Double organic modification by 3-chloropropyl and methyl groups on pure silica MCM-41 and Ti-MCM-41: efficient catalyst for epoxidation of cyclododecene

Asim Bhaumik [a,*] and Takashi Tatsumi [b]

[a] *Toyota Central R&D Lab. Inc., Nagakute, Aichi 480-1192, Japan*
E-mail: e1165@joa.tytlabs.co.jp
[b] *Division of Materials Science and Chemical Engineering, Yokohama National University, Yokohama 240-8501, Japan*

Received 25 January 2000; accepted 11 April 2000

Simultaneous surface modification by 3-chloropropyl and methyl groups on the same Si atoms resulted in hydrophobic and highly ordered mesoporous silica with a very high surface area. ^{13}C and ^{29}Si MAS NMR spectra indicate homogeneous grafting of chloropropyl and methyl groups in the silica matrix and this organically modified Ti-MCM-41 shows outstanding catalytic performance in the epoxidation of cyclododecene using *tert*-butyl hydroperoxide as oxidant.

Keywords: Ti-MCM-41, hydrophobicity, 3-chloropropyl, methyl, epoxidation

1. Introduction

Since the discovery of ordered mesoporous silica [1,2] and its titanium silicate analog Ti-MCM-41/Ti-HMS [3], there have been continuous efforts to improve their stability and catalytic performance. Titanium-containing mesoporous silica has been of great interest from academic and industrial viewpoints because of its potential to oxidize very bulky organic substrates which cannot be oxidized efficiently over microporous TS-1 [4] under liquid-phase reaction conditions. Surface modification by incorporating various organic functionalities [5–7] and silylation [8] have been proved to induce hydrophobicity together with stability in these mesoporous materials and thus the catalytic activity of Ti-MCM-41 improved considerably in the liquid-phase oxidation reactions in the presence of water. Ti content of these mesoporous titanium-containing silicas [9] can be increased by a sol–gel method. Very recently we have shown that 3-chloropropyl modification of Ti-MCM-41 [10] can result in highly ordered and hydrophobic mesoporous materials, which show drastic enhancement of catalytic activity for the epoxidation of alkenes. The present communication reports for the first time the incorporation of two organic groups, 3-chloropropyl and methyl substituents, on the same Si atoms of the mesoporous silica network. These Cl-propyl-methyl-Ti-MCM-41 materials have very high surface area ($>1400\ m^2\ g^{-1}$), being hydrophobic and efficient catalysts for the oxidation of a bulky organic substrate, cyclododecene.

* To whom correspondence should be addressed.

2. Experimental

Organically modified MCM-41 materials were synthesized using a mixture of 3-chloropropyldimethoxymethylsilane (Shin-etsu Chemicals) and tetraethyl orthosilicate (TEOS, TCI) as Si sources. Cetyltrimethylammonium bromide (CTMABr, TCI) was used as a template and tetramethylammonium hydroxide (25% aqueous TMAOH, Aldrich) was used to provide alkalinity of the medium. Tetrabutyl orthotitanate (TBOT, Aldrich) was used as Ti source. Isopropyl alcohol (IPA, Wako) was used to homogenize the organic and aqueous phases during the gel preparation. In this synthesis method silicon alkoxides were first hydrolyzed with the alkaline template solution followed by the addition of titanium alkoxide and subsequent dilution, alcohol removal, aging and hydrothermal treatment at an elevated temperature. In a typical synthesis of Cl-propyl-methyl-Ti-MCM-41 18.2 g of CTMABr was dissolved in a mixture of 50 g H_2O and 45 g IPA. To it solution A, consisting of 7.3 g 3-chloropropyldimethoxy methylsilane (ClPDMMS) and 33.5 g TEOS, and solution B, consisting of 36.4 g TMAOH and 18 g H_2O, were added together at once and the mixture was stirred vigorously at room temperature for 1 h. After 1 h, 2.3 g TBOT dissolved in 10 g IPA was added dropwise to the resultant clear solution and the stirring was continued for 1 h. Then the solution was heated at 353 K for 1 h to remove the added alcohols and those produced during the hydrolysis of the alkoxides (otherwise the presence of alcohols promotes the dissolution of micelles). Finally, the volume of the solution was adjusted with water. This gel was aged overnight (24 h) with continuous stirring. Finally, the pH of the resultant gel

Table 1
Physico-chemical properties of organically modified MCM-41.

