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Surface acidity of MCM-41 by in situ IR studies of pyridine adsorption

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Abstract

The nature and concentration of the acid sites of MCM-41 material as a function of Si/Al ratio have been monitored by in situ IR using pyridine as a probe molecule. The thermal stability of aluminium in the framework of these materials is studied using ^{27}Al MAS NMR spectroscopy. The tetrahedral to octahedral aluminium ratio is found to increase with higher aluminium incorporation. The sample with the lowest Si/Al ratio is found to exhibit higher acidity compared to the other samples. However, the acidity of these mesoporous aluminosilicates is less compared to the conventional H–Y zeolite. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: MCM-41; MAS NMR; In situ IR; Pyridine

1. Introduction

Zeolites are known for their wide application as acid catalysts in petrochemical and fine chemical industries. Of the zeolites known to date, H–Y and H–ZSM-5 are most extensively used owing to their high thermal stability and high acidity which are prerequisites for application in catalysing acid catalysed reactions. However, the pore sizes of these zeolites limit them from treating heavier feeds in petrochemical industries as well as in synthesising large molecules in fine chemical industries. In recent years considerable drive has been devoted to develop solid acid catalysts in the mesoporous range to bridge the gap between microporous materials, viz. the zeolites and the macroporous solids, viz. the amorphous

aluminosilicates. This led to the discovery of various pillared clays having layered structure and phosphate based molecular sieves. But none of these materials were found suitable for industrial applications either due to their unstable structures or low acidities.

The major breakthrough in this regard has been the synthesis of mesoporous molecular sieves designated M41S series by the Mobil group [1]. These semicrystalline materials can be prepared in a wide range of Si/Al ratio by employing a unique liquid crystal templating mechanism [2]. By varying the chain length of the surfactant templates these materials can be as well synthesised in a wide range of pores between 20 and 100 Å in diameter. The presence of these large uniform pores combined with the acidic properties have undoubtedly opened up a new era in solid acid catalysis. A considerable effort has been employed to study the nature and strength of active sites of these materials.

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The present communication deals with an in situ IR study of these materials using pyridine as a probe molecule to estimate the potential acidity of one of the materials in the M41S series, viz. MCM-41. An extensive ^{27}Al solid state MAS NMR study is also performed to look into the stability of aluminium in the framework position which accounts for the potential Bronsted sites in MCM-41. The influence of Si/Al ratio on the ratio of Bronsted to Lewis site is also presented. The results are compared with H–Y zeolite which is known for its strong acidity.

2. Experimental

Na–MCM-41 with Si/Al ratios of 60, 30 and 15 were synthesised using Ludox As-30 and aluminium sulphate as the silica and aluminium source, respectively. Cetyltrimethylammonium bromide was employed as the template. A typical gel composition for Si/Al ratio of 30 is given as follows:

59.8 SiO₂ : 1.0 Al₂O₃ : 3.8 TEAB : 13.0
CTAB : 10.5 Na₂O : 2810 H₂O

The synthesised gels were autoclaved at 383 K for 48 h. The solid material was filtered, washed several times with hot water and dried in the oven. The resultant semicrystalline powder was calcined in a flow of nitrogen for 1 h followed in air for 12 h at 823 K. HC–MCM 41 was obtained by repeated (thrice) exchange of the sodium form of the MCM-41 with 1M NH₄Cl solution at 333 K for 12 h followed by calcination of the oven-dried ammonia exchanged samples in air at 823 K for 6 h. H–Y zeolite (SiO₂/Al₂O₃=4.9) was prepared by the usual procedure reported in the literature.

X-ray powder diffraction of the H–MCM-41 samples were carried out in a Rigaku Miniflex powder

diffractometer using Co K_α radiation. BET surface area measurements were carried out by nitrogen adsorption at 77 K on a Carlo Erba sorptometer (1800). Pore-size distribution was obtained by BJH method. ^{27}Al solid state MAS NMR study was performed in Jeol GSX400 instrument using a Larmor frequency of 104.1 MHz. Data were acquired at an MAS speed of 5.5 KHz. Very short $\pi/20$ radiofrequency pulses [3] were used to ensure that the data are quantitatively reliable. Following the work of Luan et al. [4], all the samples were fully hydrated at room temperature prior to the NMR experiment.

