Comparison of mesoporous solid acid catalysts in the production of DABCO by cyclization of ethanolamine

I. Synthesis and characterization of mesoporous solid acid catalysts

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Abstract

Mesoporous silica molecular sieves MCM-41 containing zinc and aluminum ions (Zn–Al-MCM-41) with Si/(Zn + Al) ratio equal to 75, 151, 228, 304 and 380 and only aluminum ions (Al-MCM-41) with Si/Al ratio equal to 21, 42, 62, 83 and 104 respectively, were synthesized under hydrothermal conditions using cetyltrimethylammonium (CTMA+) surfactants as template in the absence of auxiliary organics. The mesoporous materials viz. Zn–Al-MCM-41 and Al-MCM-41 were characterized using several techniques, e.g. ICP-AES, XRD, FTIR, TG/DTA, Nitrogen adsorption, 27Al-MAS-NMR, SEM, TEM, XPS and pyridine acidity (TPD and FTIR) measurements. The d-spacing value and unitcell parameter in the Zn–Al-MCM-41 and Al-MCM-41 decreases by increasing the metal ions content. FT-IR studies showed that zinc ion was incorporated into the hexagonal mesoporous Al-MCM-41 materials, however, the wavenumber of the anti-symmetric Si–O–Si vibration bands (1096 cm\(^{-1}\)) in Zn–Al-MCM-41 are higher than those in Al-MCM-41 (1083 cm\(^{-1}\)). These bands should be due to the increase of the mean Si–O distance in the wall caused by the substitution of the small ionic radii of silicon by the larger ionic radii of zinc. The surface area, pore diameter, pore volume of Zn–Al-MCM-41 is smaller than that of Al-MCM-41 while the hydrothermal stability and acid sites in the Zn–Al-MCM-41 are higher than that of Al-MCM-41 due to increasing protons with the aluminum ions non-framework by the introduction of zinc ions. Thus Bronsted and Lewis acid sites in Zn–Al-MCM-41 are same, but its acid sites are higher than Al-MCM-41.

Keywords: Zn–Al-MCM-41; Al-MCM-41; Hydrothermal stability; Bronsted acidity; Lewis acidity

1. Introduction

Solid acid catalysts have served as important functional materials for the petroleum refinery industry, such as in the cracking processes, and for the production of chemicals [1]. At present, about 180 industrial processes using solid acids are in operation, featuring acids such as zeolites, oxides, mixed oxides including heteropoly acids, and phosphates [2]. In contrast, a significant number of acid-catalyzed reactions, such as Friedel–Crafts reactions, esterification, hydration, and hydrolysis, are still carried out using conventional acids, such as H\(_2\)SO\(_4\) and AlCl\(_3\). However, processes involving conventional acids are typically associated with problems of high toxicity, corrosion, catalyst waste, use of large amounts of catalyst, and difficulty of separation and recovery. Because solid acids are environmentally friendly with respect to corrosiveness, safety, less waste, and ease of separation and recovery, replacement of these liquid acids with solid acids is desirable in the chemical industry.

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Zeolites possess several catalytically desirable properties: a high surface area; adjustable pore size; hydrophilicity; acidity; high thermal and chemical stability. Therefore, they are gaining importance in the quest for cleaner processes. Industrial examples [2,3] include aromatic alkylation [4], the synthesis of tert-butylamine from ammonia and isobutene over zeolites MFI [5], the conversion of methanol and ammonia to mono- and dimethylamine over modified mordenites [6] or zeolites Rho [7], and the hydration of cyclohexane to cyclohexanol over ZSM-5. Furthermore, zeolites have found widespread applications in oil refining processes [8,9].

A disadvantage of zeolite catalysts is their limited pore size (up to 1.0 nm), which renders useless as catalysts in the conversion of larger sized reactants.

The discovery of the mesoporous material MCM-41 [10–12] has greatly enlarged the window of porous materials applicable as catalyst for organic reactions. Unfortunately, the acid strength of MCM-41 resembles that of the amorphous silica aluminas rather than that of the more strongly acidic zeolites [13]. Although the material is valuable for many organic conversions [14,15], enhancement of its acidity is desirable for extension of its applicability.

Several approaches aimed at increasing the acid strength of the material. Kozhevnkov et al. showed that heteropoly acids (HPA) supported on MCM-41 are excellent catalysts in several reactions [16–19]. However, the lack of stability of this catalyst in case polar or products are involved, concerning mainly the dispersion of the HPA [20] and leaching of the HPA the support, prevents its introduction in industrial applications. Another possibility is the use of sulfonic acid groups covalently attached to the MCM-41 pore wall via an organic spacer [21,22].

Selvaraj et al. [23,24] reported the synthesis and characterization of Al-MCM-41 with Si/Al = 93 and 104, and Zn–Al-MCM-41 with Si/(Zn + Al) = 340 and 380. However, the hydrothermal stability, hydrophobicity and catalytic activity in Zn–Al-MCM-41 are higher than that of Al-MCM-41 while the materials have been used for highly selective synthesis of p-cymene [21,22].

