

Catalysts from MCM-41: framework modification, pore size engineering, and organic–inorganic hybrid materials

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Abstract

The mesoporous material, MCM-41, is characterized by an extremely high surface area and a one-dimensional system of cylindrical pores with a narrow size distribution in the mesopore range. Adjustment of the pore size over the range 2.0–4.0 nm can be easily achieved by selection of a templating agent. However, the material has little intrinsic catalytic activity. In order to take advantage of the unique opportunities inherent in the defined porosity, catalytic activity has to be introduced. This can be done by inorganic ions, or by affixing organic/metal-organic active groups on the material. We describe catalysts for high temperature gas-phase reactions where functionalization has been achieved by the introduction of framework alumina and platinum. For liquid-phase reactions, we developed solid bases as well as solid Lewis acids based upon modified MCM-41. Through pore size engineering, i.e. matching the pore size to the size of the reacting molecules, the selectivity of the catalyst can be increased, as shown for the preparation of linear alkyl benzenes. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Since their first description in 1992 [1], the mesoporous materials of the M41S family have attracted much interest. They had been developed at Mobil research with the expectation to create zeolite-like materials with bigger pores, which should extend the range of zeolite applications towards bulkier molecules. The driving force behind the development was the need of the refining industry to process heavier crudes as higher-quality deposits become depleted. However, the promises in the field of petrochemical processing have only partially been fulfilled. Two problems were early recognized: low catalytic activity due to low

intrinsic acidity, and insufficient hydrothermal stability. In this paper, we discuss some attempts towards the improvement of these materials for practical applications. Examples for the use of MCM-41 based catalysts for high temperature gas-phase reactions and for liquid-phase processes at lower temperature will be presented.

2. Synthesis and characterization

The M41S materials, of which MCM-41 is the best characterized subgroup, are prepared by a micelle templating method [2]. A silica source is subjected to mild hydrothermal conditions in the presence of a micelle-forming cationic detergent such as a cetyl trimethylammonium (CTMA) salt. An alkaline pH is adjusted with NaOH, NH₃, tetramethylammonium

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hydroxide (TMAOH) or CTMAOH. Various silica sources have been evaluated, such as Ludox (colloidal silica), Aerosil (high surface area fumed silica) or molecular precursors, e.g. sodium silicate or tetraethylorthosilicate (TEOS). Likewise, different sources of alumina were tried: NaAlO_3 ; AlCl_3 ; $\text{Al}(\text{O}-i\text{-Pr})_3$; $\text{Al}(\text{NO}_3)_3$. Many groups have developed their own methods, and have identified critical parameters, e.g. the need to control and adjust the pH during crystallization [3].

For characterization, three methods have to be combined: low-angle X-ray diffraction, electron microscopy, and gas adsorption measurements. The X-ray diffraction pattern of the MCM-41 materials has reflexes only at low-angles: one dominant peak at about 2° (2θ) is followed by four or more lines of decreasing intensity, which can be indexed on a hexagonal lattice. No reflections are observed at higher angles, indicating that the arrangement of the atoms within the walls is essentially amorphous. The structure of the walls resembles that of silica gel, with corner and edge-shared SiO_4 -tetrahedra linked in a random manner. X-ray diffraction is not capable to assess the quality of the material, and samples that give only one reflection have been found to contain considerable fractions of MCM-41 material. Schacht and Schüth [4] simulated diffraction spectra and found that even at a high defect rate, diffraction patterns can still be indexed for a hexagonal lattice, however, if the domain size decreases, the higher order reflections disappear. High resolution electron microscopy gives a qualitative picture of the size of ordered domains, but quantitative evaluation of pore size and wall thickness is difficult due to the focus problem.

Analysis of sorption isotherms is a valuable tool to assess the structure of MCM-41. With N_2 , the adsorption isotherms generally show a steep step at $p/p_0 \approx 0.4$. Materials with pores < 4 nm do not show any hysteresis. However, if the pores are bigger, or if Ar or O_2 are used as adsorbates, a well-developed hysteresis loop is observed [4]. The adsorption isotherms are frequently evaluated using the BJH theory, which is based on the Kelvin equation. Non-local density functional (NLDF) theory may give a better estimate [5] of the true pore size. If results from X-ray diffraction and pore size analysis are combined, one obtains information on the thickness of the walls that separate the individual pores.

