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RESEARCH NOTE

Pore Size Engineering on MCM-41: Selectivity Tuning of Heterogenized $AlCl_3$ for the Synthesis of Linear Alkyl Benzenes

Xucan Hu, Maw Lin Foo, Gaik Khuan Chuah, and Stephan Jaenicke[1]

Department of Chemistry, National University of Singapore, Kent Ridge, Singapore 119260, Republic of Singapore

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$AlCl_3$ has been successfully immobilized on MCM-41 mesoporous silica of different pore sizes to form a novel shape-selective catalyst for the Friedel–Crafts alkylation of benzene with long-chain olefins (linear 1-olefins with a chain length of 6 to 16 carbon atoms). The selectivity toward the monoalkylated product is strongly influenced by the pore size of the carrier material. This demonstrates the opportunities offered by the micelle-templating method to tailor shape-selective catalysts for reactions with bigger molecules. © **2000 Academic Press**

INTRODUCTION

Responsible care and *sustainable development* have become paradigms of industrial production. It is therefore required that all processes are optimized with respect to energy efficiency, chemicals utilization, and waste minimization (1, 2).

Linear alkyl benzenes (LABs) are an important starting material for the manufacture of detergents. The key step is the alkylation of benzene with linear long-chain olefins, which are derived from the dehydrogenation of the corresponding alkanes. The alkylation usually takes place in the liquid phase with Lewis ($AlCl_3$) or Brønsted acids (HF; H_2SO_4) as catalysts. The corrosive nature and potential environmental hazards in the case of HF as well as difficulties in recycling and disposal of the spent catalyst are drawbacks of these systems. Heterogeneous processes using solid catalysts are therefore highly desirable. The DETAL process (3–5) for the synthesis of LABs is one example of how a more environmentally friendly process that uses a solid acid catalyst can replace conventional technology. Heterogeneous Friedel–Crafts catalysts based on $AlCl_3$ or $ZnCl_2$ immobilized on mesoporous clays and silica gel have been described (6, 7) and demonstrated to be active for selected reactions. $AlCl_3$ immobilized on silica gel is claimed to be reusable and to show an activity comparable to the free molecule.

In 1992, the M41S family of mesoporous silica or aluminosilicate with good long-range order had been described (8–10). The pore size of the material can be controlled through the choice of the micelle-forming detergent molecules (11). Most work has concentrated on the hexagonal structure type, MCM-41, prepared with cetyltrimethylammonium bromide, a 16-carbon chain detergent. Early applications of these materials centered on their use as cracking catalysts. It was hoped that the larger pores would make these materials suitable for treatment of heavier crudes, which could not be used with conventional zeolite catalysts. However, the MCM-41 materials lack the thermal stability and the strongly acidic properties of the zeolite cracking catalysts (12). The material seems therefore more promising for the synthesis of fine chemicals under relatively mild conditions. Here, the large pore size of the material should be advantageous in shape-selective reactions. After suitable chemical modification to introduce catalytic activity, MCM-41 has been successfully used for transformations of bigger molecules (13–16). Various clay minerals have also been used to catalyze reactions between sterically demanding molecules (1, 7, 17). We therefore investigated $AlCl_3$ supported on MCM-41 for its capability to catalyze the Friedel–Crafts alkylation of benzene with linear 1-alkenes.

EXPERIMENTAL

Purely siliceous MCM-41. MCM-41[*n*]'s with different pore sizes were prepared by direct hydrothermal synthesis in an alkali-free medium (18), using the optimized recipe reported by Chen *et al.* (19). The qualifier [*n*] corresponds to the number of C atoms in the main chain of the alkyltrimethylammonium ions used as the micelle-forming agent in the synthesis of the material. The molar composition of the reactants silica, tetraethylammonium hydroxide (TEAOH), alkyltrimethylammonium bromide

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[1] To whom correspondence should be addressed. E-mail: chmsj@nus.edu.sg.