Sample No.	TEOS/ CPDMMS	Si/Ti mole ratio		BET surface area[b] ($m^2\ g^{-1}$)
		Gel	Product[a]	
1	4	$\propto$	–	1079
2	3	$\propto$	–	1134
3	4	30	34.2	1436
4	3	30	29.7	1483

[a] As measured by ICP.
[b] Measured from N_2 adsorption isotherm at $P/P_0 = 0$–0.3.

was measured (varying from 11.8 to 11.9) and the gel was heated in a closed polypropylene bottle at an elevated temperature (typically 353 K) under static conditions. The molar ratio of the various constituents in the synthesis mixture was: $4TEOS : ClPDMMS : 1.25C_{16}TMABr : 2.5TMA\text{-}OH : 0.167TBOT : 300H_2O$.

Hydrothermal treatment was carried out at 353 K for 2 to 4 days. In the case of organically modified pure silica MCM-41, an identical procedure was followed except the addition of a Ti source. After the hydrothermal treatment the products were filtered, washed thoroughly with water and dried to produce the as-synthesized form of the organically modified Ti-MCM-41. Surfactant was removed from this as-synthesized form by repeated treatment with HCl/EtOH to give the almost template-free organically modified pure silica MCM-41 and Ti-MCM-41. The resultant materials were characterized by XRD, FT-IR, UV-Vis, ^{13}C and ^{29}Si MAS NMR spectroscopies and N_2 and H_2O adsorption measurements. Chemical analysis was carried out by ICP.

In a typical example for the oxidation reaction, to a solution of cyclododecene (1.66 g) in dry acetone (8 g), *tert*-butyl hydroperoxide (TBHP, 80% in di-*tert*-butyl peroxide, 1.2 g, substrate : TBHP = 1 : 1 mol/mol) was added, followed by the catalyst addition (sample 3, 0.33 g). The resulting mixture was refluxed at 333 K with vigorous stirring for 6 h. After the reaction, the catalyst was filtered and the reaction products were analyzed by a capillary GC (Shimadzu R 14A) using a FID detector. Identification of the products was performed by the known standards and GC-MS (HP 6890).

3. Results and discussion

3.1. Characterization

In figure 1 XRD patterns of the acid-extracted form of pure silica Cl-propyl-methyl-MCM-41 (a) and Cl-propyl-methyl-Ti-MCM-41 (b) are shown. As shown in the figure, 100, 110, 200 and 211 diffractions [1,2] are noticeable, indicating hexagonal ordering. Apart from the usual bands of mesoporous silica, the FT-IR spectrum (not shown) of sample b shows a strong band at 960 cm^{-1}, implying the incorporation of Ti. UV-Vis spectra (not shown) of Cl-propyl-methyl-Ti-MCM-41 also show a strong absorption band in the 220–240 nm region, indicating the presence of isolated tetrahedral Ti, and no absorption above the 300 nm band responsible for octahedral or occluded Ti [11].

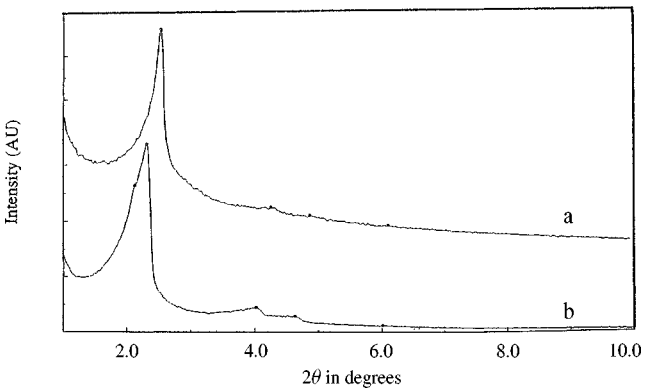

Figure 1. XRD patterns of pure silica Cl-propyl-methyl-MCM-41 (sample 1, pattern a) and Cl-propyl-methyl-Ti-MCM-41 (sample 3, pattern b) after surfactant removal.

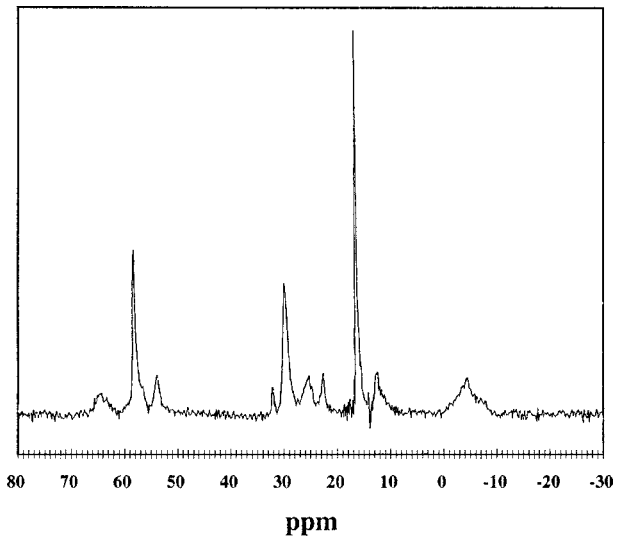

Figure 2. ^{13}C MAS NMR spectrum of Cl-propyl-methyl-Ti-MCM-41 (sample 3, after first HCl/EtOH extraction).