3. Al-substitution

Already, the first disclosure on MCM-41 materials mentioned Al-substitution. It is well known that the introduction of Al^{3+} into a tetrahedral site of the SiO_2 framework leads to the trapping of a counter-ion for charge compensation; if the counter-ion is H^+ , Brønsted acidity results. At higher temperature, the material will dehydrate, and Brønsted sites are transformed into Lewis acid sites. However, it had also been observed early on that introduction of Al led to material with reduced long-range order. Many attempts were made to improve the material, particularly by varying the chemistry of the synthesis gel, the composition, the sequence of addition of the ingredients, and the time and temperature of the hydrothermal treatment. Our results on the influence of synthesis temperature on the pore size and wall thickness are shown in Fig. 1 [6]. A higher synthesis temperature leads to a decrease in the pore diameter, together with a moderate increase in the wall thickness. The walls of our material are relatively thick compared to the value reported by other groups; at approximately 2 nm, the thickness corresponds to about five linked SiO_4 -tetrahedra. This may be the reason for a relatively good thermal stability of the material.

For the introduction of alumina into the framework, two strategies were pursued: direct synthesis from gel compositions that contained both silica and alumina, and post-synthesis modification of a purely siliceous

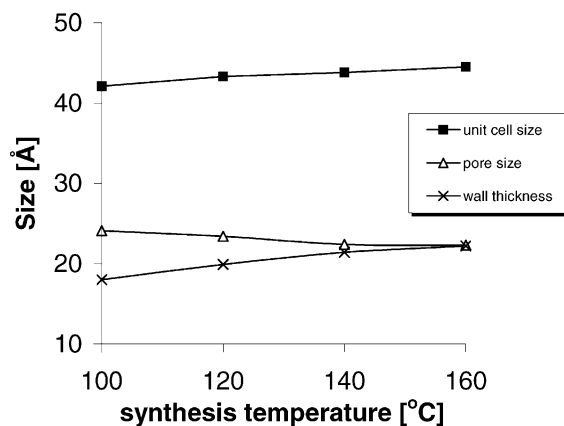


Fig. 1. Influence of the synthesis temperature on pore size and wall thickness of Al-MCM-41 (Si/Al = 10).