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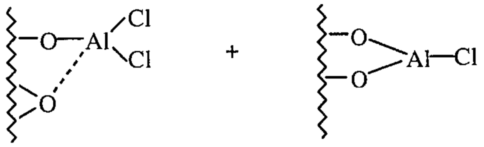
(C_nTAB), and water was 1.00 : 0.21 : 0.28 : 24. A typical synthesis using cetyltrimethylammonium bromide ($C_{16}TAB$) was as follows: 21.2 g of TEAOH solution (20 wt%) and 14 g of $C_{16}TAB$ were added to 60 g of deionized water with stirring and were slightly heated to obtain a clear solution. After an additional 10 min of stirring at room temperature, 8.2 g of fumed silica (DEGUSSA Aerosil 200) was gradually added to the solution. The mixture was first stirred for 2 h at 80°C and then aged for 24 h at room temperature before being placed in a Teflon-lined stainless steel autoclave and subjected to hydrothermal treatment at 150°C. The reaction products were removed after 2 days, filtered, and washed free of bromide. The solid was finally calcined in a muffle furnace at 550°C for 8 h with a heating rate of 1°C/min.

$AlCl_x$-MCM-41[n]. One gram of the respective support was thoroughly dried (300°C for 8 h). It was then allowed to cool to room temperature in an atmosphere of dry nitrogen, and 20 ml of dry benzene was added. Thereafter, 0.2 g (1.5 mmol) of anhydrous $AlCl_3$ was added. The slurry was stirred and heated to reflux for 1 h under dry nitrogen. After filtration and washing with two portions of hot benzene, the catalyst was obtained as a yellow powder.

Activity test. Ten millimoles of the respective alkene was added dropwise at room temperature over a period of 30 min to a vessel containing 1.65 g (20 mmol) of benzene (dried over sodium metal) and 0.1 g of the catalyst. Throughout the reaction, a slow flow of dry nitrogen was passed through the reactor. Thirty minutes after the last drop of alkene was added, a sample was withdrawn with a filter syringe and analyzed by gas chromatography.

RESULTS AND DISCUSSION

Pure silica MCM-41 was prepared using different cationic detergents with chain lengths of $10 \leq n \leq 18$ carbon atoms. The resulting mesoporous material had pore sizes ranging from 22 to 39 Å, depending on the alkyltrimethylammonium salt used (Table 1). It was then reacted with $AlCl_3$ in dry benzene. The evolution of about 1.1 mol of HCl/mol of $AlCl_3$ suggests the formation of $\boxed{S}$–O–$AlCl_2$ species by reaction with surface OH groups of the support, together with some $\boxed{S}$–$(O)_2$–AlCl as shown in Scheme 1. Getty and Drago (6) confirmed with solid state MAS-NMR that tetrahedrally coordinated Al is present on $AlCl_3$-treated silica.



SCHEME 1. Possible structures for the supported $AlCl_x$ species [after Ref. (6)].

X-ray diffraction patterns of MCM-41[*n*] samples are shown in Fig. 1. As *n* increases, the 2θ value of the main peak (100 reflex) shifts to a lower angle, corresponding to a larger lattice parameter. An incremental increase by two C_2H_4–units leads to an increase in the lattice constant by ~4 Å, in good agreement with previous reports (9, 10). With increasing chain length, the (100) reflex becomes narrower and more intense, and additional peaks that can be indexed as (110), (200), and (210) for a hexagonal lattice are observed. Apparently, the long-range order of the material increases with an increase in the chain length of the micelle-forming detergent. However, this relation holds no longer for C_{18}. The pore size distribution was calculated from the desorption branch of the N_2-adsorption isotherm using the Barrett–Joyner–Halenda formula (Fig. 2). All samples have pore sizes narrowly distributed about a mean pore diameter, which increased with chain length. MCM-41[16] has the best long-range order according to its X-ray diffraction pattern and also the narrowest pore size distribution. The structural order is probably related to the solubility of the amphiphilic molecules in the aqueous phase, which

