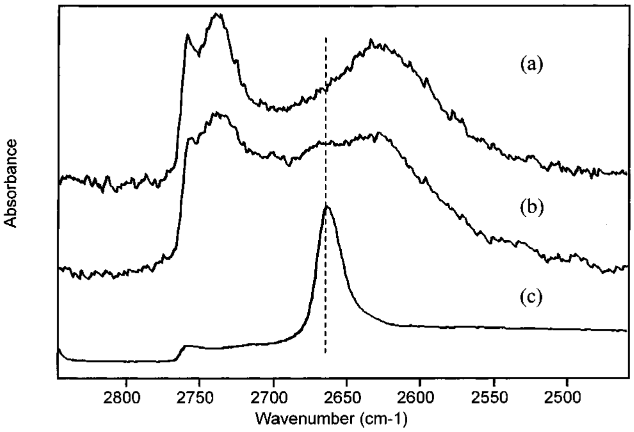

Figure 3. Infrared spectra of (a) MCM-41, (b) MCM-41/ZSM-5 (procedure 2), and (c) ZSM-5, after activation in vacuo and selective deuteration with deuteriobenzene at 323 K (see text).

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Table 1. N_2 Adsorption Data of Recrystallization Experiments Using Procedures 2 and 4

	procedure 2 (m^2/g)	procedure 4 (m^2/g)
parent MCM-41	855	855
TPA/MCM-41	822	822
1 h, 170 °C	74	530
2 h, 170 °C	40	90

3560 cm^{-1}) which have been tentatively assigned to silanol groups and hydrogen-bonded bridging, zeolite-like deuterioxyl groups. Exchange of silanol groups is much more pronounced in MCM-41 than in other materials, an observation which is discussed in more detail in ref 26. In the spectrum of the recrystallized material, a weak additional feature is present at approximately 2667 cm^{-1}. Bridging deuterioxyl groups in ZSM-5 display a peak at 2664 cm^{-1}.

Heptane hydroconversion experiments with MCM-41/ZSM-5 did not show any increased acidity as compared to the parent MCM-41.

In procedure 3, TPA-Br was used as a template in an effort to decrease the damage of the MCM-41 structure, caused by the impregnation with TPA-OH. To obtain the same alkaline conditions as in procedure 2, the pH was adjusted to pH 9 by addition of NaOH prior to the hydrothermal treatment. Formation of ZSM-5 crystallites did not occur after 1 h, but in the samples, which were subjected to 2 and 3 h of hydrothermal treatment, some ZSM-5 crystallites were formed. As expected, the impregnation with TPA-Br did not affect the MCM-41 framework. The effect of the hydrothermal treatment, however, was the same as when TPA-OH was used as a template.

To avoid rapid collapse of the framework during hydrothermal treatment it was investigated (procedure 4) whether supporting the framework with a template molecule was of benefit. After the impregnation with TPA-OH, MCM-41 was impregnated with hexadecylamine, a molecule frequently used for the synthesis of mesoporous materials of the HMS type.[27] XRD indicates the MCM-41 structure to be retained longer compared to the other experiments. N_2 adsorption experiments showed that mesopores were still present after 1 h of hydrothermal treatment. The surface area decreased to 530 m^2/g compared to 74 m^2/g in the experiment where the MCM-41 structure was not supported (see Table 1). However, the MCM-41 structure also collapsed ultimately: after 2 h of hydrothermal treatment, N_2 adsorption showed no sign of mesopores anymore and only a small d_{100} signal was still present in the XRD spectrum. Again small signals at 23° in 2θ appeared in the XRD pattern, indicating formation of small ZSM-5 crystals.

Discussion

Of the four recrystallization methods, the methods using impregnation with TPA as a way of offering the template were successful in generating small zeolite crystallites. By impregnation of Na-MCM-41 with TPA-OH a substantial amount of OH^- ions is occluded in the MCM-41 pores. Due to their strong mineralizing ability, these OH^- ions can give the Si and Al species the mobility necessary for recrystallization. When TPA is offered to the MCM-41 by ion exchange, no basicity is generated in the MCM-41 pores, and as a consequence, no recrystallization occurs. The high basicity required for recrystallization also causes serious damage to the MCM-41 material and ultimately leads to a complete collapse of the framework. By contrast, the MCM-41 framework was not affected by impregnation with TPA-Br. To generate the required basicity, the pH of the synthesis mixture was adjusted to 9 with NaOH. This resulted in the same rapid collapse of the material as observed when TPA-OH was applied as a template.