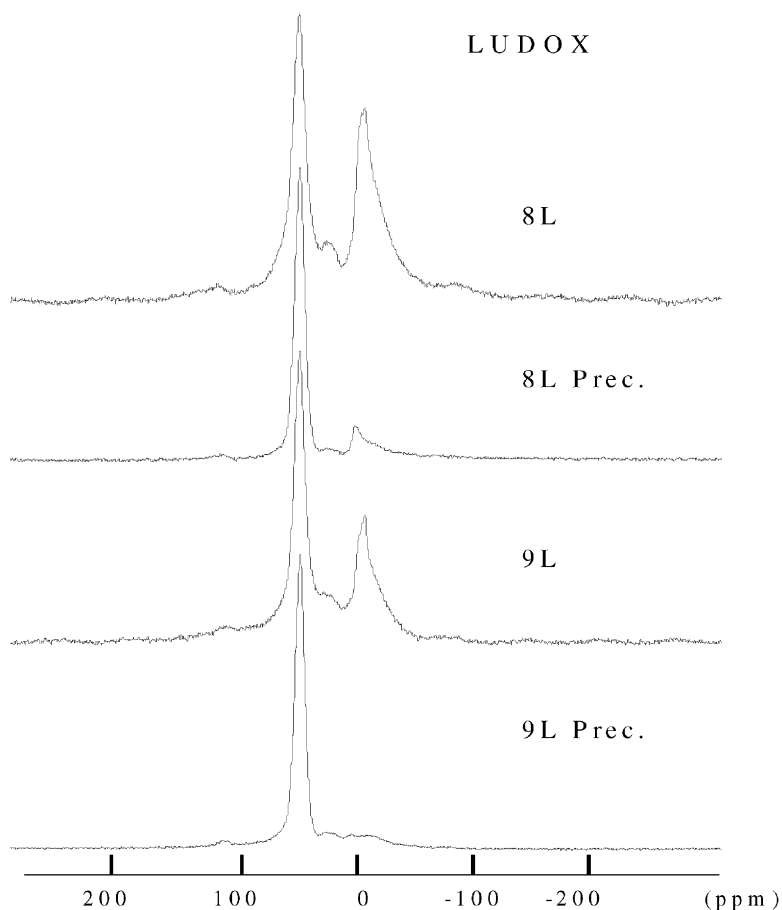


Fig. 2. ^{27}Al MAS-NMR of samples 8L (Si/Al = 5) and 9L (Si/Al = 10) before and after calcination. Samples before calcination are labeled precursor.

material with reagents such as AlCl_3 or $\text{Al}(\text{O}-i\text{Pr})_3$, where $i\text{-Pr} = -\text{CH}(\text{CH}_3)_2$. ^{27}Al MAS-NMR (Fig. 2) proves that the as-synthesized material contains most of the Al-ions in tetrahedral coordination as indicated by the single resonance at +50 ppm relative to a standard of Al^{3+} (aqueous). At the higher Al-content (e.g. sample Al 8L with Si/Al = 5), about 10% of the Al is in an hexagonal environment already in the as-synthesized form. On calcining, some of the alumina leaves the framework and forms particles in the pores. The alumina in these particles is hexagonally coordinated and gives rise to a signal at 0 ppm. Post-synthesis modification leads to a higher incorporation of alumina; we were able to prepare materials with Si/Al = 2 that maintained the MCM-41 structure

and contained a large fraction of the aluminum ions in the framework. However, the acidity of these materials is only moderate, comparable to that of amorphous silica–alumina gels.

Fig. 3 shows the number of Brönsted acid sites, estimated from the relative intensity of the band at 1548 cm^{-2} in the IR spectra of adsorbed pyridine, as a function of the Al-content of the material. For material prepared by direct synthesis and by grafting of alumina from $\text{Al}(\text{O}-i\text{Pr})_3$, we observe an increase in the number of acid sites with increasing Al-content. However, if AlCl_3 is used for post-synthesis modification of siliceous MCM-41, the reverse trend is observed: at low Al-content (17 mol%), the concentration of acid sites is comparable to that of material

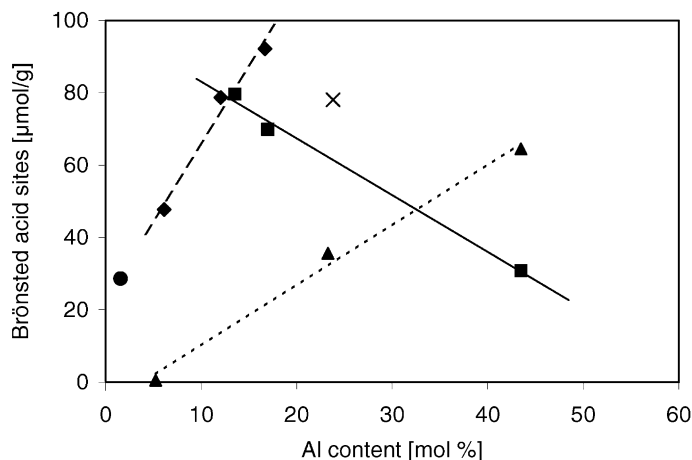


Fig. 3. Concentration of Brønsted acid sites (determined from IR of adsorbed pyridine) as function of the Al-content: direct synthesis (◆); post-synthesis modification with Al(O-*i*Pr)₃ (▲); ion-exchange with Al(NO₃)₃ (●); post-synthesis modification with AlCl₃ (■); post-synthesis modification with NaAlO₂ (×).

