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Mesoporous materials prepared using coal fly ash as the silicon and aluminium source

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Coal fly ash was converted into two types of porous materials, MCM-41 and SBA-15 (both of hexagonal structure), using the supernatant of the fly ash. It was found that most of the Si and Al components in the fly ash could be effectively transformed into mesoporous materials, depending on the hydrothermal conditions, and that fusion is essential. Investigation by ^{29}Si and ^{27}Al MAS NMR demonstrated that fusion plays an important role in enhancing the hydrothermal conditions for synthesis of these materials. A high concentration of Na ions in the supernatant of the fused fly ash was not found to be critical in the formation of Al-MCM-41 when prepared under controlled pH conditions. Pyridine adsorption experiments on Al-MCM-41 prepared from coal fly ash revealed the presence of Brönsted and Lewis acid sites. It was also found that the catalytic activity in the cumene cracking reaction is linked only to the accessible aluminium, and not to the total incorporated aluminium present in the Al-MCM-41.

Introduction

Porous solids are an important class of materials due to their wide applications in various separation, purification and catalytic processes. Although there are many kinds of amorphous porous materials which contain micropores, mesopores and macropores, there were no materials possessing uniform mesopores until the early 1990s, when Kuroda *et al.* and Mobil scientists first reported the M41S family of materials.[1,2] Presently, however, both the economic and environmental costs for the large-scale manufacture of these materials are high due to the cost and toxicities of both the templates and the preferred silica source. A variety of silica sources have been reported, including sodium silicate and silicon tetraethoxide.[3] Interestingly, the original work by Mobil was performed using a synthetic precipitated silica[1] and many researchers favor the use of solid fumed silica.[4] The industrial manufacture of mesoporous materials is likely to be economically prohibitive if silicon alkoxides and fumed silica in particular are selected.

Coal combustion in the world accounts for about 37% of the total electricity production and, in turn, results in huge amounts of fly ash as waste material.[5] The problem with fly ash lies in the fact that its disposal requires large quantities of land and water. In addition to that, if not managed well, its fine particles can become airborne by virtue of their very low masses.[6,7] Nearly 500 million metric tons of fly ash are produced annually in the world, with a global recycling rate of only 15%.[8] Most of the ash is at present used as a fine aggregate to substitute for portland cement in concrete, deposited in landfills and/or coal mines or sea-side docking areas and used as a lining for hazardous waste dumps. Since the major chemical compounds contained in fly ash are SiO_2 and Al_2O_3 (60–70 wt% and 16–20 wt%, respectively), resource recovery from coal fly ash is one of the most important issues in waste management at present.[5–8] Recently, intensive efforts have been made to promote the recycling of fly ash through its zeolitization. These treated fly ash materials (zeolite-like) with relatively higher cation exchange capacities (CECs) were used to evaluate the practical application of removing heavy metals or ammonia from waste water.[9]

Conventionally, coal fly ash has been converted to microporous materials (zeolites) by alkaline hydrothermal treatment, which is analogous to the formation of natural zeolites from volcanic deposits.[9,10] Several groups around the world have studied the conversion of fly ash into zeolites.[7–15] Very recently, a molten-salt method involving thermal treatment with $NaOH$–$NaNO_3/KNO_3$ without any addition of water at very high temperature was also suggested as an alternative for fly ash conversion into zeolites.[7,10] However, in all these studies the zeolite products still contain significant amounts of residual fly ash. In addition to that, the co-existance of several crystalline phases and the presence of impurities are typical characteristics of such zeolite materials and therefore limit their applications.[16] We have also studied the synthesis of a variety of zeolites using the fusion approach and, under controlled synthesis conditions, we were successful in preparing pure zeolites.[17] The use of coal fly ash as a silica and aluminium source for the preparation of mesoporous materials is very rare in the literature[18] and has not been explored in detail. Here, we report the direct synthesis of Al-MCM-41 showing increased stability and a periodic pore structure by appropriate pH adjustment using coal fly ash as the source of silica and aluminium. The aluminium-containing MCM-41 thus obtained has been further tested for acidity and as a catalyst for cumene cracking. An attempt has also been made to prepare siliceous SBA-15-type material using coal fly ash for the first time.

