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Probing the active sites of aluminated mesoporous molecular sieve MCM-41 by secondary synthesis in the conversion of cyclohexanol

Salasiah Endud, *University Technology Malaysia*

Hadi Nur, *University Technology Malaysia*

Halimatun Hamdan, *University Technology Malaysia*

Probing the active sites of aluminated mesoporous molecular sieve MCM-41 by secondary synthesis in the conversion of cyclohexanol

Salasiah Endud, Hadi Nur and Halimatun Hamdan

Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia
KB 791, 80990 Johor Bahru, Malaysia

The active sites of H-Al-MCM-41 aluminated by secondary synthesis have been probed by the conversion of cyclohexanol and compared with those of H-Al-MCM-41 prepared by direct synthesis, purely siliceous MCM-41, $\text{AlPO}_4\text{-5}$ and H-ZSM-5. Conversion of cyclohexanol produces cyclohexene, cyclohexanone and 3-methylpentane in the presence of Brönsted, basic and Lewis acid sites respectively. Whereas cyclohexanol is converted to polyaromatic compounds in the presence of very strong acid sites as those found in H-ZSM-5. The formation of cyclohexene as the only product of conversion over H-Al-MCM-41 prepared by direct and secondary synthesis indicates the presence of Brönsted acid sites in both systems, which is not observed in the purely siliceous MCM-41 and $\text{AlPO}_4\text{-5}$ samples. The larger amount of cyclohexene formed over H-Al-MCM-41 by secondary synthesis suggests that there is a higher degree of Brönsted acidity in this system than that of H-Al-MCM-41 by direct synthesis. However, the strength of acidity in H-Al-MCM-41 by secondary synthesis is weaker than that of H-ZSM-5. In addition, the results of this reaction, supported by IR spectroscopy study, do not indicate the presence of Lewis acidity in H-Al-MCM-41 prepared by secondary synthesis.

1. INTRODUCTION

Mesoporous molecular sieve MCM-41 attracts much attention because of its unique properties [1,2] and potential as catalysts in reactions involving large organic molecules [3-6]. Purely siliceous MCM-41 does not show significant catalytic activity as it lacks the ion exchange capability due to its electrically neutral framework. However, the isomorphous substitution of the framework Si by aluminium or other trivalent cations offers a mechanism for generating acidity and for modifying the chemical properties of the purely siliceous MCM-41. The incorporation of aluminium into the framework of MCM-41 is particularly important as it gives rise to Brönsted acid sites. It has been reported that

calcined Al-MCM-41 has acid properties similar to those of amorphous silica [7]. However, it has not been firmly established whether the acidity is due to the Brönsted acidic protons which are ion-exchanged in order to balance the necessary number of framework negative charges introduced by the incorporation of aluminium, or attributed to the formation of extraframework aluminium which are associated with the presence of Lewis acidity.

In a recent communication [8], we have succeeded in preparing mesoporous aluminosilicate MCM-41 materials by isomorphous substitution via secondary synthesis. The success of preparing Al-MCM-41 by such a technique offers great advantages in tailoring Al-MCM-41 as catalyst with variable acidic properties for specific reactions. Therefore, it is of interest to identify and understand the nature of active sites present in these materials; whether it is acidic, basic or cationic. In previous acidity studies [9,10], pyridine or ammonia adsorption is most often used to determine the concentration and strength of the Brönsted and Lewis acid sites in zeolitic materials. In our study presented here, the cyclohexanol conversion has been chosen as the probe reaction.

In the conversion of cyclohexanol, two reactions can occur: the dehydration into cyclohexene and water and the dehydrogenation leading to cyclohexanone. The dehydration of cyclohexanol occurs due to the presence of Brönsted acid sites, whereas the dehydrogenation of cyclohexanol takes place in the presence of surface basic sites (Figure 1). Therefore besides identifying the nature of active sites, it is possible to estimate the relative acidity of H-Al-MCM-41 prepared by both direct and secondary synthesis based on this diagnostic test reaction. In addition, the catalytic behaviour of these materials in cyclohexanol conversion is compared with other catalysts: $\text{AlPO}_4\text{-5}$ that possesses some weak basic sites and H-ZSM-5, which is strongly acidic and has been shown to be an excellent catalyst for the conversion of alcohol to gasoline [11,12].