with similar Al-content prepared by direct synthesis. However, at higher Al-content, the number of acid sites decreases. XRD and sorption isotherms show that the MCM-41 structure remains unchanged. AlCl₃ reacts vigorously with surface silanol groups. In this way, the entire surface can be terminated with Al-species, which upon calcinations form a continuous alumina-like overlayer. Only very few bridging –OH groups of the type Al–(OH)–Si, which are believed to be responsible for the Brønsted acidity, are present. The less reactive aluminum alkoxide will bind only to one surface silanol group. The bulky nature of the precursor prevents two aluminum centers to approach each other closely. On calcination, the Al-species are incorporated into the wall of the MCM-41. Thus, Al and Si will be well dispersed. However, the acidity at any given alumina content is lower than that of directly synthesized samples.

The catalytic properties of Al-substituted MCM-41 have been tested with cumene cracking in the gas-phase as the test reaction [7]. The cumene cracking reaction correlates well with the concentration of Brønsted acid sites as determined by IR of adsorbed pyridine (Fig. 4). The catalysts show good initial activity; the activity is higher than that of a commercial mordenite. However, the activity decreases rapidly because of coke formation. The activity of the catalyst can be maintained at a high level if it is doped

with Pt at a level of 0.25–1.0%, and if hydrogen is fed together with the cumene. Without hydrogen, the activity of the Pt-containing catalyst is lower than that of the parent material. We attribute this to the fact that on impregnation, the Pt-crystallites deposit preferentially at the acid sites, and therefore, reduce the acidity that is required for the cracking reaction.

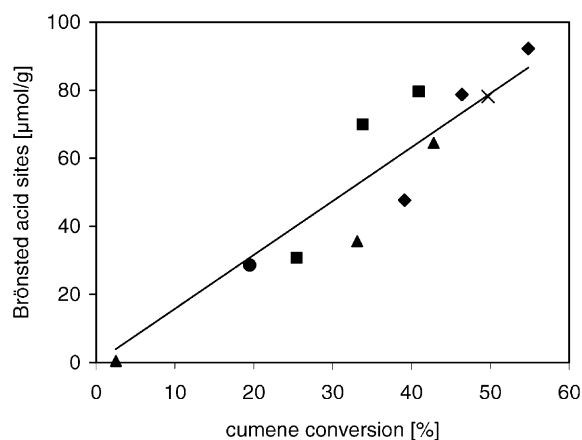


Fig. 4. Correlation between cumene conversion at 300°C and concentration of Brønsted acid sites on Al-MCM-41 prepared by different methods: direct synthesis (◆); post-synthesis modification with Al(O-*i*Pr)₃ (▲); ion-exchange with Al(NO₃)₃ (●); post-synthesis modification with AlCl₃ (■); post-synthesis modification with NaAlO₂ (×).

However, in the presence of hydrogen, a spillover effect [8] comes into action: hydrogen adsorbs and dissociates on the Pt-particles. The H-atoms diffuse to Lewis acid sites where they lose an electron and transform to H^+ . In this way, the acidity is enhanced, and the cracking reaction proceeds smoothly. The active hydrogen reacts also with the coke precursors, and prevents the deposition of a fouling layer that could block access to the active sites.

The thermal stability of the MCM-41 material prepared in this way is good; the material can be used to temperatures of 700°C with little decrease in surface area. Higher heating, however, leads to irreversible collapse of the pore system. Framework substitution of Si by Al leads to a certain decrease in thermal properties. Nevertheless, the thermal stability is still reasonably good. We were able to regenerate cracking catalysts based on Al-MCM-41 for at least six times. The re-generation consisted of slow burn-off of the deposited coke in a stream of air at 550°C . After the first re-generation cycle, the materials recovered only about 50–60% of the initial activity, but there was little further decrease in activity after subsequent re-generations.