Namba et al. [25] first reported that the maximum activity in H-ZSM-5 was observed at Si/Al = 47. As will be described here, as Si/Al ratios increases, the surface of the zeolite becomes more hydrophobic and possesses stronger affinity for organic reactant but the number of acid sites decreases while thermally and mechanically are less stable. Herein our present study, as the same problem occurs in Al-MCM-41, but, the acid sites in Zn–Al-MCM-41(75) do not decrease. Because the thermal, mechanical and hydrothermal stability in Zn–Al-MCM-41 are higher than those of Al-MCM-41 due to the introduction of zinc ions. However, tetrahedral aluminum is replaced by zinc, the ion is produced two negative ions with tetrahedral environment and the ions are associated to Bronsted acid sites while the tetrahedral aluminum ions became into octahedral aluminum ions and their are associated to the Lewis acid sites. Thus Bronsted and Lewis acid sites in Zn–Al-MCM-41 are same, but its acid sites are higher than Al-MCM-41.

2. Experimental

2.1. Materials

The syntheses of Zn–Al-MCM-41 and Al-MCM-41 materials were carried out hydrothermally using sodium metasilicate (Na$_2$SiO$_3$·5H$_2$O), aluminum sulfate (Al$_2$(SO$_4$)$_3$·18H$_2$O), zinc chloride (ZnCl$_2$), cetyltrimethylammonium bromide (C$_{16}$H$_{33}$N(CH$_3$)$_3$Br$^-$) and sulfuric acid (H$_2$SO$_4$). All the chemicals were purchased from M/s Aldrich & Co, USA.

2.2. Synthesis of Zn–Al-MCM-41 and Al-MCM-41

2.2.1. Synthesis of Zn–Al-MCM-41

For the synthesis of the Zn–Al-MCM-41 (Si/(Zn + Al) = 75), 21.2 g (1 mol) sodium metasilicate (44–47% SiO$_2$) dissolved in 50 g of deionized water was mixed with 0.832 g (0.0125 mol) of aluminum sulfate (dissolved in 10 g of deionized water) solution and 0.17 g (0.0125 mol) of zinc chloride (dissolved in 10 g of deionized water). This mixture was stirred for 30 min. using a mechanical stirrer at a speed of about 250 rpm and in order to reduce the pH to 10.8, 1 N of sulfuric acid was added with continuous stirring for another 30 min. at a speed of about 250 rpm until the gel formation. After that, 9.1 g (0.25 mol) of cetyltrimethylammonium bromide was added drop by drop (30 ml/h) by the dual syringe pump so that the gel was changed into suspension. After further stirring for 1 h the resulting gel was transferred into Teflon-lined steel autoclave and heated to 165 °C for 48 h. After cooling to room temperature, the material was recovered by filtration, washed with deionized water and ethanol and finally calcined in flowing air at 540 °C for 6 h.

The different Zn–Al-MCM-41 catalysts (Si/(Zn + Al) = 151, 228, 304 and 380) were also synthesized in a above similar manner wherein only the ratio of sodium metasilicate, zinc chloride and aluminum sulfate was adjusted and the input in gel molar compositions 1SiO$_2$/xAl$_2$O$_3$/yZnO/0.25CTMABr/100H$_2$O; (x = 0.00625–0.0025, y = 0.00625–0.0025).

2.2.2. Synthesis of Al-MCM-41

The different Al-MCM-41 catalysts (Si/Al = 21, 42, 62, 83 and 104) were synthesized by hydrothermal method...
using aluminum sulfate as the source for aluminum by the similar procedure as above adopted for the synthesis of Al-MCM-41 without the source for zinc and the input gel molar composition was $1\text{SiO}_2/\text{xAl}_2\text{O}_3$: 0.25CTMABr/100H$_2$O; ($\text{x}=0.025–0.005$).

2.2.3. Hydrothermal treatment of Zn–Al-MCM-41 and Al-MCM-41

Zn–Al-MCM-41 and Al-MCM-41 samples were treated in boiling water in polypropylene bottles and retained at 100 °C for 1 week in order to evaluate the hydrothermal stability of the mesoporous structure of MCM-41 materials.

2.3. Physicochemical characterization

The zinc and aluminum content in Zn–Al-MCM-41 and Al-MCM-41 materials was recorded using ICP-AES with allied analytical ICAP 9000.

The crystalline phase identification and phase purity determination of the calcined Zn–Al-MCM-41 and Al-MCM-41 samples were carried out by XRD (Philips, Holland) using nickel filtered CuK$\alpha$ radiation ($\lambda=1.5406\text{Å}$). The samples were scanned from 0.5° to 5° (20) in steps of 0.5°, with a count of 5 s at each point. In order to protect the detector from the high energy of the incident and diffracted beam, slits were used in this work.

Infra red spectra were recorded with a Nicolet Impact 410 FTIR Spectrometer in KBr pellet (0.005 g sample with 0.1g KBr) scan number 36, resolution 2 cm$^{-1}$. The data was treated with Omnic Software.

The weight loss, dehydration and dehydroxylation for as-synthesized Zn–Al-MCM-41 and Al-MCM-41 samples was evaluated by TG-DTA in a Rheometric scientific (STA 15H$^+$) thermobalance. Ten to 15 mg of as-synthesized MCM-41 was placed in a platinum pan and heated from room temperature to 1273 K at a heating rate of 2 K/min in air with flow rate of 50 ml/min. For comparison experiments, samples were dried at 323 K for the same period. The data were collected at 30-s intervals using on-line PC.

The surface area and pore properties of Zn–Al-MCM-41 and Al-MCM-41 samples before and after hydrothermal treatments were analyzed using a NOVA-1000 (QUANTACHROME, version 5.01) sorptometer. The calcined samples were dried at 130 °C and evacuated overnight for 8 h in flowing argon at flow rate of 60 ml/min at 200 °C under vacuum. Surface area, pore size, pore volume and wall thickness was obtained from these isotherms using the conventional BET and BJH equations.

