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Al_x^{n+}-grafted MCM-41 Catalysts: Probing the Influence of Temperature on the Alumination Process

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The influence of grafting temperature on Al-grafted MCM-41 catalysts prepared by reacting pure silica MCM-41 with aqueous solutions containing Al polycations was investigated by performing the alumination at room temperature (RT) or 80°C. Better retention of structural integrity was achieved at 80°C than at RT, and incorporation of Al was up to four times higher at 80°C. The higher Al content of materials grafted at 80°C translated to higher acid content and higher total conversions for the dealkylation of cumene. However, the catalytic activity per active site (TOF values) was higher for RT-grafted materials presumably due to better site isolation. © 2000 Academic Press

Key Words: **Al-grafted MCM-41; aluminosilicate MCM-41; alumination; grafting; grafting temperature; catalytic activity; acidity.**

INTRODUCTION

Mesoporous silicas such as MCM-41 possess uniform channels of diameter in the 20 to 100 Å range and are synthesized via a mechanism in which supramolecular assemblies of surfactant micelles act as structure directors for the organization of inorganic silicate precursors (1–3). There is currently considerable research interest in the preparation and use of heteroatom containing mesoporous silicas as heterogeneous catalysts (4–6). The incorporation of Al is particularly important as it gives rise to solid acid catalysts with acid sites associated with the presence of Al in framework positions. Al may be introduced into mesoporous silicates by direct (mixed-gel) synthesis (7–9) or by postsynthesis grafting methods (10–13). Recent studies have shown that unlike direct synthesis, incorporation of heteroatoms via postsynthesis grafting generates materials with readily accessible active sites on the inner walls of the mesoporous framework (10–15). Furthermore, for directly synthesized MCM-41 aluminosilicates, the presence of Al deep within the framework also results in an undesireable reduction in structural ordering and a lowering in thermal and hydrothermal ("steaming") stability (16, 17). Postsynthesis grafting of Al therefore offers distinct advantages over direct synthesis with respect to accessibility to active sites, structural ordering, and stability (12, 13, 18, 19). Due to the advantages it provides, grafting is likely to become an attractive alternative route for the preparation of mesoporous aluminosilicates derived not only from MCM-41 but also from other forms of mesoporous silicas (MCM-48, KIT-1, SBA-*n* and MSU-*n*), and therefore it deserves further investigation.

Several methods have so far been described for the postsynthesis alumination of MCM-41 using various sources of Al in either aqueous or nonaqueous media (10, 11, 18, 19). In general, alumination has been performed at temperatures below 80°C and in most cases at room temperature. There has however been no systematic study on the effect of grafting temperature on the alumination process and on the properties of the resulting aluminosilicate MCM-41 materials. The temperature at which the alumination is performed is expected to be an important factor especially in aqueous media where the "grafting" Al species exists in specific ionic form and is therefore subject to mobility considerations determined by its charge/mass ratio. Mobility considerations are particularly relevant if the grafting species exists in polymeric form. We have recently shown that alumination using Al solutions (such as aluminum chlorhydrol, ACH) which contain polymeric species (e.g., the so-called Keggin ion, Al_{13}^{7+}) is more efficient than via monomeric Al species (13). ACH solutions containing the Al_{13}^{7+} Keggin ion are more commonly used as pillaring reagent in the preparation of pillared intercalated clays (PILCs) (20) and we have previously shown that PILCs with vastly different properties can be obtained from such ACH solutions by varying the "pillaring" temperature (21). Presented here are results on the chemical, physical, and catalytic characterization of ACH-grafted MCM-41 materials prepared at either room temperature or 80°C. In order to accentuate any temperature effects, small particle pure silica, Si-MCM-41, was used in this study as the starting host material due to its greater susceptibility to structural change during the alumination process compared to larger particle Si-MCM-41 (22).

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METHODS

Materials

The small particle purely siliceous MCM-41 material was prepared according to Ref. (22). Al-grafted MCM-41 materials were prepared by adding 1.0 g of the calcined purely siliceous MCM-41 to a 50-ml solution of either 0.12 or 0.034 mol l^{-1} (w.r.t. Al) aluminum chlorhydrate (ACH) and stirring for 2 h. Three sets of materials were prepared.

Set H. Si-MCM-41 was added to the ACH solution at 80°C and stirred for 2 h at 80°C.

Set HH. The ACH solution was thermally treated at 80°C for 1 h after which the Si-MCM-41 was added and the resulting gel was stirred at 80°C for 2 h.

Set HC. The ACH solution was thermally treated at 80°C for 1 h and allowed to cool to room temperature after which the Si-MCM-41 was added and stirred for 2 h at room temperature.