ZSM-5 crystallites in the recrystallized samples could best be detected using TEM. Due to the higher density of the zeolite particles compared to the amorphous MCM-41 pore walls (1.9 g/cm^3 vs 1.1 g/cm^3) these zeolite crystallites can be seen as dark spots in the TEM micrographs. Due to the small size of the particles XRD was of limited use and a complete XRD pattern could not be obtained. However, some reflections could be observed, albeit with considerable line broadening and with low intensities. The signal at 23° in 2θ is ascribed to small ZSM-5 particles. Further support was obtained from ^{13}C NMR: although considerable resolution enhancement was necessary to visualize it, a small split-up of the methyl signal of TPA, characteristic for TPA in a ZSM-5 environment, could be observed. Burkett and Davis[28] in their study on ZSM-5 crystal growth reported a strong interaction between TPA and silica species long before any long-range ordering is found. In an early stage of crystal growth, TPA is enclathrated into a silica structure resembling the channel intersections.

The formation of 3 nm particles as shown by TEM is in agreement with the initial stage of the ZSM-5 crystal growth mechanism proposed by Dokter et al.[29] This mechanism starts with the formation of silicate−TPA clusters of ∼3 nm and is followed by an aggregation of these particles. Formation of the 3 nm particles has later been confirmed by Schoeman[30] and De Moor et al.[31] Further densification ultimately leads to the formation of ZSM-5 crystals. In our recrystallization experiments, the crystal growth stops at the 3 nm silicate−TPA cluster stage. Apparently these particles are not sufficiently mobile to allow the aggregation process. This suggests that the ZSM-5 crystallites are growing from the MCM-41 pore wall, following a semi-solid-state transformation, and not from dissolved silicate species. This idea is further supported by the homogeneous distribution of the dark spots observed in TEM.

The recrystallization procedure involves two processes: the formation of 3 nm ZSM-5 crystallites and the amorphization of the MCM-41. The latter is caused by the alkaline conditions required for the partial transformation to ZSM-5. To retard the collapse of the MCM-41 framework Kloetstra et al.[25] applied glycerol as the medium for recrystallization. Because of the low solubility of silica in this medium, the framework was better retained as compared with recrystallization in

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water. Glycerol, however, also inhibited the formation of ZSM-5 crystallites. Filling the MCM-41 pores with a “template” molecule, i.e., hexadecylamine, to support the MCM-41 framework allows the use of water as the reaction medium. In this way, formation of ZSM-5 crystallites is possible and the collapse of the MCM-41 structure is retarded, though not prevented. Table 1, however, clearly shows the benefit of filling the MCM-41 channels with an organic compound on the stability under recrystallization conditions. The exact role of hexadecylamine is unclear, and it is certainly not expected to form rodlike micelles in the MCM-41 channels. An alternative way to maintain a mesoporous structure is by using a parent material with a thicker pore wall. Then, more pore wall silica can be “consumed”, without a collapse of the mesoporous structure.

Calcination of recrystallized MCM-41 samples led to a disappearance of the dark spots in TEM and of the XRD signal at 23° in 2θ, suggesting a collapse of the ZSM-5 crystallites. The infrared spectra (Figure 3), however, indicate that a small amount of ZSM-5 like material is still present after calcination and is still retaining some acidity, albeit too little to detect in a catalytic *n*-heptane hydroconversion experiment. It should be noted that alternative interpretations for such small changes in infrared spectra are possible, and more definite statements can only be made after a treatment has been found to remove organic template material without damaging ZSM-5 crystallinity.

Conclusions

In conclusion, it is possible to partially recrystallize MCM-41 yielding homogeneously distributed 3 nm particles. Both ^{13}C NMR and small signals in XRD suggest that these particles are ZSM-5 crystals. Alkaline conditions are required, but these inevitably also lead to the collapse of the MCM-41 framework. Supporting the MCM-41 framework by means of a long-chain template molecule increases the stability of the mesoporous material. It is possible to maintain a large surface area when the material is subjected to 1 h of hydrothermal treatment, which is sufficient to achieve crystallization of small ZSM-5 crystallites. It is expected that the present method of creating small ZSM-5 particles can be applied not only to MCM-41 but also to other mesoporous alumino silicates.

Acknowledgment. The IOP (Innovation Oriented Research Program) on Catalysis and NWO-CW are acknowledged for financial support.

CM001127Q