Experimental

Materials

The coal fly ash used in this study was obtained from the Nanao-Ota power plant, Hokuriku, Japan, and was used as obtained, its chemical composition was analyzed and is listed in Table 1. Apart from the main constituents such as silica and alumina, the other impurities found in the ash were Fe_2O_3,

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Table 1 Elemental compositions (wt%) of coal fly ash, fused fly ash powder and the materials synthesized

Sample	Elemental compositions/wt% Si	Al	Na	K
Coal fly ash	31.357	10.149	0.241	0.441
Fused fly ash	27.866	8.173	26.865	nd
Al-MCM-41	33.015	2.301	1.618	nd
SBA-15	34.357	0.005	0.041	nd

CaO, MgO, K_2O, TiO_2, Cr_2O_3, P_2O_5 and SO_3 with contents of 3.6, 2.0, 0.7, 0.9, 0.8, 0.9, 0.3 and 0.7%, respectively. The specific surface area (BET) and cation exchange capacity (CEC) of the coal fly ash were found to be 4.5 $m^{2\ -1}$g and 0.8 meq per 100 g, respectively.

Synthesis of Al-MCM-41

The surfactant used in the synthesis of the MCM-41 was $C_{16}H_{33}(CH_3)_3NBr$ (CTAB). Because larger amounts of Si and Al species can be dissolved by employing the fusion method, we adopted this approach in our study. Coal fly ash was treated with sodium hydroxide (1 : 1.2, fly ash : alkali by weight) at 823 K for 1 h to obtain a fused mass, which was cooled to room temperature and milled overnight. The obtained fused fly ash powder was mixed with water in a weight ratio of 1 : 4 and aged for 1 day at room temperature with agitation. The resultant suspension was then filtered to obtain the supernatant. The concentrations of Si, Al and Na in the supernatant measured by atomic absorption spectroscopy (Perkin Elmer AS-800) are 11000, 380 and 35000 ppm, respectively. In a typical MCM-41 synthesis, 0.867 g of $C_{16}H_{33}(CH_3)_3NBr$, 15 ml water and 0.75 g aq. NH_4OH were combined with 38 ml of the supernatant and the mixture hydrothermally treated at 97 °C for 4 days. The synthesis pH was threefold adjusted at 10.2 by using dilute acetic acid from time to time. For comparison, aluminium-containing MCM-41 was prepared by post-synthesis alumination of MCM-41 using trimethylaluminium [$Al(CH_3)_3$]. It was found that post synthesis alumination with $Al(CH_3)_3$ is effective for the incorporation of aluminium into the framework of MCM-41.[19] The siliceous MCM-41 was prepared by using pure chemicals following the procedure described in the literature.[20] The materials obtained were washed, dried and calcined at 550 °C for up to 8 h to decompose the surfactant.

Synthesis of SBA-15

The surfactant used in the synthesis of the SBA-15 was triblock polymer $(EO)_{20}(PO)_{70}(EO)_{20}$. SBA-15 was prepared by using a clear solution of 3.6 g of triblock polymer dissolved in 150.0 ml aq. HCl (2 M), and then 40.0 ml of the supernatant and 6.4 g of sodium metasilicate was added at room temperature under vigorous stirring. To this reaction mixture, 10.0 ml of 35% HCl and 50.0 ml of distilled water was quickly added. The resulting gel was aged at room temperature for 1 day and subsequently heated at 90 °C for 3 days. All samples were calcined at 550 °C for up to 6 h.