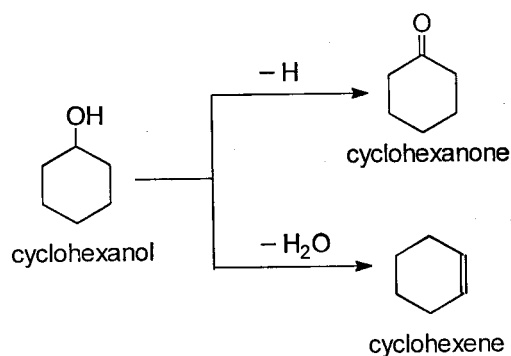


Figure 1. Schematic representation of the dehydrogenation of cyclohexanol to cyclohexene and the dehydration of cyclohexanol to cyclohexene.

2. EXPERIMENTAL

Sample of H-ZSM-5 was supplied by N. E. Chemcat, Japan and $\text{AlPO}_4\text{-5}$ molecular sieve was synthesized as described elsewhere [13]. The synthesis, treatment and characterization of purely siliceous MCM-41 and aluminosilicate MCM-41 ($\text{Si}/\text{Al} = 2.8, 3.6$ and 3.8) is made according to the procedure described previously [8]. Calcined Al-MCM-41 sample ($\text{Si}/\text{Al} = 3.6$), is used for the protonic ion exchange procedure performed with $1\text{ M NH}_4\text{NO}_3$ solution at 90°C (with liquid-to-solid ratio of 50 ml/g). H-Al-MCM-41 was obtained by deammoniating the ammonium form of Al-MCM-41 at 550°C in air. Sample of Al-MCM-41 by direct synthesis was prepared according to a literature method [2]. The cyclohexanol conversion reaction was performed over 0.5 g of H-Al-MCM-41, H-ZSM-5 (Si/Al ratio ≈ 38), $\text{AlPO}_4\text{-5}$ and purely siliceous MCM-41 using a continuous flow, fixed bed microreactor at 400°C and atmospheric pressure, with a feed rate of 0.05 ml/min . Cyclohexanol was a BDH product with 99% purity and used as received. Product distribution was determined by a Shimadzu GC-14B gas chromatograph equipped with an FID detector and a 50 m fused silica capillary column with helium as carrier gas. The products were identified on the basis of their mass spectra using Hewlett Packard 5890 Series II gas chromatograph and Hewlett Packard 5982A mass spectrometer. For IR studies on MCM-41 materials, thin self supporting wafers of about 10 mg/cm^2 were prepared and activated in situ in the IR cell fitted with CaF_2 windows at 400°C in vacuum for 16 h . The infrared spectra were recorded in the range of $4000\text{--}1300\text{ cm}^{-1}$ using a Perkin Elmer 1600 spectrometer with a resolution of 2 cm^{-1} .

3. RESULTS AND DISCUSSION

The infrared spectra of hydroxyl groups of the purely siliceous MCM-41 and secondary aluminated MCM-41 are shown in Figure 2(i) in the region of stretching vibrations of O-H bands. A very intense band at 3744 cm^{-1} was observed in the IR spectrum of the parent MCM-41 corresponding to terminal silanol groups. These groups have been previously observed on amorphous silica and microporous zeolites and reported to reveal a very weak acid character [14]. The IR results clearly show that the MCM-41 samples have very large amount of silanol groups, the largest population being in the purely siliceous MCM-41.