The nature of acid sites were investigated using pyridine as the probe molecule. Rectangular self-supported wafers of the H–MCM-41 samples were prepared applying 6 ton pressure. All the samples were subjected to vacuum in the sample holder until a pressure of 10⁻⁶ mbar was attained followed by activation at 573 K to obtain a pressure of 10⁻⁷ mbar. Pyridine vapour was admitted in doses until the catalyst surface is saturated. This is ensured from the IR spectra of the –OH region [5]. Pyridine was then desorbed until a pressure of 10⁻⁶ mbar was obtained to ensure that there is no more physisorbed pyridine on the wafers. IR spectra was recorded using a Perkin Elmer FTIR 1760 instrument. The wafers containing chemisorbed pyridine were subjected to thermal treatment at 323, 373, 423, 473, 523 and 573 K and the IR spectra were recorded in situ.

3. Results and discussion

The XRD pattern of all the H–MCM-41 samples shown in Fig. 1 exhibited low angle peaks characteristic of these materials [1]. The bulk Si/Al ratios of the as-synthesised samples (determined from chemical analysis) along with the lattice parameter ‘*a*’ are given in Table 1. An interesting feature that evolves is the

Table 1
Composition and textural properties of the calcined MCM-41 samples

Sample	Si/Al ratio (as-synthesised)	<i>a</i> (Å)	Pore diameter (Å)	Surface area (m ² g ⁻¹)
Si–MCM-41	∞	43.5	31	1170
S-I	60	43.2±1	31	1160
S-II	30	42.8±1	30	1080
S-III	15	40.5±1	30	980

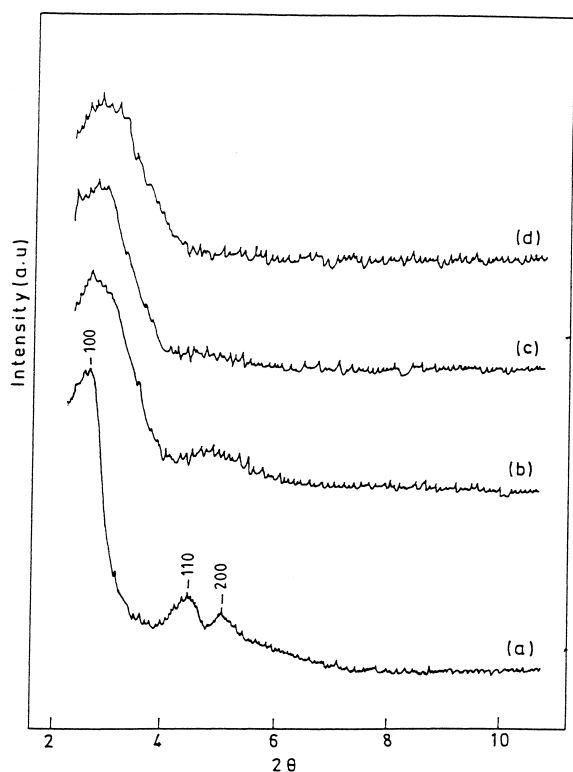


Fig. 1. XRD patterns of (a) siliceous MCM-41(∞) (calcined form stirred with 1 M NH_4Cl solution and calcined at 823 K), (b) H-form of S-I, (c) H-form of S-II and (d) H-form of S-III samples

deterioration of the pattern with aluminium incorporation. Higher aluminium loading brought about gradual lowering in the intensity of the 100 plane and resulted in the overlap of the 110 and 200 peaks into a broad hump which is almost absent in the S-III with Si/Al ratio of 15. Thus, introduction of aluminium during the synthesis procedure decreases the ordering and brings down the structural uniformity in the aluminium containing MCM-41 samples compared to the siliceous material. The structural deterioration is further reflected in the BET surface of the samples determined by N_2 adsorption study at 77 K. The values of surface areas given in Table 1 reflects that aluminium incorporation results in lowering in the values of the surface area of the catalysts. Adsorption isotherms (type IV) with hysteresis were recorded on all the samples (figures not shown). Apart from the inflection at lower relative pressures ($\sim p/p^0 < 0.3$) the aluminosilicate samples exhibited another sharp inflection at higher relative pressures ($p/p^0 > 0.9$) whereas the