Analysis and characterization

Powder X-ray diffraction patterns were obtained using Cu-Kα radiation with a MAX18X^{CE}. The chemical composition was analyzed by the $Li_{12}B_4O_4$ method using the X-ray fluorescence (XRF) technique (Philips PW2400). BET surface area measurements were made by N_2 adsorption at liquid nitrogen temperature (Belsorp 28SA) and the morphology was ascertained by scanning electron microscopy (SEM) using a Hitachi S-4100. Transmission electron microscopy (TEM) was carried out with a JEOL 2010. The FT-IR spectra of self supporting wafers were measured with a JEOL JIR-7000. TG-DTA was performed using a Rigaku TG-8120. Solid-state ^{29}Si and ^{27}Al NMR spectra were obtained on a Varian VXP-400.

Catalytic activity

The cumene cracking was performed in an atmospheric pressure flow system. The sample was placed in the quartz tube reactor of 10 mm internal diameter and dehydrated at 673 K for 1 h in a nitrogen stream. The temperature was then brought up to reaction temperature (623 K). The reactant was fed into the catalyst bed with a micro-feeder. Nitrogen was used as the carrier gas (40 ml min^{-1}), the contact time (W/F) was 0.20 h, and the partial pressure of the cumene was 7.9 kPa. On-line product analysis was done on a Shimadzu GC-17A gas chromatograph (FID) with GL-Science TC-1 capillary column (30 m).

Results and discussion

The most important physical characteristics determining the reactivity of coal fly ash is the particle size. The mean particle size of the coal fly ash used in this study was 18.3 μm (Fig. 1). Generally, smaller particles are more easily cooled in the combustor, resulting in more disordered and more reactive species. Fig. 2 summarizes the XRD patterns of the fly ash (a) and the fused fly ash (b) at 823 K. It can be seen that the major crystalline phases found in the fly ash are quartz, mullite

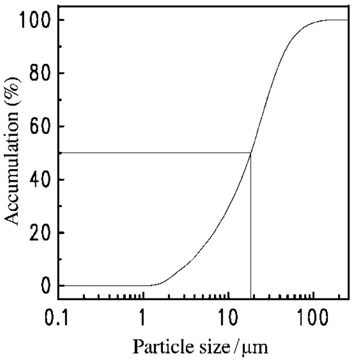

Fig. 1 Particle size distribution of coal fly ash.

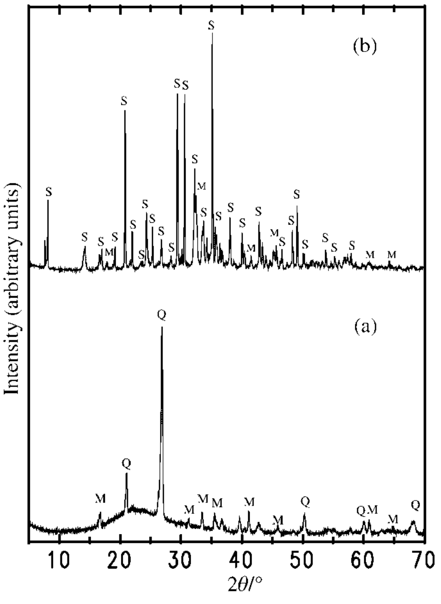

Fig. 2 X-Ray diffraction profiles of the fly ash (a) and the fused fly ash (b) at 823 K. M = mullite, Q = quartz, S = sodium silicate.

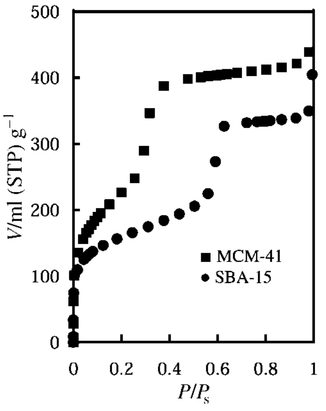

Fig. 3 N_2-adsorption isotherms for Al-MCM-41 and SBA-15.

and aluminosilicate glass and are contained as an amorphous phase. On the other hand, a large amount of sodium silicate exists in the fused fly ash [Fig. 2(b)], which implies that fusion is effective in extracting silicon from quartz. Most of the quartz and mullite species have reacted with the NaOH, resulting in the disappearance of their respective peaks in the fused fly ash pattern.