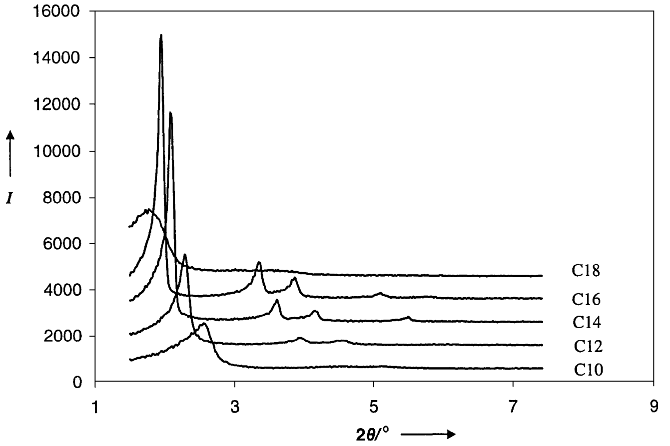


FIG. 1. X-ray diffraction patterns for MCM-41 prepared with different detergent molecules of the type $C_nH_{2n+1}(CH_3)_3N^+Br^-$.

TABLE 1

Textural and Microstructural Properties of the MCM-41 Materials

Sample	$d_{100}{}^a$ (Å)	Rel. intens.[a] (%)	D^b (Å)	SA^c ($m^2 g^{-1}$)
MCM-41[10]	34.5	17.8	22.5	1067
MCM-41[12]	38.3	35.1	26.0	1063
MCM-41[14]	42.0	79.9	30.9	962
MCM-41[16]	44.7	100	33.4	1140
MCM-41[18]	50.0	25.8	39.2	812

[a] From X-ray diffraction.

[b] Pore diameter, from N_2 sorption measurements.

[c] BET surface area.

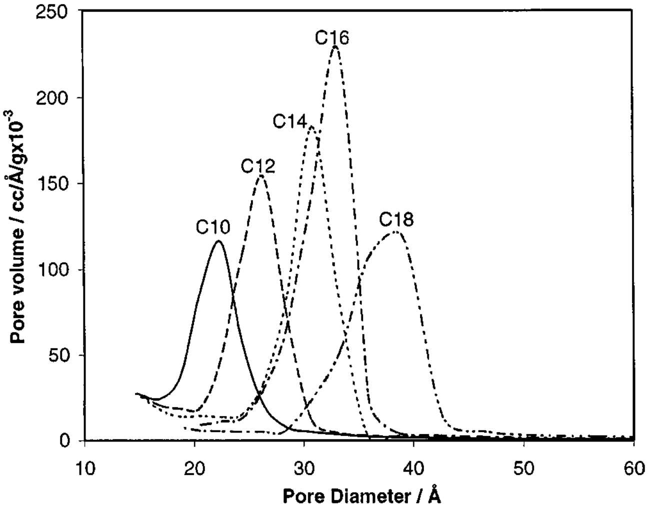


FIG. 2. Pore size distribution (calculated from the desorption branch of the N_2-sorption isotherm) for MCM-41 prepared with different detergent molecules of the type $C_nH_{2n+1}(CH_3)_3N^+Br^-$.

increases with decreasing chain length, so that less stable micelles form in the case of the shorter chains. With very long-chain detergent molecules, structural flexibility increases, leading to deviations from a rodlike shape.

At a loading of 1.5 mmol/g, $AlCl_3$ was completely immobilized on the surface of the MCM-41 after 1 h refluxing in benzene. The complete uptake of $AlCl_3$ was confirmed by analysis of the supernant liquid: analysis for Al in the filtered solution showed only traces in the ppm range. To test whether $AlCl_3$ leaches from the support, we kept the catalyst for 3 h in boiling benzene. The solid catalyst was removed, and 1-octene was added to the filtrate. The absence of any alkylation reaction proves that no $AlCl_3$ leached form the support. Analysis (ICP-AES) of the extract for aluminium was also negative, whereas the analysis of the catalyst after the support was digested yielded a value of 1.46 mmol/g in excellent agreement with the designed loading. The MCM-41 structure was unaffected by the reaction with $AlCl_3$. This was confirmed by XRD and sorption measurements on the spent catalysts.