The $^{27}$Al MAS NMR spectra were recorded at a frequency of 75.512 MHz and a spinning rate of 8 kHz with a pulse length of 4 µs, a pulse interval of 1 s and approximately 1000 scans. $^{27}$Al chemical shifts are reported relative to 1 M Al(NO$_3$)$_3$.

The SEM microscopes of a typical sample of Zn–Al-MCM-41 and Al-MCM-41 materials were obtained on a JEOL 2010 microscope operated at 200 KV from a thin film dispersed on a holly carbon grid in ethanol solvent.

TEM images were recorded using a JEOL JEM-200CX electron microscope operating at 200 KV with modified spectrum stage with objective lens parameters $C_x=0.41\text{ mm}$ and $C_c=0.95\text{ mm}$, giving an interpretable point resolution of $\approx 0.185\text{ nm}$. Samples for analysis were prepared by crushing the particles between two glass slides and spreading them on a holly carbon film supported on a Cu grid. The samples were briefly heated under tungsten filament light bulb in air before transfer into the specimen chamber. The images were recorded at magnifications of 100,000x.

X-ray photoelectron spectroscopy (XPS) data were recorded on a VG scientific photoelectron spectrometer using AlK$\alpha$$_2$$_1$ radiation (1486.8 eV) from an X-ray source operating at 13 kV and 10 Pa. Working pressure was kept below $2\times10^{-8}\text{Torr}$. The spectra were recorded at a photoelectron take-off angle of 45°. Binding energies were referenced to the C 1s peak from adventitious carbon surface deposit at 284.8 eV.

Temperature programmed desorption of pyridine was studied on Zn–Al-MCM-41 and Al-MCM-41 samples under chromatograph conditions [26].

IR spectra were recorded with JASCO FTIR-610 spectrometer, fully controlled by the OMNIC software, and an all-glass high-vacuum system. Finely ground catalyst samples, equilibrated with water vapor at room temperature, were pressed in self-supporting thin wafers (10–15 mg cm$^{-2}$), having a surface area of 1.0 cm$^2$ on each face. Before pyridine adsorption, all wafers were pre-treated. Both clean sample reference spectra after pyridine adsorption were collected at room temperature, as an average of 60 runs with a 2 cm$^{-1}$ resolution. Preliminary investigations showed that these were the optimal recording conditions.

In the series of experiments carried out to evaluate the proportionality coefficient between the integrated absorbance ($A_1$) and the amount of adsorbed probe, accurately measured amounts (0.1–0.3 µmol) of pyridine vapor were successively adsorbed on the catalyst sample at 150 °C. The amount of pyridine was determined volumetrically via the ideal gas law, after emission of pyridine vapor in a 492 cm$^3$ compartment of the vacuum system. Complete adsorption was found to occur within a 5 min contact time. The pressure was measured by means of a barocel 600-capacitance type pressure-meter. The walls of the glass vacuum system were maintained at 150 °C, in order to minimize pyridine adsorption on them. The total amount of pyridine adsorbed on the different catalysts was in the range of 1–3 µmol. Between each adsorption step, the samples were pumped off to
1.33×10⁻³ Pa and cooled down to room temperature, as usual, to collect the spectrum.

After this preliminary calibration, FTIR analysis was carried out by equilibrating the catalyst wafers for 30 min at 150 °C at a probe molecule vapor pressure of 500 Pa, followed by evacuation for 10 min at the same temperature, while maintaining the walls of the vacuum system at 150 °C. Constant values of integrated absorbance were obtained by prolonging evacuation up to 500 min.

Only the 1270–1700 cm⁻¹ part of the IR difference spectra, obtained by subtracting the absorbance reference spectrum from the absorbance spectra recorded after probe adsorption, was considered.

3. Results and discussion

3.1. ICP-AES

All Al-MCM-41 and Zn-Al-MCM-41 samples were analyzed by ICP-AES, which gave the corresponding Si/Al=21, 42, 63 and 104 and Si/(Zn+Al) ratio of 75, 151, 228, 304 and 380 respectively, in bulk sample. The observed zinc and aluminum content in Al-MCM-41 and Zn-Al-MCM-41 have been presented in Table 1.

3.2. XRD

Fig. 1a and b illustrate the X-ray powder diffraction patterns of calcined Al-MCM-41 and Zn–Al-MCM-41 samples having Si/Al=21, 42, 63 and 104 and Si/ Zn+Al=75, 151, 228, 304 and 380 gel molar ratio, respectively. The X-ray diffractograms of Al-MCM-41 and Zn–Al-MCM-41, after calcinations in air at 540 °C for 6 h, contain a sharp d₁₀₀ reflection line in the range 2θ=2.05–2.3 and 1.95–2.33 respectively. Additionally two broad peaks at 2θ = 3.6° and 4.1° approximately are obtained except for Zn-Al-MCM-41 samples. These peaks have been attributed to higher reflection lines due to small particles [27]. Physicochemical properties of these mesoporous materials are summarized in Table 1. For example, the pore-to-pore distance of Al-MCM-41 could be determined by the XRD patterns. The XRD patterns of calcined Al-MCM-41 (21) with characteristic peaks of hexagonal (p6mm) symmetry and with d₁₀₀ of 38.41' are shown in Fig. 1a (Si/Al = 21). The repeating distance (a₀) between pore centers was 44.35'. The hexagonal unit cell parameter (a₀) was calculated using the formula as a₀ = 2d₁₀₀/√3 from d₁₀₀, which was obtained from the peak in the XRD pattern by Bragg’s equation (2d sinθ = λ, where λ = 1.5406' for the CuKα line). The value of a₀ was equal to the internal pore diameter plus one pore wall thickness. The increase in the unit-cell parameter on zinc incorporation is probably in Al-MCM-41 materials due to the larger size of Zn²⁺ (radius 74 pm) compared with Al³⁺ (radius 53 pm) and Si⁴⁺ (radius 40 pm). It is also observed that the unit-cell parameter decreases with increasing zinc content. These clear peaks indicate that the long-range order structure was achieved and the regular mesoporous structure was retained after the introduction of metals. These Bragg peaks were broadened and shifted slightly to higher angle with increasing metal content, although the hexagonal structure still remained intact. Each diffraction pattern was the same as those of MCM-41 materials as described by Beck et al. [12].