^{13}C MAS NMR spectra of Cl-propyl-methyl-Ti-MCM-41 (sample 3 taken as representative after first HCl/EtOH extraction) show peaks at -4.5, 16.5, 29.8 and 58.0 ppm corresponding to methyl and α, β and γ carbon atoms of $–C(\alpha)H_2C(\beta)H_2C(\gamma)H_2Cl$, respectively, as shown in figure 2. The peaks at 13, 23, 27, 32, 54 and 65 ppm are ascribed to residual surfactant molecules [5]. In figure 3 the ^{29}Si MAS NMR spectrum of Cl-propyl-methyl-Ti-MCM-41 (sample 4) is shown. Apart from Q^3 and Q^4 peaks, the presence of the D^2 peak [12–14] at -17.6 ppm (with respect to TMS) indicates the incorporation of chloropropyl and methyl moieties on the same silicon atom in these mesoporous materials. Absence of any further shifted signals (for MeRSi(OSi–)OH [13] observed chemical shift $\delta \approx -12$ ppm) indicates absence of silanol on this Si and the $Cl–(CH_2)_3(CH_3)Si(O–)_2$ moieties are grafted at the middle of the two Q^3 Si units. Mild signals at -64.5 and

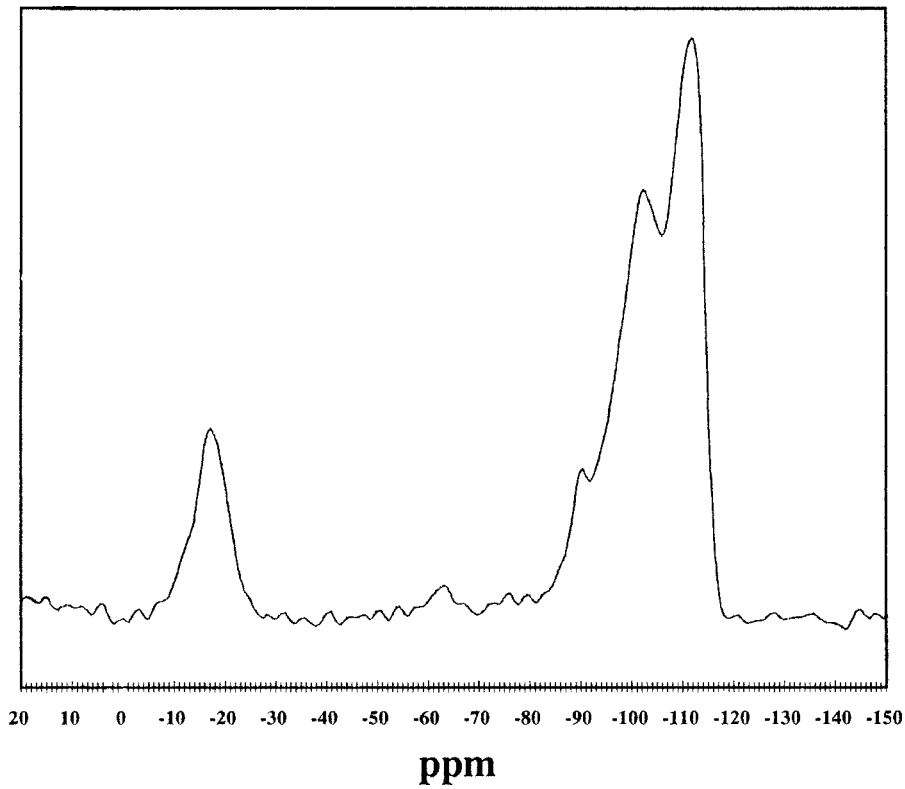

Figure 3. ^{29}Si MAS NMR spectrum of Cl-propyl-methyl-Ti-MCM-41 (sample 4) recorded on a Bruker MSL 300. Chemical shift δ measured with respect to TMS.

−58.0 ppm could be ascribed to T^3, Me–Si(OSi)$_3$ and T^2, Me–Si(OSi)$_2$OH, which might be formed through the cleavage of 3-chloropropyl–Si bonds probably during hydrothermal synthesis.