Fig. 3 shows the N_2-adsorption isotherm of the Al-MCM-41, featuring a type IV isotherm with a sharp capillary condensation step at P/P_s *ca.* 0.35, typical of a uniform material. Similarly, for SBA-15 this step occurs at P/P_s *ca.* 0.6, which is characteristic of capillary condensation with uniform pores. The P/P_s position of the inflection points is related to pore diameters in the mesopore range and the sharpness of these steps indicates the uniformity of the mesopores.

The XRD pattern of a calcined sample of the Al-MCM-41 [Fig. 4(a)] clearly displays at least four reflections that are consistent with indexing to a hexagonal cell, which is typical of an MCM-41 product. If we assume hexagonal pore symmetry, the main d_{100} peak at 3.87 nm corresponds to a unit cell with $a_o = 4.46$ nm. The observation of three higher angle reflections other than the d_{100} indicates that the product is likely to possess the symmetrical hexagonal pore structure typical of Al-MCM-41.

Fig. 4(b) shows the XRD pattern of the SBA-15 after calcination. The spectrum exhibits one very intense line and two weak lines, which testify to the excellent textural uniformity of the material. The X-ray diffraction data therefore indicates that the supernatant of the fused fly ash can be successfully used in the synthesis gel to prepare mesoporous materials which exhibit characteristics similar to those found in the literature.

A high Na ion concentration in the precursor solutions has been known to favor the formation of zeolite and hinder the formation of the Al-MCM-41 phase.[11] We observed that the high concentration of Na ions present in the supernatant of fused fly ash is not critical in the formation of the Al-MCM-41 when prepared under controlled pH conditions. The quality of the obtained Al-MCM-41 material is strongly influenced by the pH during the synthesis.[20,21] The Si/Al ratio and the yield of the Al-MCM-41 before the first pH adjustment indicate that essentially all the aluminium originally present in the supernatant was incorporated in the structure. The further increase of the Al-MCM-41 yield upon continued synthesis with pH adjustment, together with the observed increase in the Si/Al ratio suggest that the additional amounts of silica were incorporated as a consequence of the pH adjustment. For pure silica MCM-41, similar conclusions were drawn by Ryoo and Kim, who observed an increase in the yield of MCM-41 based on the amount of silica recovered,[20] and also by Edler and White, based on crystallite sizes determined from XRD line broadening.[22] However, in the case of the SBA-15, incorporation of aluminium into the siliceous framework was not observed because of the strongly acidic medium (2 M HCl), where most of the aluminium present in the supernatant remained in the dissolved state.

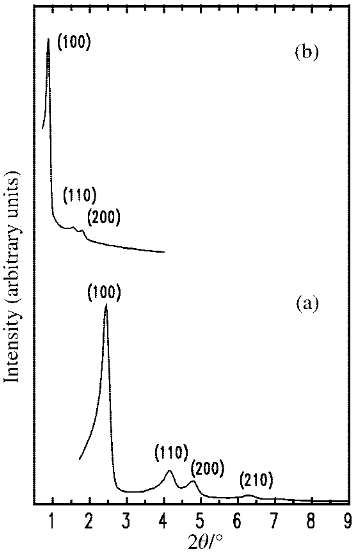

Fig. 4 XRD profiles of the Al-MCM-41 (a) and SBA-15 (b).

The other physicochemical properties of the typical products are presented in Table 2. We note that the BET surface areas and pore volumes of the samples prepared in this work are slightly lower than those that may be obtained from more reactive silica sources. The values obtained are nevertheless similar to those reported in the literature and indicate high overall total porosity. The calculated pore diameters and wall thicknesses are within the range of those that have been previously reported for Al-MCM-41 and SBA-15-type materials prepared from other silica sources.[3,20] Based on these observations, the possibilities of using the dissolved silica and aluminium present in the supernatant of fused fly ash as a precursor for the synthesis of porous materials are fairly good and this general approach can be used to prepare synthetic materials. However, the use of the high Si content fly ash would be a better choice.