inflection in the same region for the siliceous material is not so sharp. The second inflection as also observed by Luan et al. [6] in their MCM-41 samples may be attributed to macropore filling or to the filling of the interparticle pores. These macropores and interparticle pores result from calcination and subsequent thermal treatments of the aluminosilicates which bring about partial collapse of structure probably due to formation of extraframework aluminium. All the samples showed a narrow uniform pore-size distribution around 30 Å thereby revealing the effectiveness of the synthesis procedure. However, slight broadness in the distribution was observed for samples with higher aluminium content (figure not given). The details are given in Table 1.

3.1. ^{27}Al MAS NMR spectra

Figs. 2–4 show the ^{27}Al solid-state MAS NMR spectra of the as-synthesised, calcined and H-form

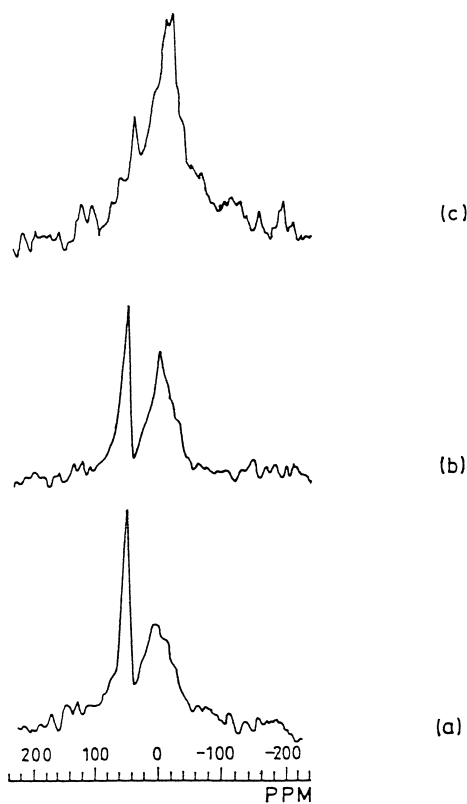


Fig. 2. ^{27}Al MAS NMR spectra of (a) as-synthesised, (b) calcined and (c) H-form of the S-I sample.

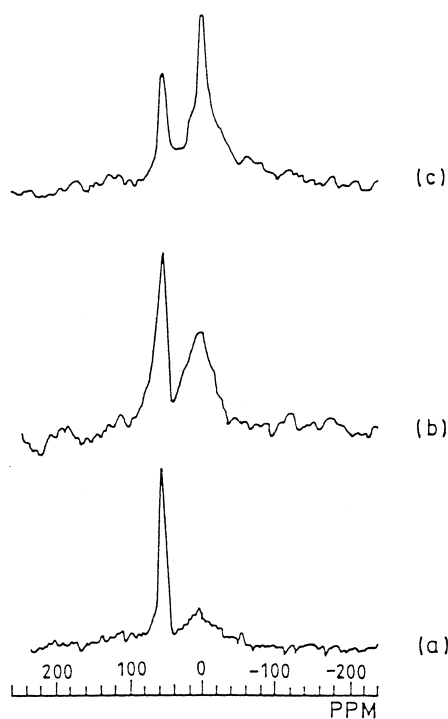


Fig. 3. ^{27}Al MAS NMR spectra of (a) as-synthesised, (b) calcined and (c) H-form of the S-II sample.