In all cases the resulting solid was obtained by filtration and thoroughly washed with distilled water (until free of Cl^- ions), dried at room temperature, and calcined in air at 550°C for 4 h. The Al-grafted MCM-41 samples were designated HX, HHX, or HCX, where X is 2 for materials derived from 0.12 mol l^{-1} ACH or 10 for 0.034 mol l^{-1} ACH-derived materials (see Table 1).

Characterization

Elemental compositions were determined by X-ray fluorescence (XRF). Powder X-ray diffraction (XRD) patterns were recorded using a Philips 1710 powder diffractometer with Cu $K\alpha$ radiation (40 kV, 40 mA), 0.02° step size and 1 s step time. Textural properties (surface area and pore volume) were determined using a Micromeritics ASAP 2400 sorptometer (13). ^{27}Al magic-angle-spinning (MAS) NMR spectra were obtained according to Ref. (13). The acidity was measured using thermal programmed desorption of cyclohexylamine as previously described (12, 13, 23). The conversion of cumene was used to evaluate the catalytic activity of the Al-grafted materials. The reaction was performed in a tubular stainless steel, continous-flow, fixed-bed microreactor system with helium as carrier gas at 300°C and WHSV of 5.5 as previously described (13).

TABLE 1

Composition and Textural Properties of the Parent Pure Silica Si–MCM-41 and Al-Grafted Materials

Sample	[Al] (in grafting sol.) (mol l^{-1})	Si/Al	d_{100} (Å)	Surface area (m^2/g)	Pore volume (cm^3/g)
Si–MCM-41			33.8	1110	0.93
H2	0.12	9.8	35.6	859	0.55
HH2	0.12	9.2	39.7	797	0.67
HC2	0.12	39.5		810	0.44
H10	0.034	16.9	34.8	1047	0.66
HH10	0.034	19.2	39.2	886	0.74
HC10	0.034	72.3		772	0.42

RESULTS AND DISCUSSION

Chemical Composition

Elemental compositions (bulk Si/Al ratio) of the Al-grafted materials are shown in Table 1. The grafting temperature has a marked influence on the amount of Al incorporated; the Al content of set H and HH samples (prepared at 80°C) is relatively similar and much higher than that of set HC samples prepared at room temperature. Indeed the Al content of H and HH samples is nearly four times higher than that of HC samples prepared from similar ACH solutions. A comparison between H and HH samples indicates that prior thermal treatment of the grafting solution has no significant effect on the amount of Al incorporated as long as the grafting is performed at 80°C. A comparison between HH and HC samples is pertinent because the only difference in their preparation is the grafting temperature; the grafting species is expected to be the same due to similar pretreatment of the grafting solution (i.e., heating at 80°C for 1 h). The large variation in the amount of Al incorporated between set HH and HC samples is most likely caused by the difference in the mobility of the grafting Al species; in both cases a significant proportion of the grafting Al species exists in polymeric form (21). Grafting at 80°C enhances mobility and improves the interaction between the grafting species and the host silica matrix. This is consistent with the expectation that the transportation of the bulky grafting species into the pores of the host MCM-41 is more effective at 80°C than at RT. The ^{27}Al MAS NMR spectra in Fig. 1 show that the materials contain both tetrahedrally coordinated (framework) and octahedrally coordinated (nonframework) Al with resonance at ca. 53.0 and 0 ppm, respectively. The majority of the Al is however in tetrahedral coordination.

Physical Properties

Powder X-ray diffraction patterns of the parent Si-MCM-41 and Al-grafted samples prepared from 0.12 mol l^{-1} ACH solutions are shown in Fig. 2a. The patterns for samples H2 and HH2, which were grafted at 80°C, are fairly similar and comparable to that of the parent Si-MCM-41 indicating good retention of structural ordering for these samples. For sample HC2, there is a large reduction in the intensity of the (100) peak suggesting that extensive degradation of long range structural ordering occurs during alumination at room temperature. (Similar trends in the nature of the patterns were observed for materials prepared from

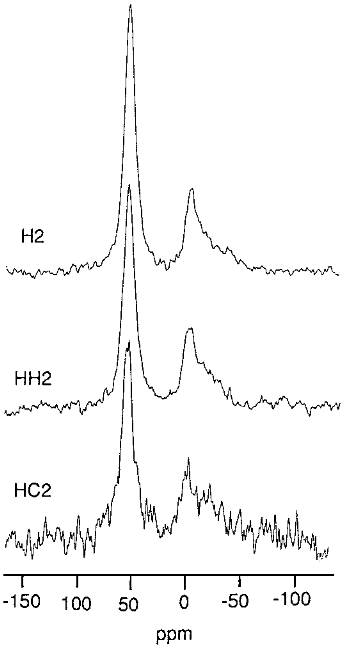

FIG. 1. ^{27}Al MAS NMR spectra of calcined Al-grafted MCM-41 samples prepared from 0.12 mol l^{-1} ACH solutions. See Methods section for sample designation.