3.3. Fourier transform infra red spectroscopy

Infra red spectroscopy had been used extensively for the characterization of transition-metal cation modified zeolites. The as-synthesized Zn–Al-MCM-41 and

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Zn contenta (wt%)</th>
<th>Al contenta (wt%)</th>
<th>d-spacingb (Å)</th>
<th>Unit cell parametera, b a₀ (Å)</th>
<th>Surface areab (m²/g)</th>
<th>Pore sizeb D (Å)</th>
<th>Pore volumeb (cm³/g)</th>
<th>Wall thicknessd (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-MCM-41(21)</td>
<td>–</td>
<td>0.499</td>
<td>38.41</td>
<td>44.35</td>
<td>830</td>
<td>27.5</td>
<td>0.866</td>
<td>16.85</td>
</tr>
<tr>
<td>Al-MCM-41(42)</td>
<td>–</td>
<td>0.234</td>
<td>39.26</td>
<td>45.33</td>
<td>880</td>
<td>29.8</td>
<td>0.907</td>
<td>15.53</td>
</tr>
<tr>
<td>Al-MCM-41(62)</td>
<td>–</td>
<td>0.159</td>
<td>41.09</td>
<td>47.44</td>
<td>920</td>
<td>32.1</td>
<td>0.958</td>
<td>15.34</td>
</tr>
<tr>
<td>Al-MCM-41(83)</td>
<td>–</td>
<td>0.122</td>
<td>43.09</td>
<td>49.76</td>
<td>978</td>
<td>34.6</td>
<td>0.976</td>
<td>15.10</td>
</tr>
<tr>
<td>Al-MCM-41(104)</td>
<td>–</td>
<td>0.982</td>
<td>44.84</td>
<td>51.78</td>
<td>1099</td>
<td>36.8</td>
<td>0.996</td>
<td>14.94</td>
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<tr>
<td>Zn–Al-MCM-41(75)</td>
<td>0.123</td>
<td>0.220</td>
<td>37.91</td>
<td>43.77</td>
<td>820</td>
<td>22.8</td>
<td>0.852</td>
<td>20.97</td>
</tr>
<tr>
<td>Zn–Al-MCM-41(151)</td>
<td>0.060</td>
<td>0.123</td>
<td>38.41</td>
<td>44.35</td>
<td>867</td>
<td>25.6</td>
<td>0.893</td>
<td>18.75</td>
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<tr>
<td>Zn–Al-MCM-41(228)</td>
<td>0.040</td>
<td>0.079</td>
<td>38.91</td>
<td>44.92</td>
<td>912</td>
<td>27.0</td>
<td>0.944</td>
<td>17.90</td>
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<tr>
<td>Zn–Al-MCM-41(304)</td>
<td>0.031</td>
<td>0.060</td>
<td>39.98</td>
<td>46.15</td>
<td>970</td>
<td>29.3</td>
<td>0.963</td>
<td>16.85</td>
</tr>
<tr>
<td>Zn–Al-MCM-41(380)</td>
<td>0.020</td>
<td>0.049</td>
<td>41.09</td>
<td>47.44</td>
<td>1071</td>
<td>32.2</td>
<td>0.983</td>
<td>15.20</td>
</tr>
</tbody>
</table>

a The results obtained from ICP-AES.
b Values obtained from XRD studies.
c Values obtained from N₂-adsorption results.
d Wall thickness (t)=unit cell parameter (a₀) – pore size (D).
Fig. 1. (a) X-ray diffraction patterns of calcined Al-MCM-41 samples and (b) X-ray diffraction patterns of calcined Zn–Al-MCM-41 samples.