It is seen that incorporation of aluminium in the purely siliceous MCM-41 samples leads to a decrease in the intensity of the IR band assigned to terminal Si-OH hydroxyls (3744 cm^{-1}) which is shifted to 3742 cm^{-1} . This is presumably connected with structural redistributions resulting from the insertion of Al species into the mesoporous structure during alumination. After adsorption of pyridine at room temperature, the OH stretch band at 3742 cm^{-1} shows a loss in intensity and broadens as seen in Figure 2(ii), due to the interaction with the pyridine molecules, indicating the presence of weak acid sites.

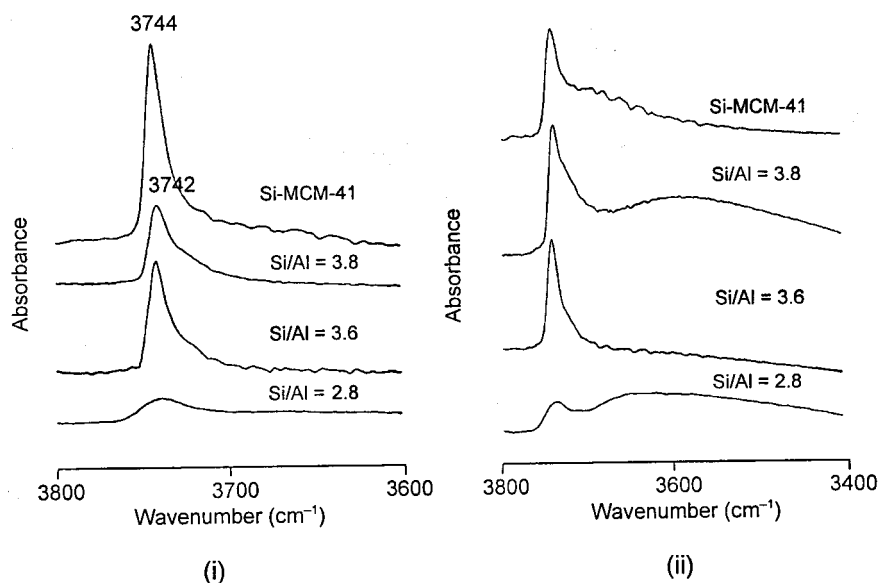


Figure 2. FTIR spectra of the hydroxy groups of (i) activated MCM-41 samples and (ii) after pyridine adsorption.

Figure 3(i) depicts the spectrum of pyridine chemisorbed on the purely siliceous MCM-41, showing no Brønsted acidity and a weak Lewis acidity. The same IR bands due to pyridinium ions and to pyridine bonded to Lewis sites but of lower intensities were observed with the desorption of pyridine at higher temperatures. Secondary aluminated MCM-41 of various concentrations exhibit two IR bands associated with Brønsted acidity (B) at 1540 cm^{-1} and Lewis acidity (L) at 1450 cm^{-1} respectively as shown in Figures 3(ii)–(iv). It is observed that the amount of Brønsted acidity increases as the amount of aluminium in the framework of secondary Al-MCM-41 increases. The ratio of observed intensity of the Brønsted band, I_B , to the Lewis band, I_L , for Al-MCM-41 with the Si/Al = 2.8 is $I_B/I_L = 2.3$. The formation of a small amount of strong Lewis acid sites, *i.e.* octahedrally coordinated Al species in the aluminosilicate sample may be affiliated with the presence of octahedral Al in the MCM-41 framework [15]. We note that these acid sites are rather strong in Al-MCM-41 as pyridine is still present on the sample after outgassing at $400\text{ }^{\circ}\text{C}$. Moreover, when the experiment was performed with purely siliceous MCM-41, the peaks hardly persist upon evacuation of the sample at $250\text{ }^{\circ}\text{C}$. That was an additional evidence that strong Lewis acid sites were generated upon substitution of framework Si^{4+} by Al^{3+} .