of MCM-41 samples. In the as-synthesised samples, majority of the incorporated aluminium are found in the tetrahedral environment, i.e., in the framework position. Also assuming that the concentration of the tetrahedral and octahedral aluminium are proportional to the respective intensities of the resonances at $\delta(53.0 \pm 1)$ and $\delta(0.0 \pm 2)$, it is observed that the ratio of aluminium in the tetrahedral to that of aluminium in the octahedral environment ($\text{Al}_{\text{Td}}/\text{Al}_{\text{Oh}}$) is maximum for the S-III sample and minimum for the S-I sample. This somewhat unexpected result contrary to literature reports apparently indicates that incorporation of higher amount of aluminium is probably favourable in these materials when prepared by the present synthetic procedure. As the concentration of octahedral aluminium is the least in the as-synthesised S-III sample, it may also be deduced that the peak at low frequency region may not be exclusively due to extra-framework aluminium but also due to framework aluminium maintaining higher coordination by bonding with water/template which is not a common observation in microporous zeolites. This possibility

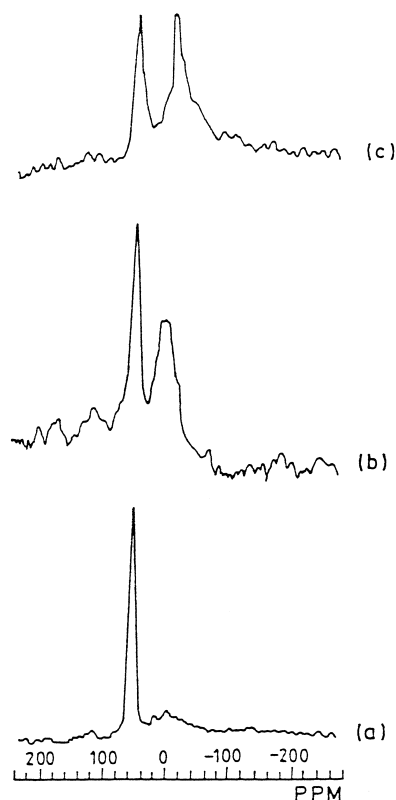


Fig. 4. ^{27}Al MAS NMR spectra of (a) as-synthesised, (b) calcined and (c) H-form of the S-III sample.

decreases with increasing aluminium content as coordination of water/template to the adjacent aluminium sites causes steric hindrance which is energetically unfavourable. This may be a reason for the apparent decrease in the concentration of aluminium in the octahedral environment with increase in aluminium incorporation. With calcination, aluminium comes out of the framework for all the samples, the extent of dealumination being maximum for the S-III sample. On calcining the NH_4^+ -exchanged forms of the samples, severe dealumination occurs thereby resulting in further decrease of the $\text{Al}_{\text{Td}}/\text{Al}_{\text{Oh}}$ ratio as given in Table 2. This may be due to the steaming effect caused by the adsorbed water molecules in the samples as it is already established that these mesoporous molecular sieves have large adsorption capacities [1]. Thus it is found that tetrahedral aluminium is more stabilised in the MCM-41 samples with higher aluminium content.

Table 2

Ratio of the relative intensities of the ^{27}Al MAS NMR peaks from 4-coordinated and 6-coordinated aluminium in the as-synthesised, calcined and H-form of the MCM-41 samples

Sample	$\text{Al}_{\text{Td}}/\text{Al}_{\text{Oh}}$		
	As-synthesised	Calcined	H-form
S-I	2.4	1.5	0.4
S-II	5.3	1.8	0.6
S-III	9.5	2.0	1.0

3.2. Hydroxy groups in H-MCM-41

Infra red spectra of the hydroxy groups in the H-MCM-41 samples measured at 323 K under 10^{-6} mbar pressure show bands at 3740 cm^{-1} for all the samples (Fig. 5(a)–(c)). This band can be assigned to the non-acidic silanol (Si–OH) groups. In addition to this, a broad band is observed at 3555 cm^{-1} for all the samples. Owing to the considerable width at half height, this may be assigned to the hydrogen bonded hydroxy groups. There is another low intensity band at 3672 cm^{-1} for all the samples which may be due to –OH groups attached to the extraframework aluminium. Another small band is observed at 3713 cm^{-1} for the S-II and S-III samples having higher aluminium incorporation. The shift of this band to lower wavelength compared to the silanol group indicates a lateral interaction of the silanol groups with defect sites which are expected to be more in samples having higher aluminium.