Fig. 2. (a) FTIR spectra of Zn–Al-MCM-41 samples (a—as-synthesized and c—calcined) and (b) FTIR spectra of Al-MCM-41 samples (a—as-synthesized and c—calcined).
Al-MCM-41 samples exhibit absorption bands around 2921 and 2851 cm\(^{-1}\) corresponding to \(n\)-C–H and \(\delta\)-C–H vibrations of the surfactant molecules (Fig. 2a and b). The broad bands around 3500 cm\(^{-1}\) have concluded that water molecules are adsorbed on the surface silanol groups (Si–OH) but not on Si–O–Si groups [28]. It can therefore be reasoned that the hydrophobic character of the dehydroxylated \(\text{SiO}_2\) surface is due to the non-polar Si–O–Si groups. Because the pores of mesoporous materials, which consist mainly silica, are constructed with tetrahedral \(\text{SiO}_4\), ideal pores do not possess silanol groups and should be highly hydrophobic. The hydrophobicity in Zn–Al-MCM-41(75) is higher than that of Al-MCM-41 and other Zn–Al-MCM-41 due to the higher negative ions and highly exchangeable capacity within the pore by increasing of zinc ions. However, if some \(\text{Si}^{4+}\) atoms becomes partly substituted by \(\text{Al}^{3+}\) and \(\text{Zn}^{2+}\) atoms, a negative charge would result on the oxygen atom of \((\text{AlO}_4)^-\) and \((\text{ZnO}_4)^2-\) respectively. Each Zn-ion in Zn–Al-MCM-41 is donated two negative ions but, Al-ion is donated one negative ion on silica surface. While deformational vibrations of adsorbed molecules cause the adsorption bands at 1623–1640 cm\(^{-1}\). The substitution of silicon by zinc and aluminum causes shifts of the lattice vibration bands to lower wavenumbers. Compared to the Si-MCM-41, the wave number of the anti-symmetric Si–O–Si vibration band of Al-MCM-41 and Zn–Al-MCM-41 samples decreases to 1083 and 1096 cm\(^{-1}\), respectively (Fig. 2a and b). Theses shifts should be due to the increase of the mean Si–O distance in the walls caused by the substitution of the small silicon (radius 40 pm) by the larger size of \(\text{Zn}^{2+}\) (radius 74 pm) and \(\text{Al}^{3+}\) (radius 53 pm) [29]. The observed shifts, which depend as well on the change in the ionic radii as on the degree of substitution, are comparatively small. Therefore, only a low degree of substitution is suggested. Interestingly, the wavenumber shifts decrease in the series Al-MCM-41 > Zn–Al-MCM-41, although the ionic radius of aluminum is smaller than those of zinc. While the wave number of the anti-symmetric Si–O–Al and Si–O–Zn vibration bands of Al-MCM-41 and Zn–Al-MCM-41 samples decreases to 955 and 965 cm\(^{-1}\), receptively (Fig. 2a and b). By the disappearing peaks at 2851 and 2921 cm\(^{-1}\), one could conclude that calcination of the original framework was complete and the identity of organic molecule completely disappeared from the calcined Zn–Al-MCM-41 (Fig. 2a) and Al-MCM-41 (Fig. 2b).

Upon introduction of higher metal content, most of the bands shifted to higher wave numbers, consistent with their incorporation in lattice positions. Additionally, an absorption band in the range 953–967 cm\(^{-1}\) assigned to a stretching vibration of Si–O–M\(^{+}\) linkage was observed (Fig. 2a and b). This is generally considered to be a proof of the incorporation of the heteroatom into the framework. Cambler et al. [30] have reported similar stretching vibrations of Si–OH groups present at defect sites.

### 3.4. Thermal analysis

Thermogravimetric analysis of the catalysts show distinct weight losses that depend on framework composition. Representative thermograms are given in Fig. 3a (Zn–Al-MCM-41) and 3b (Al-MCM-41). Generally, when the metal content increases, there is a decrease in organic content and increase in water content. Three distinct regions of weight loss are noted in the temperature range 50–150, 150–350 and 350–550 °C. The first weight loss (~4.6–16.6%) corresponds to the desorption and removal of the water and/or ethanol molecules physisorbed on the external surface of the crystallites or occluded in the macropores and mesopores present between the crystallites aggregates. A second weight loss (~38.58–40.5%), between 150 and 350 °C is attributed to the removal of the organic template. Finally, a third weight loss (~1.51–1.9%) between 350 and 550 °C is related to water loss from the condensation of adjacent silanol groups to form siloxane bond [31]. The total weight loss at 1000 °C of the Zn–Al-MCM-41 and Al-MCM-41 samples are in the 44.69–59.01% range. However, the distribution of successive weight loss depends on the framework or substituted silicon to metal ratio [32]. Thus, weight loss was higher in the low metal contents of MCM-41 materials than that in the high metal contents of MCM-41 materials.

### 3.5. Adsorption isotherm of nitrogen

Fig. 4a and b illustrate the isotherm of nitrogen adsorption by calcined Zn–Al-MCM-41 and Al-MCM-41 respectively, measured at liquid nitrogen temperature (77 K). Three well-defined stages may be identified: (1) A slow increase in nitrogen uptake at low relative pressure, corresponding to monolayer–multilayer adsorption on the pore walls; (2) a sharp step at intermediate relative pressures indicative of capillary condensation within mesopores; and (3) a plateau with a slight inclination at high relative pressures associated with multilayer adsorption on the external surface of the crystals [33]. A fourth stage, characterized by a sharp rise in \(N_2\) uptake filling all other available pores as the pressure reaches saturation (\(\phi/\phi_0=1.0\)), may be identified in some isotherms. Each isotherm showed type IV character, which is a typical shape for mesoporous MCM-41. The adsorbed amount increased gradually with increasing relative pressure by multilayer adsorption. A steep rise in the adsorbed amount was observed at a relative pressure in the range of 0.2–0.44 and 0.21–0.48 being caused by capillary condensation of nitrogen in the mesopores in the range of 27.5–36.8 and 22.8–32.2 Å diameter in the Al-MCM-41 and Zn–Al-MCM-41 respectively. This rise
became more gentle and was shifted to lower relative pressure with increasing metal content, which suggests that the pore size was narrowed and distributed. In the figures, the desorption phenomena can also be seen along with the adsorption isotherms of each sample. The specific surface area values of samples determined by the BET method lie in the range of 830–1099 and 820–1071 m²/g for Al-MCM-41 and Zn–Al-MCM-41 respectively. The surface area, pore size, pore volume and wall thickness are given in Table 1. It is observed that as the silicon to metal ratio decreases in the range 380–75 for Zn–Al-MCM-41 and 104–21 for Al-MCM-41 (the concentration of metal ion increases accordingly), the surface area, pore diameter and pore volume decrease while the wall thickness increases for both Al and Zn incorporation. This may be due to the creation of negative charge raised on the surface of pore walls by increasing Zn²⁺ and Al³⁺ ions. The average pore diameter became narrowed by the increasing of metal ions incorporation.