0.034 mol l^{-1} ACH solutions). The trends observed from the XRD patterns in Fig. 2a are mirrored by the nitrogen sorption isotherms shown in Fig. 2b. A well-defined step, characteristic of capillary condensation (filling) into uniform mesopores, in the sorption isotherm of mesoporous solids is a good indicator of pore uniformity (24). A mesopore filling step is clearly observed for the parent pure silica material. For the Al-grafted materials, the height and steepness of the mesopore filling step is reduced to varying degrees depending on the mode of alumination. The sorption isotherms obtained for samples H2 and HH2 are comparable indicating the similarity in their mesopore structure. On the other hand, sample HC2 exhibits an isotherm almost devoid of mesoporous character. The information derived from the isotherms and XRD patterns points to good retention in structural ordering and porosity for materials grafted at 80°C and poorer retention in structural ordering for materials grafted at room temperature.

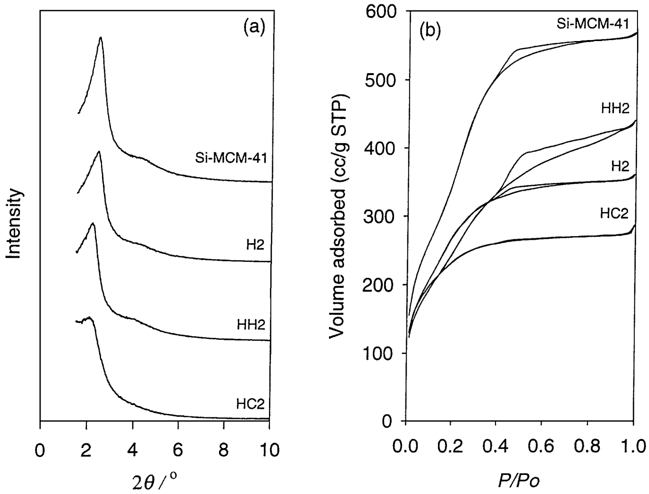

FIG. 2. (a) Powder XRD patterns and (b) nitrogen sorption isotherms of calcined purely siliceous (Si–MCM-41) and Al-grafted MCM-41 samples prepared from 0.12 mol l^{-1} ACH solutions. See Methods section for sample designation.

Table 1 shows the textural properties for the parent Si-MCM-41 materials and the corresponding Al-grafted materials. (It was not possible to accurately obtain basal spacing for HC sampes due to their ill-defined 100 peak). In all cases, alumination leads to a decrease in both the surface area and pore volume. The thicker walls of the Al-grafted materials (12, 13), the presence of nonframework Al in the pores, and structural degradation may, to various degrees, be responsible for the observed decrease in surface area and pore volume. The surface area and especially pore volume of materials grafted at room temperature are reduced to a greater extent than for materials prepared at 80°C. It is possible that the lower surface area and pore volume observed for the room temperature grafted HC samples is due to the deposition of Al polycations at the pore mouth, which results in pore blocking. This is a likely scenario due to the lower mobility of the polycations at room temperature. However, to fully understand the unusual effects of grafting temperature on the structural integrity of the Al-grafted materials it is necessary to consider the behavior of the parent Si-MCM-41 in pure water under alumination conditions, i.e., Si-MCM-41 stirred in pure water at room temperature or 80°C. After stirring for 2 h in pure water (at the respective temperatures) Si-MCM-41 suffered structural degradation at both temperatures. The structural degradation was greater at 80°C, which is the reverse of what is observed when Si-MCM-41 is stirred in ACH solutions.

It is generally accepted that structural degradation of Si-MCM-41 in water occurs due to hydrolysis of Si–O–Si bonds (17, 25). In pure water, as hydrolysis proceeds, the proportion of terminal silanol groups increases thus accelerating the destruction of the silica framework. Furthermore, hydrolysis proceeds faster in hot water than in cold water, hence the observation that structural degradation of Si-MCM-41 is greater in pure water at 80°C than at RT. Alumination, on the other hand, is thought to occur on silanol groups and/or defect sites (26). Alumination uses up silanol groups and is in some respects the reverse of hydrolysis and therefore serves to stabilize the mesoporous framework. Once formed, Si–O–Al bonds are relatively stable to further attack from water (17); the presence of Al in tetrahedral positions creates a negative charge on the surface of the pore walls, repelling OH$^-$ ions which catalyze the hydrolysis of siloxane bonds. While only hydrolysis occurs in water, in ACH solutions both hydrolysis and alumination will occur and it is their relative dominance that will determine the extent of structural degradation. At 80°C, due to the enhanced mobility of the grafting Al species, alumination predominates resulting in excellent Al incorporation and good retention of structural ordering. Furthermore, the effects of hydrolysis are readily reversed by Al insertion. At room temperature the interaction between the grafting species and the host matrix is poor due to the lower mobility of the grafting species. Consequently, alumination occurs to a lesser extent, resulting in lower Al incoporation. Since the hydrolysis of siloxane bonds is not readily reversed (as is the case at 80°C) structural degradation is relatively more extensive. It follows from the foregoing discussion that better preservation of structural ordering can be achieved by reducing the extent to which hydrolysis of siloxane occurs by using a host Si-MCM-41 matrix with less strained Si–O–Si linkages.