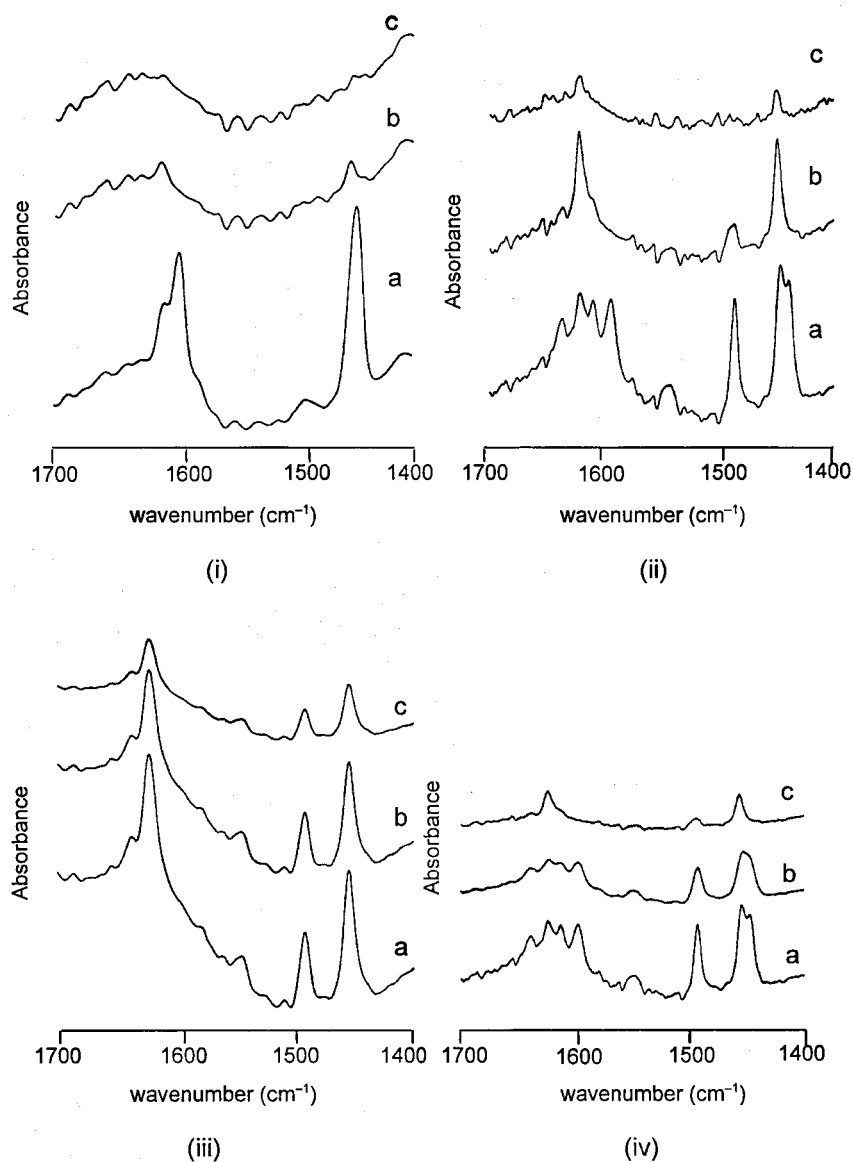


Figure 3. FT-IR spectra of adsorbed pyridine on (i) purely siliceous MCM-41 and Al-MCM-41 samples with (ii) Si/Al = 2.8, (iii) Si/Al = 3.6 and (iv) Si/Al = 3.8 evacuated at a = 25 °C, b = 250 °C and c = 400 °C