When the samples are heated at 573 K till a pressure of 10^{-7} mbar is attained, all the bands except the one at 3740 cm^{-1} disappear (Fig. 5(a')–(c')). This proves that at higher calcination temperature, the weak H-bonds and the coordinations related to the defect sites disappear. There is no band found corresponding to the Bronsted site, viz. $\text{Si}(\text{OH})\text{Al}$ which is well documented for the existing zeolites like HZSM-5, H–Y, etc. Normally this band appears in the range $3600\text{--}3680\text{ cm}^{-1}$ and its intensity increases with increasing aluminium incorporation. The NMR data suggest that appreciable amount of tetrahedral aluminium is present in S-II and S-III samples. Thus the absence of –OH band corresponding to Bronsted site is quite unexpected. Even there is no band corresponding to the –OH stretch owing to the presence of octahedral

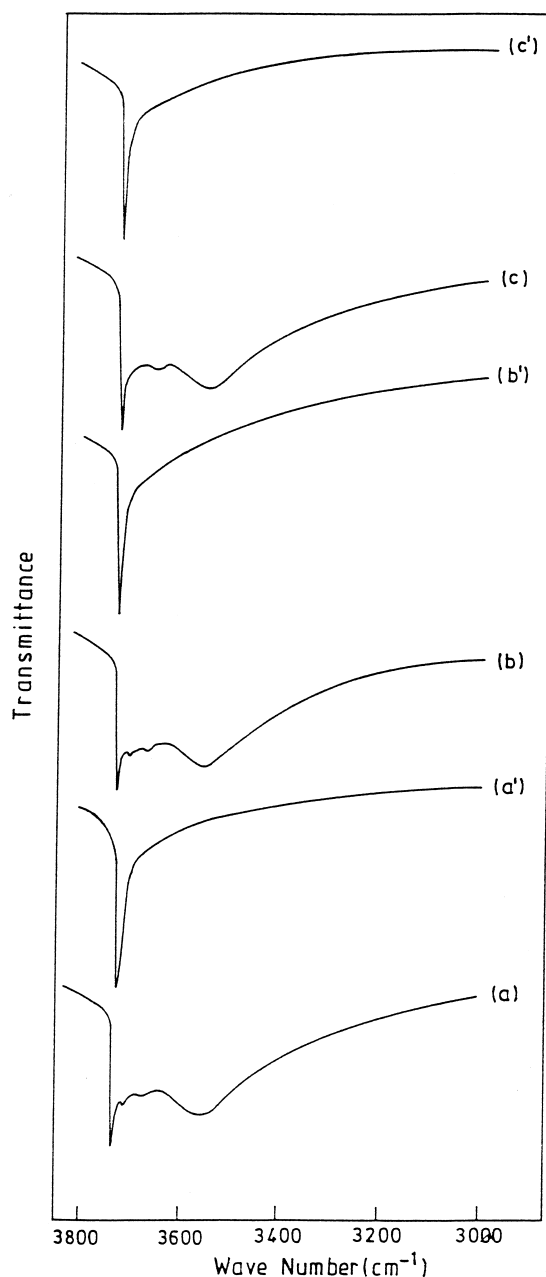


Fig. 5. Infra red spectra of the hydroxy region of (a) S-III, (b) S-II and (c) S-I samples recorded at 323 K under 10^{-6} mbar pressure and of (a') S-III, (b') S-II and (c') S-I samples recorded at 573 K under 10^{-7} mbar pressure.

aluminium. This led to the suspicion whether majority of the –OH species remain buried in the inorganic matrix or the pressure exerted on these mesoporous

materials for making pellets led to the rupture of the pores. Jentys et al. [5] also did not observe any band corresponding to the Bronsted acid site. However, Corma et al. [7] reported a weak band at 3604 cm^{-1} for the MCM-41 sample with Si/Al ratio of 14 which they assigned to the -OH bond stretching in Si(OH)Al species. It is also to be noted that this band was observed when the sample was calcined under vacuum whereas the samples calcined in air did not exhibit this band.