The remarkable improvement of hydrothermal stability due to the higher metal-incorporation is further evidenced by the measurement of N₂-adsorption. The surface areas of all the MCM-41 materials were measured after they had been treated in boiling water for 1 week. The surface areas slightly decreased from 830–1099 to 801–980 m²/g in the Al-MCM-41 samples and also slightly decreased from 1071 to 1020 m²/g in Zn–Al-MCM-41 (380), but the surface area does not decrease in other Zn–Al-MCM-41 samples [24]. The Si–O–Al and Si–O–Zn bonds are relatively stable to further attack from boiling water [34]; the presence of Al³⁺ and Zn²⁺ creates a negative charge on the surface of the pore walls, repelling OH⁻ ions and therefore, preventing the hydrolysis of siloxane bonds and also resulting in an increase in the number of acid sites. The surface area in the Al-MCM-41 and Zn–Al-MCM-41 (380) samples decreased due to low metal incorporation/non-framework as it does not create sufficient negative charges on the surface of the pore walls. But the surface area of other Zn–Al-MCM-41 samples does not decrease due to repelling OH-ions higher on the pore walls. Hence, it is concluded that Zn is irreversibly incorporated into the structure of Zn–Al-MCM-41 samples. Thus the hydrothermal stability is higher in Zn–Al-MCM-41 (75) than that in other Zn–Al-MCM-41 and Al-MCM-41 samples.

### 3.6. Solid-state NMR spectroscopy

Fig. 5a shows solid-state ⁷⁷Al-MAS spectra of Al-MCM-41 of different Si/Al ratios 21, 42, 62, 83 and 104. Each chemical shift peak spectrum shows a strong
and sharp signal at 53 ppm as well as a weak and broad signal at around 0 ppm regardless of the Al content. The signal at around 53 ppm could be assigned to tetrahedrally coordinated framework aluminum (T\(_4\)-Al), which was observed in aluminosilicate zeolites [35]. The signal at around 0 ppm was ascribed to octahedrally coordinated (O\(_6\)) non-framework aluminum [35]. Kosslick et al. [36] reported that calcinations of the as-synthesized Al-MCM-41 to remove the template led to the appearance of a signal at −5 ppm assigned to octahedrally coordinated extraframework aluminum species. Similarly, in the present study, the signal at around 0 ppm assigned to O\(_6\)-Al would be extraframework species formed intrinsically during synthesis. The signal assigned to non-framework T\(_4\)-Al, observed at 30–40 ppm as an Al residue in dealuminated zeolites [37] was not clearly seen in the present case. The aluminum was then incorporated mainly with tetrahedral coordination.

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Fig. 4. (a) N\(_2\)-adsorption isotherms of calcined: (A) Zn–Al-MCM-41(75), (B) Zn–Al-MCM-41(122) and (C) Zn–Al-MCM-41(380); (b) N\(_2\)-adsorption isotherms of calcined: (A) Al-MCM-41(21), (B) Al-MCM-41(62) and (C) Al-MCM-41(104).
in the MCM-41 framework. The intensities of these signals increased with increasing Al content or with low Si/Al ratio. This result suggests that the amount of T-Al in the MCM-41 structure can be regulated by controlling the ratio of sodium metasilicate and aluminum sulfate.

When the sample containing more Al was calcined, a substantial intensity loss of the Si(2Si, 2Al) and Si(3Si, 1Al) occurred, while octahedral aluminum appeared. These results could be explained by assuming that calcination leads to “dealumination”. It is important to bear in mind these results when considering the use of these materials for acid-catalyzed reactions, in which the Bronsted acidity should be associated to the presence of tetrahedral aluminum and also Lewis acidity should be associated to the presence of octahedral aluminum. But Bronsted acidity is higher than Lewis acidity due to higher aluminum tetrahedral coordinated on the silica surface.

Fig. 5b shows solid-state $^{27}\text{Al}$-MAS spectra of Zn–Al-MCM-41 of different Si/(Zn+Al) ratios 75, 151, 228, 304 and 380. Each chemical shift peak spectrum shows a strong and sharp signal at 0 ppm regardless of the Al content. The intensities of these signals increased with increasing Zn$^{2+}$ and Al$^{3+}$ ions content or with low Si/Zn+Al ratio. From the above results, it is inferred that when the Zn$^{2+}$ ion is incorporated in the Al-MCM-41, the Al$^{3+}$ ion is non-framework on the silica surface under ion-exchange method. Thus the Lewis acidity should be associated with the presence of octahedral aluminum in the Zn–Al-MCM-41.