4. Lewis acids

Lewis acid catalysts can be obtained by immobilizing AlCl_3 or other Lewis acids on MCM-41. The immobilization reaction, which takes place at moderate temperature is due to a specific interaction between the AlCl_3 -species and surface silanol groups. Grafting of AlCl_3 can be from the gas or the liquid-phase. For this study, AlCl_3 was immobilized on calcined MCM-41 by a liquid-phase reaction. Benzene is the preferred solvent. In order to establish shape selectivity, a series of materials with different pore diameter was prepared [9]. For the templating step, alkyl trimethylammonium salts with alkyl chains of 10–18 carbon atoms in length were used. The test reaction was the Friedel–Crafts alkylation of benzene with linear 1-alkenes. Linear alkyl benzenes (LABs) are important intermediates in the production of bio-degradable detergents. Our catalyst shows high activity already at room temperature, and affords linear alkylbenzenes with very high selectivity and in good yields. The mesoporous support does not interfere with the

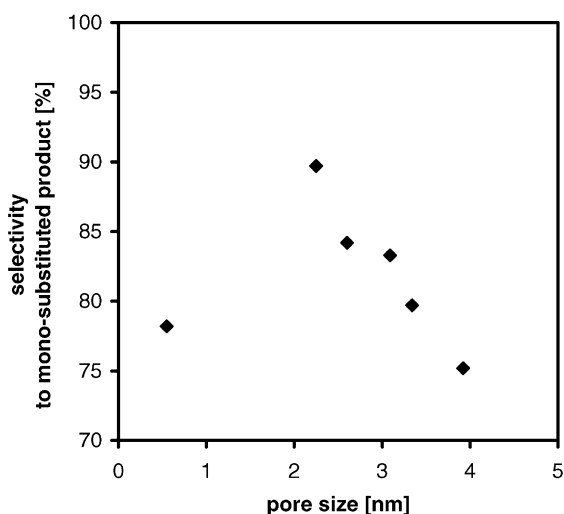


Fig. 5. Selectivity to mono-alkylation products as function of the pore size over $\text{AlCl}_3/\text{MCM-41}$.

activity of the AlCl_3 , but enhances the selectivity to the mono-substituted products. The catalyst directs the benzene ring preferably to the second-position of the alkyl chain as expected if the reaction proceeds via the more stable carbonium ion. Substitution at other positions along the alkyl chain, which results from double bond migration, is a serious problem in the presently used process with an homogeneous HF catalyst. A shape-selective effect could be demonstrated, and the mono-alkylation selectivity is clearly related to the pore size. However, from Fig. 5, one extrapolates the optimum pore size for this reaction to be around 1.0 nm—considerably smaller than the smallest pore size available with our mesoporous materials. At too small a pore size, the selectivity is again poorer as shown for a zeolite (ZSM-5) with micropores of about 0.5 nm. The reaction here takes presumably place at the outer surface, and a shape-selective effect is not to be expected. The strategy of adapting the pore size to the size of the reactants could open the door to the active design of environmentally friendly catalysts that are tailored to the specific application.

The catalyst has been found useful for several other reactions. 2-(2,4-difluorophenyl) propane is a key intermediate in the manufacture of Fluconazole, an anti-fungal agent [10]. It can be obtained by alkylation of 1,3-difluorobenzene with either *i*-propanol,

Table 1

Catalyst	Reaction conditions (°C, h)	Mole ratio ^a (mol mol ⁻¹)	Conversion ^b (%)	Selectivity			
				Mono-		Poly-	
				Product	Others	Di-	Tri-
AlCl ₃	25, 0.5	1:1	100	57.1	Trace	38.7	4.2
AlCl ₃	25, 0.5	2:1	100	78.2	Trace	20.8	1
AlCl ₃	35, 0.5	4:1	100	86.7	0	12.3	1
AlCl ₃ /SiO ₂	35, 0.5	2:1	100	75.5	Trace	20.3	3.2
AlCl ₃ /MCM-41	35, 0.5	2:1	100	75.8	Trace	20.5	3.7
AlCl ₃ /MCM-41 ^c	35, 0.5	2:1	100	75.5	Trace	20.8	3.7

^a Ratio difluorobenzene:isopropanol.

^b Conversion of isopropanol.