Transmission electron microscopy images of micro-sectioned

Table 2 Physical properties of the raw material and the synthesized products

Sample	Si/Al	S_{BET}/m^2 g^{-1}	Pore volume[a]/ cm^3 g^{-1}	Pore diameter[a]/nm	d(100)/nm	a_o[b]/nm	Wall thickness[c]/nm
Fly ash	3.0	4.5	—	—	—	—	—
Al-MCM-41 (coal fly ash)	13.8	842	0.75	3.7	3.87	4.46	0.76
SBA-15 (coal fly ash)	653	483	0.53	5.5	10.03	11.58	6.08
Al-MCM-41[d]	17.9	940	0.85	2.7	4.01	4.60	1.9
SBA-15[d]	—	770	0.81	6.1	9.8	11.31	5.51

[a]Determined by the Dollimeore–Heal method. [b]Lattice parameter from XRD using the formula, $a_o = 2d(100)/\sqrt{3}$. [c]Pore wall thickness, a_o−pore diameter. [d]Pure samples prepared using standard methods.

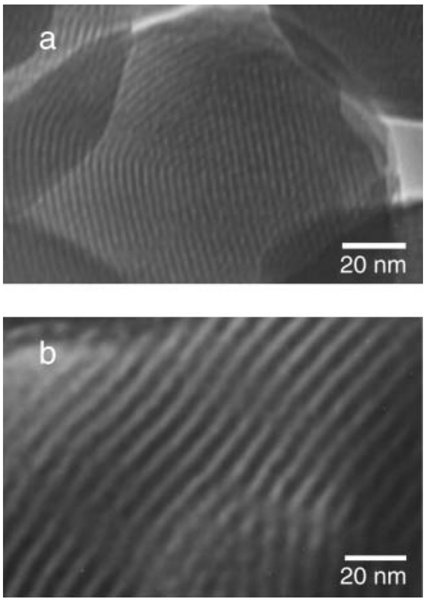

Fig. 5 TEM images of (a) Al-MCM-41 and (b) SBA-15, prepared using fly ash as the starting material.

samples (Fig. 5) show well-ordered hexagonal arrays of 1D mesoporous channels and confirm that the materials indeed possess the pore system symmetries that were inferred from the X-ray patterns and N_2 isotherms. Fig. 5(b) shows a TEM image of the SBA-15 sample. The distance between two consecutive corners of the hexagonal pores estimated from the TEM image is *ca.* 10 nm. The average thickness is around 6 nm, which is much larger than for the Al-MCM-41, and the pore diameter is around 5 nm, in agreement with the N_2-adsorption measurements. Although some areas (not shown) of the various samples are not highly ordered, significant areas of hexagonal order are observed, allowing the conclusion to be drawn that the materials are indeed porous structures.

To investigate the effect of alkali fusion at different fusion temperatures, and to obtain further information about the possible types of SiO_4 tetrahedra with neighboring AlO_4 tetrahedra, ^{29}Si MAS NMR spectra were measured for different samples. ^{29}Si MAS NMR experiments were performed at a resonance frequency of 79.49 MHz. Chemical shifts are referenced to DSS (1.53 ppm) and at least 2000 scans were acquired for each spectrum with a pulse length of 7.6 µs and a recycle time of 10 s. Fig. 6 shows ^{29}Si MAS NMR spectra for fly ash (a), fused fly ash powders obtained at 773 K (b) and 823 K (c) and Al-MCM-41-type material (d) prepared from fused fly ash powder (823 K). The most intense peak in spectrum (a), centered at -107 ppm, is assigned to highly polymerized Q^4 Si sites [Si(4Si)] and attributed to quartz. After fusion of the fly ash at 773 K [spectrum (b)], the Q^4 peak completely disappears and two marked peaks centered at *ca.* -76 and -85 ppm appear. The small peak at -76 ppm is assigned to Q^1 silicon sites [Si(1Si)], while the peak at –85 ppm is an indicative of either Si–O–Al linkages [Si(2Si, 2Al)] or Q^3 silicon sites [Si(3Si)OH)]. This implies that fusion can accomplish both depolymerization and dissolution of silicates and aluminosilicates from fly ash. The intensities of both these Q sites are significantly improved at the higher fusion temperature [spectrum (c)], suggesting more extraction. The spectrum of the calcined Al-MCM-41 [spectrum (d)] shows the presence of both Q^4 and Q^3 resonances at -109 and -102 ppm, respectively, which are significantly broader than is observed for pure SiO_2 materials. The presence of Q^3 and Q^4 species is evidence for a higher degree of condensation of the silanol groups when the synthesis is carried out with pH adjustment, and is in agreement with the findings of other authors.[19,20] Furthermore, the presence of a significant number of Al nuclei in the sample (Table 1) causes quadrupolar broadening of the Si signals observed in the spectrum of Al-MCM-41 [spectrum (d)].