3.7. Scanning electron microscopy

All calcined Zn–Al-MCM-41, Al-MCM-41 materials are having micellar rod-like shape hexagonal or spherical edges, as shown in the Fig. 6a (Zn–Al-MCM-41(75)) and 6b (Al-MCM-41(21)). Each rod, itself transformed into the MCM-41 hexagonal-phase mesostructure. Because all materials have been synthesized using cetyltrimethylammonium bromide as surfactant in the liquid crystal template mechanism, Steel et al. [38] postulated that CTMABr surfactant molecules assembled directly into the hexagonal liquid crystal phase upon addition of the silicate species, based on $^{13}$NMR spectroscopy.

3.8. Transmission electron microscopy

The TEM image of all calcined Zn–Al-MCM-41 and Al-MCM-41 (Fig. 7a for Zn–Al-MCM-41(304) and 7b for Al-MCM-41(83)) samples exhibit ordered hexagonal arrays of mesopores with uniform pore size [11]. The corresponding electron diffraction pattern also shows reflections contrast in the TEM image of the sample, the distance between mesopores are estimated, in good agreement with the value determined from XRD and N$_2$-adsorption measurements values.

Both pore channels and hexagonal symmetry can be clearly identified in the TEM image for a large number of Zn–Al-MCM-41 and Al-MCM-41 samples which indicates that the MCM-41 samples have only one uniform phase as inferred from the XRD results. The pore sizes, as observed by TEM analysis, are in agreement with the results obtained from N$_2$-adsorption measurements.

3.9. X-ray photon spectroscopy

X-ray photoelectron spectroscopy (XPS) was performed so as to determine the distribution of Zn and
Al, and also to characterize the Al and Zn species on the external surface of the MCM-41 sample. The surface Si/Zn+Al, Si/Al ratio and binding energies (BE) for Zn–Al-MCM-41 and Al-MCM-41 samples with different Si/Zn+Al and Si/Al ratios respectively, along with data for related reference materials are given in Table 2. The surface Si/M (M=Al, Zn and both metals) ratio of the metal incorporated samples indicate that the surface/near surface region has high metal content while Zn-ion penetrates the small particles to a greater extent. This is consistent with the incorporating procedure in which metals first come in contact with the outer surface of the silica matrix before being distributed into the bulk. The metal content increases with increasing binding energies of Zn 2p, Al 2p, Si 2p and O 1s.

Table 2
Binding energies for Al-MCM-41 and Zn–Al-MCM-41 samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>Binding energies/eV</th>
<th>Zn 2p</th>
<th>Al 2p</th>
<th>O 1s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si 2p</td>
<td>Zn 2p</td>
<td></td>
<td>Al 2p</td>
</tr>
<tr>
<td>Al-MCM-41(21)</td>
<td>290.5</td>
<td>–</td>
<td>74.6</td>
<td>102.9</td>
</tr>
<tr>
<td>Al-MCM-41(42)</td>
<td>290.4</td>
<td>–</td>
<td>74.5</td>
<td>102.8</td>
</tr>
<tr>
<td>Al-MCM-41(62)</td>
<td>290.3</td>
<td>–</td>
<td>74.4</td>
<td>102.7</td>
</tr>
<tr>
<td>Al-MCM-41(83)</td>
<td>290.2</td>
<td>–</td>
<td>74.3</td>
<td>102.5</td>
</tr>
<tr>
<td>Al-MCM-41(104)</td>
<td>290.1</td>
<td>–</td>
<td>74.2</td>
<td>102.3</td>
</tr>
<tr>
<td>Zn–Al-MCM-41(75)</td>
<td>289.1</td>
<td>1024.1</td>
<td>74.9</td>
<td>103.7</td>
</tr>
<tr>
<td>Zn–Al-MCM-41(151)</td>
<td>288.8</td>
<td>1023.7</td>
<td>74.8</td>
<td>103.5</td>
</tr>
<tr>
<td>Zn–Al-MCM-41(228)</td>
<td>288.5</td>
<td>1023.5</td>
<td>74.5</td>
<td>103.3</td>
</tr>
<tr>
<td>Zn–Al-MCM-41(304)</td>
<td>288.3</td>
<td>1023.3</td>
<td>74.4</td>
<td>103.1</td>
</tr>
<tr>
<td>Zn–Al-MCM-41(380)</td>
<td>288.1</td>
<td>1023.0</td>
<td>74.3</td>
<td>103.0</td>
</tr>
</tbody>
</table>
3.10. Acidity of Al-MCM-41 and Zn–Al-MCM-41

The acidities of the Al-MCM-41 and Zn–Al-MCM-41 samples were characterized by the TPD-pyridine and FTIR-pyridine.

3.10.1. Total acidity strength

The acidities of the Zn–Al-MCM-41 and Al-MCM-41 samples were characterized by the TPD of pyridine. The acidities (mmol/g) based on the pyridine desorbed by the samples beyond 100 °C are presented in Table 3. As the zinc and aluminum content increases, the total acidity for Zn–Al-MCM-41 increases in the samples with Si/Zn+Al ratio 75>151>228>304>380. Similarly, for Al-MCM-41, the total acidity increases in the order Si/Al ratio 21>42>62>83>104.