Table 1 shows the values of total conversion of cyclohexanol to cyclohexene at 400°C over H-Al-MCM-41, Si-MCM-41, AlPO₄-5 and H-ZSM-5. The results show that at 400 °C cyclohexanol conversion is the highest over secondary aluminated H-Al-MCM-41 which produces cyclohexene as the only product at nearly 100 % conversion. This confirms that secondary aluminated H-Al-MCM-41 consists only of Brönsted acid sites. H-Al-MCM-41 prepared by direct synthesis yielded a lower rate of dehydration of cyclohexanol, suggesting a lower concentration of Brönsted acid sites in this system, confirming the poor incorporation of aluminium in the framework. As expected, the purely siliceous MCM-41 did not show any catalytic activity towards the conversion of cyclohexanol to cyclohexene due to the absence of Brönsted acidity. This material has been characterized to have mainly Lewis acidity by means of IR spectroscopy using pyridine adsorption. The only product detected from the test reaction is 3-methylpentane. In contrast, cyclohexanol was converted to cyclohexene and cyclohexanone in the presence of AlPO₄-5. The formation of cyclohexanone in this reaction indicates that some basic sites are also present in AlPO₄-5, as already reported by other workers [16,17]. In the case of H-ZSM-5, cyclohexanol is mostly converted to cyclohexene with a small amount of polyaromatic compounds as minor products confirming its well-known acidic nature. In this context, H-Al-MCM-41 prepared by secondary synthesis is less acidic as compared to H-ZSM-5, which inhibits consecutive disproportionation and isomerization reactions of cyclohexene.

4. CONCLUSIONS

Secondary aluminated Al-MCM-41 contains weak Brönsted acid sites that are not present in the purely siliceous sample. The concentration of the Brönsted acid sites increases with the amount of aluminium inserted into the

Table 1
Total conversion of cyclohexanol to cyclohexene

Catalyst	Conversion wt. [%]		other products
	cyclohexene	cyclohexanone	
H-Al-MCM-41 (secondary)	100	none	none
H-Al-MCM-41 (direct)	83	none	none
Si-MCM-41	none	none	3-methylpentane
H-ZSM-5	98	none	polyaromatics
AlPO ₄ -5	78	22	None

MCM-41 framework. Catalytic conversion of cyclohexanol to cyclohexene result demonstrates that H-Al-MCM-41 prepared by secondary synthesis contains only Brönsted acid sites with a higher concentration than the one present in the directly synthesized H-Al-MCM-41. The Al-MCM-41 materials in this study is hydrothermally stable and is a potential catalyst in acid-catalyzed conversion of alcohols at moderate temperatures.

REFERENCES

1. C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 359 (1992) 710.
2. J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 114 (1992) 10834.
3. A. Corma, A. Martínez, V. Martínez-Soria and J. B. Montón, *J. Catal.* 153 (1995) 25.
4. K. Roos, A. Liepold, W. Reschetilowski, R. Schmidt, A. Karlsson and M. Stöcker, *Stud. Surf. Sci. Catal.*, 94 (1995) 389.
5. K. M. Reddy and C. Song, *Catal. Today*, 31 (1996) 137.
6. J. Aguado, D. P. Serrano, M. D. Romero and J. M. Escola, *J. Chem. Soc., Chem. Commun.*, (1996) 725.
7. C.-Y. Chen, H.-X. Li and M. Davis, *Microporous Mater.*, 2 (1993) 17.
8. H. Hamdan, S. Endud, H. He, M. N. M. Muhid and J. Klinowski, *J. Chem. Soc., Faraday Trans.*, 92 (1996) 2311.
9. J. Weglarski, J. Datka, H. He and J. Klinowski, *J. Chem. Soc., Faraday Trans.*, 92 (1996) 5161.
10. J.-H. Kim, M. Tanabe and M. Niwa, *Microporous Mater.*, 10 (1997) 85.
11. C. D. Chang, *Stud. Surf. Sci. Catal.*, 36 (1988) 127.
12. S. A. Tabak and S. Yurchak, *Catal. Today*, 6 (1990) 307.
13. S. T. Wilson and E. M. Flanigen, *European Patent Application*. 0043562, 1982.
14. A. Corma, V. Fornés, M.T. Navarro and J. Pérez-Pariente, *J. Catal.*, 148 (1994) 569.
15. E. P. Parry, *J. Catal.*, 2 (1963) 371.
16. J. B. Moffat, R. Vetrival and B. Viswanathan, *J. Mol. Catal.*, 30 (1985) 171.
17. S. P. Elangovan and V. Murugesan, *J. Mol. Catal.*, 118 (1997) 301.