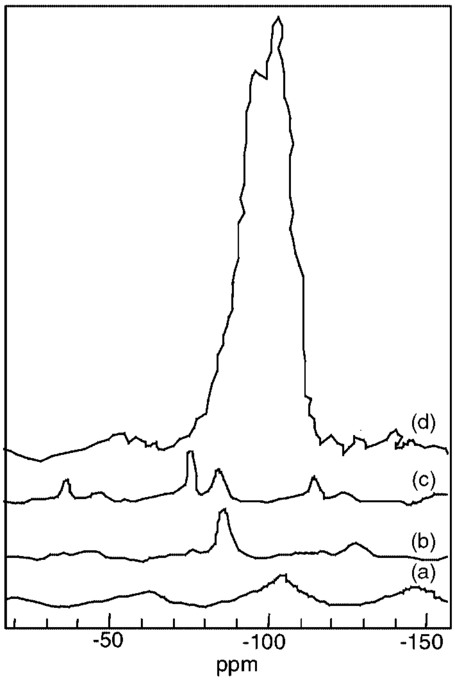

Fig. 6 ^{29}Si MAS NMR spectra for coal fly ash (a), fused fly ash powder obtained at 723 (b) and 823 K (c), and Al-MCM-41 from the supernatant of the fused fly ash powder obtained at 823 K (d).

In order to obtain information about the chemical state of the Al in the materials prepared, ^{27}Al MAS NMR spectra of the original coal fly ash (a) and calcined Al-MCM-41 (b) were measured (Fig. 7). Chemical shifts are referenced to 1 M $Al(NO_3)_3$ aqueous solution and the peak intensity was normalized based on 1 g of material. The spectrum of the fly ash does not show any peak, indicating the lack of any tetrahedrally (T_d) coordinated framework aluminium. However, a single very strong peak assigned to T_d framework

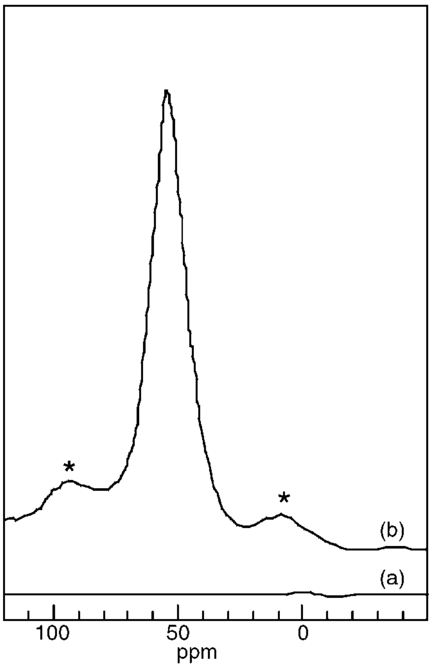

Fig. 7 ^{27}Al MAS NMR spectra for coal fly ash (a) and calcined Al-MCM-41 prepared from the supernatant of the fused fly ash solution (b). *Denotes the spinning side bands.