3.3. Pyridine adsorption study

Figs. 6–8 show the infra red spectra of the pyridine adsorbed on the aluminosilicates in the region $1650\text{--}1400\text{ cm}^{-1}$ at 10^{-6} mbar pressure subjected to different thermal treatments in the range $323\text{--}573\text{ K}$. All the samples exhibited bands due to hydrogen bonded pyridine (1445 and 1596 cm^{-1}), strong Lewis bound pyridine (1623 and 1455 cm^{-1}), weak Lewis bound pyridine at 1575 cm^{-1} , pyridinium ion ring vibration due to pyridine bound to Bronsted acid sites (1546 and 1639 cm^{-1}) and a band at 1492 cm^{-1} which can be assigned to pyridine associated with both Bronsted and Lewis sites.

The bands at 1445 and 1596 cm^{-1} for all the samples disappear at 423 K . These are the only bands found in pure siliceous material (not shown in figure). In case of the pure mesoporous silicalite, these bands disappear at 473 K as reported for pure silica. Thus pyridine forms hydrogen bonds with silanol groups. It is also noteworthy that the relative intensities of these bands decrease when compared to other diagnostic bands with decrease in Si/Al ratio as increase in aluminium incorporation leaves less number of free silanol groups in the material. This observation is consistent with the report of Mokaya et al. [8].

A careful investigation of the band position of the Bronsted acid site at 1546 cm^{-1} reveals that as we go from S-III to S-I, the peak intensity decreases. However, the decrease is expected as revealed in ^{27}Al MAS NMR. With thermal treatment, the intensity of the peak decreases for all the samples, the decrease being large for the sample with lower aluminium content, i.e., S-I. At 573 K , there is practically no Bronsted site for S-I whereas the S-III sample still retains some of the sites. This suggests that the Bronsted sites of the sample having more aluminium incorporation can

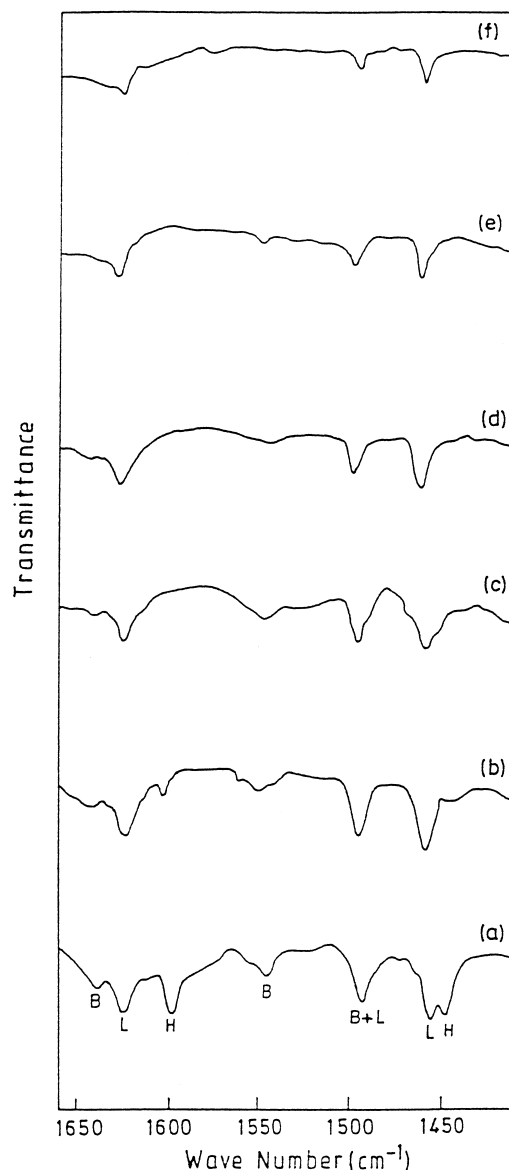


Fig. 6. Infra red spectra of pyridine adsorbed on S-I sample following thermal treatment at (a) 323, (b) 373, (c) 423, (d) 473, (e) 523, and (f) 573 K. H: Hydrogen bonded pyridine, B: Bronsted-bound pyridine, and L: Lewis bound pyridine.

retain more pyridine at higher temperature compared to the samples having higher Si/Al ratio.