Alkylation experiments with different 1-alkenes are summarized in Table 2. Grafted $AlCl_3$ catalysts show high activity for the alkylation of benzene, comparable to that of $AlCl_3$ itself. The reaction is normally complete as soon as the alkene has been added dropwise over a period of 30 min (benzene : alkene = 2 : 1. Because of the mild reaction conditions, no skeletal rearrangements take place in the alkene chain nor were any oligomers of the olefin detected. The desired linear alkyls are obtained in high yield. The supported $AlCl_3$ catalyst is significantly more selective toward monoalkylbenzene than $AlCl_3$ in a homogeneous reaction. Besides the desired monosubstituted product, only a small amount of disubstituted products forms with the MCM-41-supported $AlCl_3$, whereas substantial amounts of di- and even trisubstituted benzenes form with free $AlCl_3$. The selectivity toward the monoalkylated product increases with increasing chain length of the alkene and reaches 99% for the alkylation with 1-hexadecene. The increased selectivity toward the monoalkylated product over the supported catalyst may be attributed to the shape-selective effect of the porous support.

Since the selectivity to the monosubstituted product increased with the length of the olefin molecule for a given MCM-41[*n*], it is expected that it should be possible to optimize the selectivity for a given alkene by adjusting the pore size. Using the alkylation of benzene with 1-octene as the test reaction, we determined the selectivity toward monoalkylation products using supported $AlCl_3$ on MCM-41[*n*] with $n = 10, 12, 14, 16$, and 18. The shorter chain 1-octene was selected because of its poor selectivity in the earlier study with MCM-41[16], which makes it experimentally easier to verify selectivity changes as a consequence of changed pore radius. The improvement in selectivity toward the monoalkylation product with decreasing pore size in the support is clearly apparent (Table 3).

However, if the pore size becomes even smaller, the activity and selectivity decrease again. This is seen from the data for a catalyst prepared from a microporous zeolite, ZSM-5. Under identical reaction conditions, the conversion of 1-octene over this material was only 5%, and the selectivity of 78.2% is significantly lower than the 89.7% achieved over MCM-41[10]. ZSM-5 is classified as a medium-pore

TABLE 2

Selectivities for the Alkylation of Benzene with 1-Alkenes in the Homogeneously (Free $AlCl_3$) and Heterogeneously ($AlCl_3$ Supported on MCM-41) Catalyzed Reaction

		Selectivity toward alkylbenzenes[b]		
Alkene	Catalyst[a]	mono[c]	di	tri
1-hexene	homog.	58.6	31.1	10.3
1-hexene	heterog.	79.9	20.1	—
1-octene	homog.	66.0	24.3	9.7
1-octene	heterog.	79.7	20.3	—
1-decene	homog.	68.5	22.5	9.0
1-decene	heterog.	91.1	8.9	—
1-dodecene	homog.	72.5	27.5	[d]
1-dodecene	heterog.	96.2	3.8	—
1-tetradecene	homog.	70.1	29.9	[d]
1-tetradecene	heterog.	98.5	1.5	—
1-hexadecene	homog.	77.5	22.5	[d]
1-hexadecene	heterog.	>99.0	<1.0	—

[a] homog.: homogeneous catalysis with $AlCl_3$ (0.15 mmol); heterog.: over $AlCl_x$ MCM-41[16] (0.1 g of catalyst containing 0.15 mmol of $AlCl_x$).
[b] Determined by GC of the product mixture.
[c] Exclusively linear alkyl benzenes.
[d] Nonvolatile product, not analyzed by GC.