aluminium is observed at *ca.* 54 ppm for the sample prepared from fly ash. Despite the high aluminium concentration ($Si/Al = 13.8$) in this sample, no octahedral (O_h) non-framework aluminium peak (0 ppm) is seen. This provides direct evidence for Al incorporation in the MCM-41 framework. This result is also consistent with the retention of Q^3 Si species in the ^{29}Si NMR spectrum. It must be the unique chemical nature of the fly ash supernatant that favors T_d coordination. The other physicochemical properties (pore volume and wall thickness) are also consistent with high aluminium incorporation. In the earlier report on MCM-41 preparation from coal fly ash,[18] no such observations were made, due to the fact that the sample contained several impure phases, and direct evidence of Al incorporation in the MCM-41 phase was inconclusive. The ^{27}Al MAS NMR spectrum of SBA-15 (not shown) did not reveal the presence of any tetrahedral Al species in the framework, possibly be due to the very low pH synthesis conditions.

Fig. 8 shows the TGA curves for as-synthesized Al-MCM-41 samples prepared from coal fly ash (a) and pure chemicals (b). Two main weight losses in the samples are observed, as reported in the literature.[23] The first weight loss [*ca.* 5.6 and 5.8% for (a) and (b), respectively] between 298 and 400 K is due to adsorbed water and the second weight loss [*ca.* 37.7 and 38.7% for (a) and (b), respectively] between 400 and 1223 K is due to the decomposition of organic species. These TGA measurements indicate the different interactions of the associated template with the Al species and silanol groups. The total weight loss in both the samples is approximately 45%, in agreement with results reported by other workers.[1,23] SBA-15 prepared from coal fly ash showed a total weight loss of about 60%, associated with decomposition of the organic block polymer.

Acidity and catalytic activity

The incorporation of aluminium into silica structures is known to form acidic sites in the framework. The acidic properties of the Al-MCM-41 prepared from coal fly ash and pure chemicals were further evaluated by measuring the IR spectra of pyridine adsorbed on the samples. Pyridine vapor (*ca.* 1.3×10^2 Pa) was adsorbed at 423 K for 1 h on the samples. Fig. 9 shows the IR spectra of the samples [$Si/Al = 13.8$, 17.9 for spectra (a) and (b), respectively] after degassing at 423 K for 30 min. The spectra exhibit several peaks due to pyridinium ions on Brönsted acidic sites (1546 and 1641 cm^{-1}) and strongly Lewis-bound pyridine (1623 and 1456 cm^{-1}). The peak at 1494 cm^{-1} can be assigned to pyridine associated with both Brönsted and Lewis acidic sites.[24] Another peak due to hydrogen-bonded pyridine (1596 cm^{-1}) can also be seen. However, the majority of the acidic sites generated on both the samples were found to be Lewis acidic sites and the peaks arising from Brönsted acidic sites disappeared after thermal treatment at 523 K for 1 h, suggesting that the acidic strength of the Brönsted acidic sites in the Al-MCM-41 prepared is very weak. Nevertheless, it is interesting to observe the acidity in Al-MCM-41 derived from coal fly ash which confirms the aluminium incorporation suggested by the ^{27}Al MAS NMR analysis.

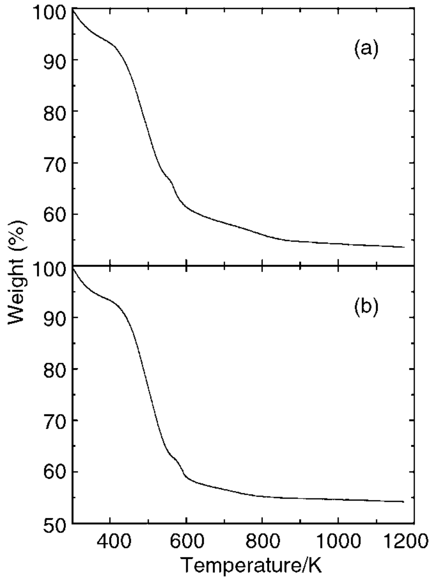

Fig. 8 TGA plots for Al-MCM-41 samples prepared from (a) coal fly ash and (b) pure chemicals.