^c Second run; after completion of the first reaction, the liquid was decanted off, and fresh difluorobenzene added followed by addition of 2-chloropropane.

propene, or 2-propylchloride. From an environmental point of view, the alcohol would be the preferred reagent. However, the water liberated in the reaction immediately deactivates the catalyst. With propene, too, the activity of the catalyst decreased rapidly, and the catalyst could not be reactivated by simple washing. TGA shows that an organic deposit had formed on the catalyst. Apparently, the propene polymerizes at the surface, poisoning the catalyst and restricting access to the active sites. The 2-chloropropane reacts smoothly at room temperature. The HCl evolved in the reaction is not soluble in the solution and can be easily separated and recovered. The immobilized catalyst promotes the reaction under very mild conditions (35 °C); its activity is equal to that of AlCl₃ in homogeneous phase (Table 1). The catalyst can be easily separated from the products, and can be re-used if the separation is done under exclusion of moisture.

The alkylation of other substituted benzenes was also evaluated. Here, one does not only face the problem of multiple substitution at the aromatic ring, but in addition, ligand rearrangement and ligand exchange are possible side reactions. It was found that a less active Lewis acid, e.g. ZnCl₂ on MCM-41, performed better than the AlCl₃-based system. ZnCl₂ was impregnated on the carrier from methanol solution. This method allows one to vary the loading over a wide range. However, it is observed that the activity reaches a maximum at about 4 mmol g⁻¹ (Fig. 6). This concentration is below that required for mono-layer coverage.

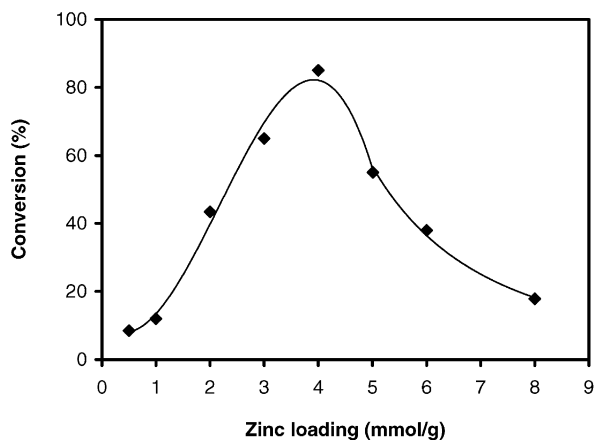


Fig. 6. Dependence of alkylation activity on ZnCl₂ loading for ZnCl₂/MCM-41 catalysts.

Obviously, the interaction of the reacting molecules with both the Lewis acid center and other surface sites is required for the reaction.

5. Organic–inorganic hybrid catalysts

Organic–inorganic hybrid materials can be prepared from MCM-41 by linking active sites to the surface through organic chains. A C₃ (propyl-) spacer was used to connect the active head group to the silica surface. The surface functionalization follows procedures well-established in the analytical field to prepare

chromatographic phases. The preferred linker is triethoxysilylpropylamine [11] or 3-trimethoxysilylpropoxymethyloxirane [12]. Strong base catalysts were obtained by anchoring triazabicyclo[4,4,0]dec-5-ene on the silica framework. These catalysts are useful, e.g. in the synthesis of mono-glycerides from glycidol and a fatty acid. Organic bases with different pK_b are available, so that the basicity can be adjusted for the targeted reaction. Such optimization is shown by comparing the catalyst for the mono-glyceride formation with that for the Knoevenagel condensation of benzaldehyde with heptaldehyde or hexaldehyde to form jasmine aldehyde and other molecules that are useful in the preparation of fragrances and perfumes [13]. However, the tethered bases show considerably less basicity than in the free form [14]. Another problem is the fact that these organic–inorganic hybrids cannot be regenerated by simply burning off all foulants.

6. Conclusion

MCM-41 is a challenge to the researcher in the field of catalysis. The possibility to synthesize materials with a controlled pore size gives a new tool at hand. However, one has to look for reactions where the specific advantages of the uniform porosity will materialize. Strategies to functionalize MCM-41 have led to much improved understanding of the material and its

interactions. But some problems, such as its limited hydrothermal stability, are still waiting for a solution.

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