Looking at the band at 1455 cm^{-1} , we find that the intensity of this band is the highest for S-III sample though the difference is not much. This cannot be explained with our NMR results according to which

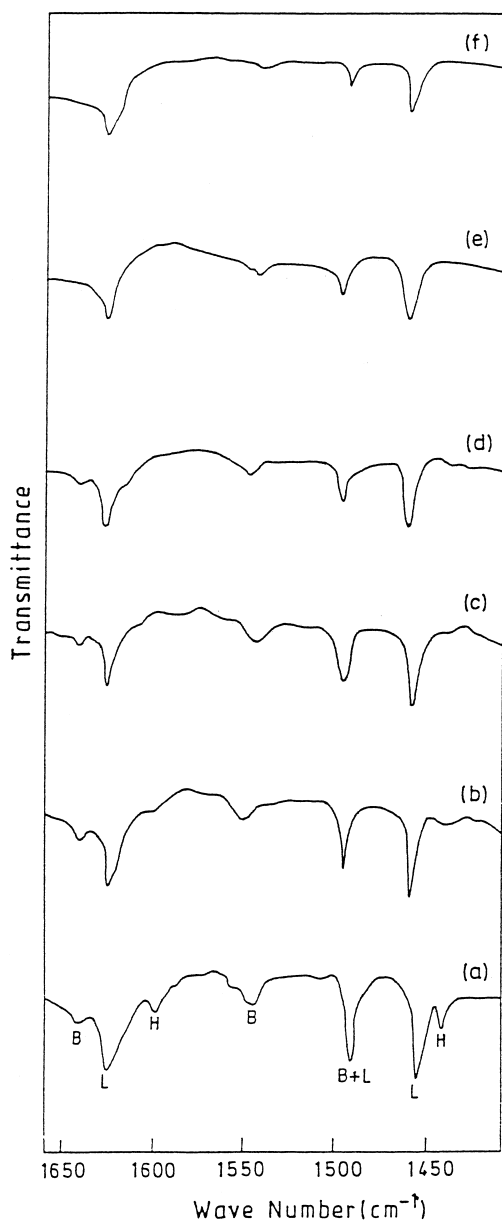


Fig. 7. Infra red spectra of pyridine adsorbed on S-II sample following thermal treatment at (a) 323, (b) 373, (c) 423, (d) 473, (e) 523, and (f) 573 K. H: Hydrogen bonded pyridine, B: Bronsted-bound pyridine, and L: Lewis bound pyridine.

the S-I sample should have much higher concentration of extraframework aluminium responsible for the Lewis acidity. With thermal treatment the decrease in the band intensity for all the samples is more or less the same. However, the decrease in the intensity of the