TABLE 3

Selectivity and Product Distribution for the Reaction of 1-Octene with Benzene Catalyzed by $AlCl_3$ Supported on MCM-41 with Different Pore Sizes

Catalyst	1-Octene conversion (%)	Monoalkylated benzene	Dialkylated benzene
$AlCl_x$/MCM-41[18]	100	75.2	24.8
$AlCl_x$/MCM-41[16]	100	79.7	20.3
$AlCl_x$/MCM-41[14]	100	83.3	16.7
$AlCl_x$/MCM-41[12]	100	84.2	15.8
$AlCl_x$/MCM-41[10]	100	89.7	11.3
$AlCl_x$/ZSM-5	5	78.2	21.8

zeolite; here, the access to internal active sites is restricted, and only the outer surface of the particles is available to catalyze the reaction. This explains the low activity and the much lower selectivity.

The supported $AlCl_3$ catalysts can be re-used as long as they are not exposed to moisture. Catalysts recovered by filtration under a nitrogen atmosphere showed unchanged activity for at least three cycles. Thus, the use of a MCM-41 material with a suitably adjusted pore size as support for $AlCl_3$ can lead to optimized catalysts for the preparation of monoalkylbenzenes. The simplicity in preparation and ease of recovery combined with high selectivity and activity let these catalysts appear to be very promising candidates to replace the liquid catalysts used today.

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REFERENCES

1. Clark, J. H., *Green Chem.* **1**, 1 (1999).
2. Sheldon, R. A., and Downing, R. S., *Appl. Catal. A: Gen.* **189**, 163 (1999).
3. de Almeida, J. L. G., Dufaux, M., Ben Taarit, Y., and Naccache, C., *J. Am. Oil. Chem. Soc.* **71**, 675 (1994).
4. Imai, T., Kocal, J. A., and Vora, B. V., *Stud. Surf. Sci. Catal.* **92**, 339 (1995).
5. Tanabe, K., and Hölderich, W. A., *Appl. Catal. A: Gen.* **181**, 399 (1999).
6. Getty, E. E., and Drago, R. S., *Inorg. Chem.* **29**, 1186 (1990).
7. Clark, J. H., Butterworth, A. J., Tavener, S. T., Teasdale, A. J., Barlow, S. J., Bastock, T. W., and Martin, K., *J. Chem. Tech. Biotechnol.* **68**, 367 (1997).
8. Yanigasawa, T., Shimizu, T., Kuroda, K., and Kato, C., *Bull. Chem. Soc. Jpn.* **63**, 988 (1990).
9. Kresge, C. T., Leonowicz, M. E., Roth, W. J., Vartuli, J. C., and Beck, J. S., *Nature* **359**, 710 (1992).
10. Beck, J. S., Vartuli, J. C., Roth, W. J., Leonowicz, M. E., Kresge, C. T., Schmitt, K. D., Chu, C. T.-W., Olson, D. H., Sheppard, E. W., McCullen, S. B., Higgins, J. B., and Schlenker, J. L., *J. Am. Chem. Soc.* **114**, 10834 (1992).
11. Behrens, P., *Adv. Mater.* **5**, 127 (1993).
12. Sayari, A., *Chem. Mater.* **8**, 1840 (1996).
13. Armengol, E., Corma, A., Garcia, H., and Primo, J., *Eur. J. Org. Chem.* **8**, 1915 (1999).
14. Climent, M. J., Corma, A., Iborra, S., Miquel, S., Primo, J., and Rey, F., *J. Catal.* **183**, 76 (1999), doi:10.1006/jcat.1998.2382.
15. van der Heijden, A. M., van Rantwijk, F., and van Bekkum, H., *J. Carbohydr. Chem.* **18**, 131 (1999).
16. Lin, X., Chuah, G. K., and Jaenicke, S., *J. Mol. Catal. A: Chem.* **150**, 287 (1999).
17. Smith, K., Pollaud, G. M., and Matthews, I., *Green Chem.* **1**, 76 (1999).
18. Cheng, C. F., Park, D. H., and Klinowski, J., *J. Chem. Soc. Faraday Trans.* **93**, 193 (1997).
19. Chen, L. Y., Ping, Z., Chuah, G. K., Jaenicke, S., and Simon, G., *Microporous Mesoporous Mater.* **27**, 231 (1999).