3.10.2. Bronsted and Lewis acidity

As one of the major fields of application of Zn–Al-MCM-41 and Al-MCM-41 are used as acid catalysts, characterization of the acidity of the above catalysts is very important. The infrared spectra region of the pyridine adsorbed on the Zn–Al-MCM-41 and Al-MCM-41 are in the region 1700–1270 cm⁻¹. Pyridine vapor was adsorbed at 159 °C for 1 h on the sample and then outgassed at the same temperature for 30 min. FTIR spectra were recorded at room temperature. All the samples show the expected bands due to hydrogen bonded pyridine (1444 and 1597 cm⁻¹), Lewis-bound pyridine (1455, 1576 and 1623 cm⁻¹), pyridine bound on Bronsted acid sites (1546 and 1638 cm⁻¹), and a band at 1496 cm⁻¹ attributed to pyridine associated with both Lewis and Bronsted acid sites [39]. The Bronsted acid sites and Lewis acid sites with various temperatures in different Si/(Zn+Al)- and Si/Al-ratio containing MCM-41 samples are listed in Table 3. In the Zn–Al-MCM-41, the number of Bronsted acid sites and Lewis acid sites are same. The number of both the acid sites increases with increasing zinc and aluminum content due to replacing the tetrahedral aluminum-ions by zinc ions under ion-exchange method; however, the zinc ion produced two negative ions at the tetrahedral position, and the replaced aluminum is non-framework on the silica surface. The Zn–Al-MCM-41 sample exhibits absorption bands around 1444 and 1597 cm⁻¹ due to hydrogen-bonded pyridine in the temperature range from room temperature – 300 °C. Both Lewis and Bronsted acid (L+B) sites decreases with increasing temperature due to the desorbed pyridine molecule and as shown in Fig. 8a for the Zn–Al-MCM-41(151).

The number of Bronsted acid sites and Lewis acid sites with various temperatures in different Al-MCM-41 samples and as listed in Table 3. In Al-MCM-41, the number of Bronsted acid sites increases with increasing aluminum content due to the 90% aluminum tetrahedrally coordinated to silica matrix. Thus the numbers of Bronsted acid sites are higher than the Lewis acid sites in Al-MCM-41 materials. The number of Bronsted acid sites (1545 cm⁻¹) increases and also both Lewis and Bronsted (L+B) sites (1495 cm⁻¹) increases with increasing temperatures (up to 300 °C) due to the desorbed pyridine molecule and as shown in Fig. 8b for the Al-MCM-41(42).


Table 3

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Total acidity from TPD-pyridine studies (mmol pyridine/g)</th>
<th>Bronsted acidity (μmol pyridine/g)</th>
<th>Lewis acidity (μmol pyridine/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature (0 °C)</td>
<td>R 100  200  300</td>
<td>Temperature (0 °C)</td>
</tr>
<tr>
<td>R</td>
<td>100  200  300</td>
<td>R 100  200  300</td>
<td>R 100  200  300</td>
</tr>
<tr>
<td>Al-MCM-41(21)</td>
<td>0.099</td>
<td>23.8 18.3 12.3 11.3</td>
<td>11.9 10.3 8.3 6.3</td>
</tr>
<tr>
<td>Al-MCM-41(42)</td>
<td>0.092</td>
<td>18.5 15.4 10.4 10.1</td>
<td>9.25 8.5 6.7 4.2</td>
</tr>
<tr>
<td>Al-MCM-41(62)</td>
<td>0.073</td>
<td>15.3 12.3 8.3 8.0</td>
<td>7.65 6.35 5.2 3.5</td>
</tr>
<tr>
<td>Al-MCM-41(83)</td>
<td>0.052</td>
<td>12.4 10.4 4.5 4.0</td>
<td>6.20 5.40 4.5 3.2</td>
</tr>
<tr>
<td>Al-MCM-41(104)</td>
<td>0.031</td>
<td>10.2 8.5 4.0 3.8</td>
<td>5.10 4.80 3.7 2.8</td>
</tr>
<tr>
<td>Zn–Al-MCM-41(75)</td>
<td>0.103</td>
<td>27.5 20.3 2.3 13.5</td>
<td>40.3 35.6 30.5 25.3</td>
</tr>
<tr>
<td>Zn–Al-MCM-41(151)</td>
<td>0.095</td>
<td>23.4 19.2 16.3 12.4</td>
<td>38.3 30.3 27.3 23.5</td>
</tr>
<tr>
<td>Zn–Al-MCM-41(228)</td>
<td>0.076</td>
<td>19.5 17.3 14.2 10.3</td>
<td>25.4 24.5 24.3 20.2</td>
</tr>
<tr>
<td>Zn–Al-MCM-41(304)</td>
<td>0.055</td>
<td>17.4 15.4 12.4 6.7</td>
<td>20.6 20.4 20.3 18.3</td>
</tr>
<tr>
<td>Zn–Al-MCM-41(380)</td>
<td>0.035</td>
<td>14.3 13.2 9.5 5.3</td>
<td>17.7 15.3 14.5 15.6</td>
</tr>
</tbody>
</table>

*R*—Room temperature.

*Values obtained from FTIR-Pyridine studies.*
4. Conclusions

Mesoporous Zn–Al-MCM-41 and Al-MCM-41 molecular sieves with different Si/Zn + Al and Si/Al ratio respectively, were synthesized using sodium metasilicate, zinc chloride, aluminum sulfate as the reagents in sulfuric acid medium and cetyltrimethylammonium bromide as the template under hydrothermal conditions. From the physico-chemical characterization of the materials it was concluded that all the synthesized materials have good Zn–O–Si and Al–O–Si framework, high surface area, good hydrothermal stability and good hydrophobicity. The acid sites in the Zn–Al-MCM-41 are higher than that of Al-MCM-41 due to the aluminum ions non-framework by the introduction of zinc ions. Thus Bronsted and Lewis acid sites in Zn–Al-MCM-41 are same, but its acid sites are higher than Al-MCM-41.

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References