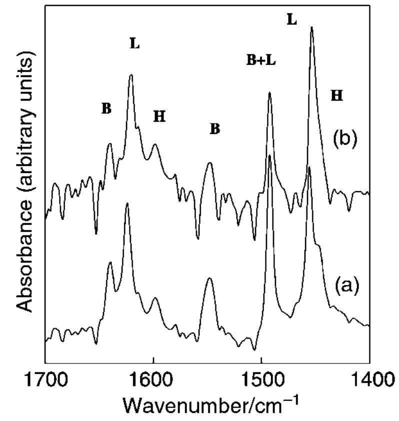

Fig. 9 Infrared spectra of pyridine adsorbed on Al-MCM-41 samples prepared using (a) coal fly ash and (b) pure chemicals. L: Lewis-bound pyridine; B: Brönsted-bound pyridine; H: H-bonded pyridine.

The catalytic activity of the Al-MCM-41 was also evaluated using the cumene cracking reaction, which requires medium to strong acidic sites.[25] The conversion of cumene obtained after different times on stream is illustrated in Fig. 10. The initial activity of the coal fly ash-derived material is lower compared to that of Al-MCM-41 prepared from pure chemicals. Taking into account the fact that a large difference in the intensity of the 1546 cm^{-1} IR absorption due to pyridine ions on Brönsted acidic sites was not observed between these two materials and that the peaks derived from Brönsted acidic sites disappeared after thermal treatment at 523 K, suggests that the acidic strength of Brönsted acid sites of Al-MCM-41 (pure chemicals) is similar to that of the material prepared from the supernatant of coal fly ash. In other words, all the aluminium present in the

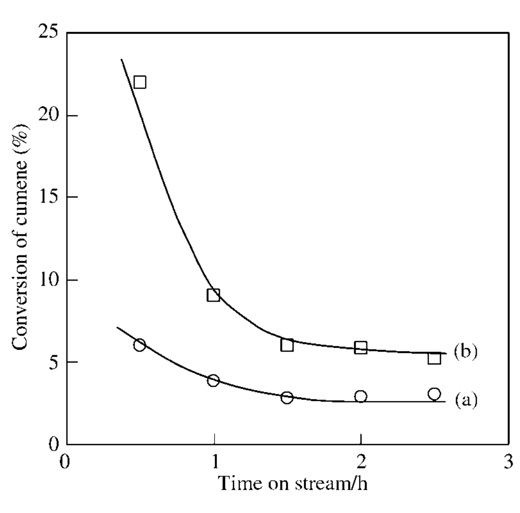

Fig. 10 Conversion profiles of cumene on Al-MCM-41 samples prepared from (a) coal fly ash and (b) pure chemicals. Reaction conditions: $T = 623$ K, $W/F = 0.2$ h, partial pressure of cumene = 7.9 kPa.

Al-MCM-41 prepared from fly ash is not catalytically active. A number of reports provide evidence for the partial inaccessibility of aluminium due to its incorporation in separate aluminium phases or in the MCM-41 walls if aluminium is added to the initial synthesis gel.[26,27] Our observations in this study provide further support for this point that the number of catalytic active sites is not connected with the aluminium concentration, but linked to the amount of accessible aluminium, preferably at the surface of the MCM-41 walls.

Conclusions

In summary, it has been shown that the intermediate adjustment of the pH of the synthesis gel during Al-MCM-41 formation using the supernatant of the coal fly ash is very effective. ^{29}Si MAS NMR data suggest that most of the quartz and mullite present in the fly ash, apart from the amorphous aluminosilicate glass, can be used as an aluminosilicate source. Very high aluminium incorporation in tetrahedral positions is revealed in Al-MCM-41 prepared using the fly ash and results in Brönsted and Lewis acidic sites which may be useful for certain catalytic applications. Furthermore, the preliminary results suggest the possibility of synthesizing highly ordered mesoporous silica using the supernatant of coal fly ash as the silica source and amphiphilic block copolymers as the structure-directing agents. The experimental data reported here suggest that coal fly ash could be a economical and environmentally friendly source of silicon/aluminium for the preparation of well-ordered mesoporous materials.

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