The N_2 adsorption–desorption isotherm of the sample 3 (taken as a representative in figure 4) is of type IV in nature and indicates the presence of mesopores. Relatively small pore diameter (pore size distribution measured by the BJH method is shown in the inset of figure 4), mesopore volume of 0.767 $cm^3\,g^{-1}$ and thicker pore wall compared to Cl-propyl-Ti-MCM-41 [10] suggests that 3-chloropropyl and methyl groups line up at the pore wall. BET surface areas of Ti-containing samples are especially high and are 1436 (sample 3) and 1483 $m^2\,g^{-1}$ (sample 4), respectively. H_2O adsorption capacity of Cl-propyl-methyl-Ti-MCM-41 was 0.67 molecules nm^{-2} compared to 2.73 and 1.16 molecules nm^{-2} for organic-free Ti-MCM-41 and Cl-propyl-Ti-MCM-41 (TEOS/organosilane = 4), respectively, indicating high hydrophobicity of Cl-propyl-Ti-MCM-41. The Si/Ti molar ratios of Cl-propyl-methyl-Ti-MCM-41 after surfactant removal were 34.2 and 29.7 for samples 3 and 4, respectively, which are considerably lower than the Ti-MCM-41 without any organic modification [3].

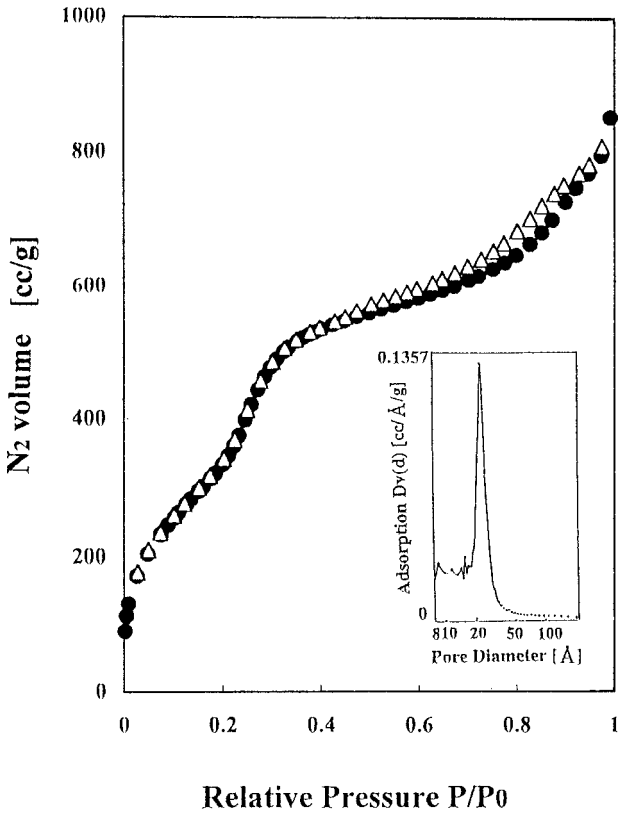

Figure 4. N_2 adsorption–desorption isotherm of Cl-propyl-methyl-Ti-MCM-41 (sample 3) recorded on Autosorb-1, Quantachrome: adsorption points (•) and those of desorption (△).

3.2. Catalysis

Catalytic activity of this Cl-propyl-methyl-Ti-MCM-41 was measured in the epoxidation of cyclododecene using TBHP as oxidant. For sample 3, 52.4 mol% (TON =

767.4 mole per mole of Ti h^{-1}) of cyclododecene is converted to the corresponding epoxide (*cis*:*trans* $\approx$ 1:3) after 6 h reaction time at 333 K using acetone as solvent. Increase in organic loading in sample 4 resulted in 53.5 mol% (TON = 736.2 mole per mole of Ti h^{-1}) conversion of cyclododecene under identical conditions, indicating enhanced hydrophobicity and increased Ti content of mesoporous silica are responsible for efficient oxidation. However, little decrease in TON can be attributed to the increase in solid density of the catalyst with the increase in organic loading from sample 3 to 4. It is pertinent to mention that Ti-MCM-41 without organic modification and merely 3-chloropropyl-modified Ti-MCM-41 gives only 3.4% (Si/Ti = 61.0, TON = 71.7 mole per mole of Ti h^{-1}) and 18.2% (Si/Ti = 38.8, TON = 275.6 mole per mole of Ti h^{-1}) conversions of cyclododecene under identical conditions, indicating catalytic efficiency is drastically improved by simultaneous modification by 3-chloropropyl and methyl groups.

Acknowledgement

AB wishes to thank Dr. S. Inagaki for helpful discussions and Toyota CRDL, Inc. for allowing publication of this work.

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