Acidity and Catalytic Activity

Table 2 gives the acid content of the Al-grafted materials obtained from thermal desorption of cyclohexylamine and reports the population of acid sites which are strong enough to retain the base after heat treatment of base-containing samples at 80 (total acidity) or 250°C (medium to strong acid sites) (12, 13, 23). The acid content is higher for set H and HH materials prepared at 80°C. The proportion of medium to strong acid sites, as a percentage of total acid content, is higher for set HC samples. The conversion of cumene which was used to evaluate the catalytic activity of the Al-grafted materials requires medium to strong acid sites (12, 13, 27, 28). The catalytic data in Table 2 shows that total conversion is higher for H and HH samples prepared at 80°C which is consistent with their higher acid content. However, HC samples exhibit higher TOF values compared to H and HH samples. It is generally accepted that the activity of acid sites in aluminosilicates can be influenced by the following two factors: (i) acid site isolation and (ii) the presence of nonframework Al in positions adjacent to the acid sites (29, 30). In the right circumstances both these factors tend to increase the catalytic activity of acid sites. It is likely that acid-site isolation is greater in HC samples, which have lower Al contents, than in H and HH samples. With regard to the presence of nonframework Al, the amounts calculated from ^{27}Al NMR and the bulk Si/Al ratios are 25–35% for H and HH samples as compared to ca. 41% for HC samples. Any beneficial effects of acid-site isolation and the presence of nonframework Al are therefore likely to be greater for HC samples. The rate and extent of catalytic deactivation did not vary much between samples prepared at 80°C or RT implying that all the samples have acid sites of similar strength. It is therefore likely that the higher TOF values for HC samples is simply due to better acid site isolation rather than intrinsically stronger acid sites. This is supported by the fact that the TOF values of H and HH samples generally increase as the Al content decreases; i.e., TOF increases with an increase in acid-site isolation.

TABLE 2

Acidity and Catalytic Activity of Al-Grafted MCM-41 Materials

	Acidity (μmol H^{+}/g)		Cumene conversion	
Sample	80°C	250°C	Initial rate[a]	TOF (h^{-1})
H2	880	520	1172	2.25[b] (0.75)[c]
HH2	750	500	1103	2.21 (0.70)
HC2	290	210	872	4.15 (2.12)
H10	600	380	955	2.51 (1.02)
HH10	500	350	1019	2.91 (1.23)
HC10	200	150	708	4.72 (3.00)

[a] Obtained after 10 min on stream in μmol (g cat h)$^{-1}$.

[b] Obtained by dividing initial rate by the content of medium and strong acid sites (i.e., at 250°C).

[c] Obtained by dividing initial rate by the total Al content.

Concluding Remarks

The temperature at which alumination (or grafting) is performed is an important factor which influences the properties of Al-grafted MCM-41 catalysts obtained by reacting pure silica MCM-41 with aqueous solutions of Al polycations. The grafting temperature has a marked influence on the amount of Al incorporated with materials grafted at 80°C incorporating up to four times as much Al as those prepared at room temperature (RT). The insertion of Al into the MCM-41 framework results in some structural degradation with the extent of structural degradation being higher for grafting at RT than at 80°C. It is proposed that there are two competing reactions that occur on the host pure silica MCM-41 surface during alumination: (i) hydrolysis of Si–O–Si linkages via water attack resulting in the destruction of the framework and (ii) insertion of Al (with silanol groups acting as anchoring sites) resulting in the formation of Si–O–Al bonds, which stabilize the framework and offer protection against water attack. The relative dominance of the hydrolysis and Al insertion reactions determine the extent of structural degradation. At 80°C, Al insertion predominates resulting in excellent Al incorporation and good retention of structural ordering. At RT, Al insertion is lower and therefore hydrolysis of siloxane bonds is more pronounced resulting in greater structural degradation. The higher Al content of materials grafted at 80°C is accompanied by higher acid content and higher total conversion levels for the dealkylation of cumene. However, the catalytic activity per active site (TOF values) is higher for RT-grafted materials due to better site isolation occassioned by their lower Al content.

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