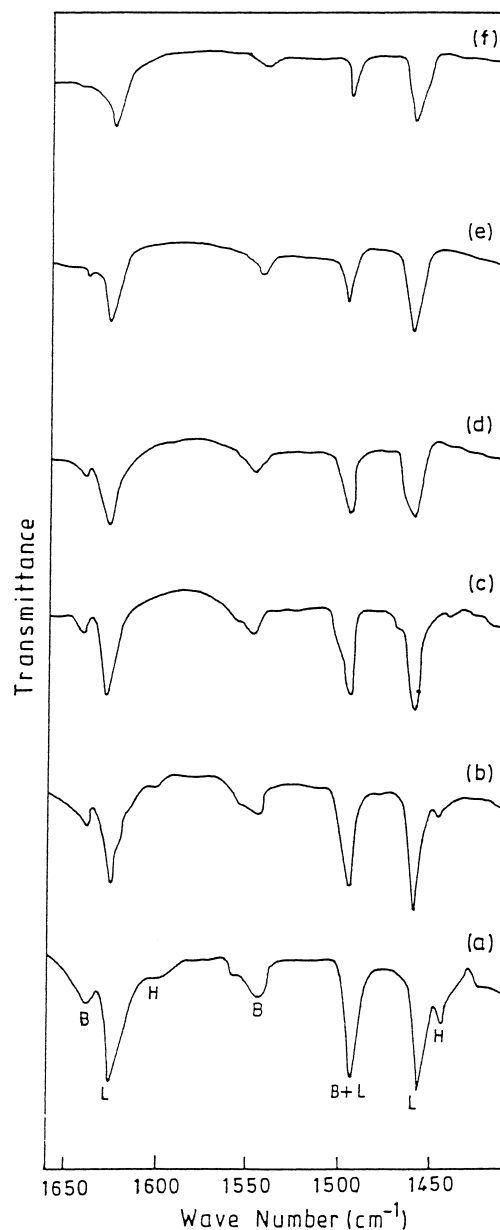


Fig. 8. Infra red spectra of pyridine adsorbed on S-III sample following thermal treatment at (a) 323, (b) 373, (c) 423, (d) 473, (e) 523, and (f) 573 K. H: Hydrogen bonded pyridine, B: Bronsted-bound pyridine, and L: Lewis bound pyridine.

band at 1456 cm^{-1} seems to be relatively less than that at 1546 cm^{-1} for all the samples.

An attempt has been made to estimate quantitatively the ratio of the Bronsted to Lewis (B/L) site for all the three catalysts at temperatures 323 and 573 K

Table 3
Ratio of Bronsted (B) to Lewis (L) acidity in the H-MCM-41 samples at two different desorption temperatures

Sample	B/L ratio	
	323 K	573 K
S-I	0.50	0.03
S-II	0.57	0.12
S-III	0.64	0.20
H-Y	0.85	0.44

(Table 3). This is based on the work of Emeis [9]. However, we have assumed that the ratio of the molar extinction coefficients, viz. (ϵ_B/ϵ_L) will remain the same in the temperature range 323–573 K. Thus for Bronsted site and Lewis site, the values of integrated molar extinction coefficients chosen are 1.67 and 2.22 cm/ μmol , respectively. At low temperature of desorption of pyridine the B/L ratio does not vary with Si/Al ratio to an appreciable extent whereas at higher temperature, the ratio is extremely low for the S-I sample. Thus at a temperature of 573 K, the sample with more aluminium content shows appreciable acidity. When this value is compared with that of H-Y zeolite we find the value is higher for the H-Y zeolite thus proving that the H-Y zeolite has higher acidity compared to these mesoporous aluminosilicates.

4. Conclusion

Aluminium incorporation in the framework of MCM-41 generates both Bronsted and Lewis sites. ^{27}Al MAS NMR spectra revealed that the relative intensities of the Bronsted to Lewis site increases with aluminium incorporation. The IR spectra of adsorbed

pyridine indicate that the B/L ratio is extremely sensitive to higher desorption temperatures. It is observed that the Bronsted site of the H-MCM-41 samples with lower Si/Al ratio retains considerable amount of pyridine at higher temperature compared to the samples with higher Si/Al ratios. However, the acidity of these mesoporous aluminosilicates is found to be less compared to H-Y zeolite.

Acknowledgements

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References

- [1] 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, J.L. Schlenker, *J. Am. Chem. Soc.* 114 (1992) 10834.
- [2] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, *Nature* 359 (1992) 710.
- [3] P.P. Man, J. Klinowski, A. Trokiner, H. Zanni, P. Papon, *Chem. Phys. Lett.* 151 (1988) 143.
- [4] Z. Luan, C.F. Cheng, H. He, J. Klinowski, *J. Phys. Chem.* 99 (1995) 10590.
- [5] A. Jentys, N.H. Pham, H. Vinek, *J. Chem. Soc., Faraday Trans.* 92 (1996) 3287.
- [6] Z. Luan, H. He, W. Zhou, C.F. Cheng, J. Klinowski, *J. Chem. Soc., Faraday Trans.* 91 (1995) 2955.
- [7] A. Corma, V. Fornes, M.T. Navarro, J. Perez-Pariente, *J. Catal.* 148 (1994) 569.
- [8] R. Mokaya, W. Jones, Z. Luan, M.D. Alba, J. Klinowski, *Catal. Lett.* 37 (1996) 113.
- [9] C.A. Emeis, *J. Catal.* 141 (1993) 347.