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Acidity and Stability of MCM-41 Crystalline Aluminosilicates

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MCM-41 samples with different Si/Al ratios have been synthesized, and their stability and acidity characteristics have been studied. It has been shown that MCM-41 is readily dealuminated upon thermal treatment both in air and in N_2 atmosphere. After calcination the sample shows an acidity of medium strength as compared with a USY zeolite. Calcination in N_2 atmosphere leads to samples with better textural and acid characteristics.

INTRODUCTION

Zeolites are widely used catalysts in acid-catalyzed reactions for the production of petrochemicals and fine chemicals. Among the different types of molecular sieves Y and ZSM-5, i.e., a large-pore and a medium-pore zeolite, are the ones used in larger quantities.

In recent years the necessity for treating heavier feeds, as well as for synthesizing large molecules used as commodities and fine chemicals, has created the demand for molecular sieve structures with pores wider than those of faujasite. Following this line, pillared layered silicates were produced, but their practical utility is still limited (1). In the field of zeolites new very large pore structures such as VPI-5 (2) and cloverite (3) were synthesized, but they have not found, so far, use as catalysts.

Very recently, a new family of mesoporous crystalline aluminosilicates designated as M41S has been discovered (4, 5). One of the members of this family called MCM-41 shows a hexagonal array of uniform mesopores ranging between 2 and 10 nm pore diameter, depending on the template and synthesis conditions used. These materials can be synthesized in a large range of framework Si/Al ratios, and therefore can develop acidity.

There is no doubt that the presence of these very large uniform pores combined with acidic properties opens new possibilities for processing and/or producing large molecules. Thus, it is of interest to study the acid characteristics of these materials and its dependence on the activation procedures. This has been done in this work on two MCM-41 samples with two different Si/Al ratios.

EXPERIMENTAL

Two samples of MCM-41 with Si/Al ratios of 14 (S1) and 100 (S2) were synthesized following the procedure given in Ref. (6) using hexadecyltrimethylammonium (Panreac 98 wt%) cation as the template, and pseudoboehmite (Catapal B, Vista) as the aluminum source. The samples were activated following two procedures: calcination in air at 813 K during 7 h (SA), and calcination in N_2 during 1 h and in air during 6 h at the same temperature (SN). X-ray powder diffraction patterns were carried out, using Cu$K\alpha$ radiation, on a Phillips PW diffractometer equipped with a graphite monochromator. Surface area measurements were obtained on an ASAP-2000 apparatus following the BET procedure. Pore diameter distribution was obtained using argon as adsorbate and following the Horvath–Kawazoe method (7). Solid state ^{27}Al and ^{29}Si MAS NMR spectra were recorded on a Varian Unity VXR-400 WB spectrometer at 104.2 and 79.5 MHz, respectively. Experimental conditions are included in Ref. (8). IR spectra were obtained on a Nicolet 710 FTIR spectrophotometer, using wafers of 10 mg cm^{-2} treated in a vacuum cell at 673 K during 16 h. Pyridine was then admitted at room temperature, and after saturation the samples were degassed at 423, 523, and 623 K, and in vacuum during 1 h. Spectra for *in situ* thermal desorption were carried out by treatment of the sample at increasing temperatures (473, 573, 673, and 773 K) in vacuum 1 h each time. Finally, NH_3 TPD experiments were made in a TPD-2900 from Micromeritics by using a heating rate of desorption of 10 K min^{-1}.

RESULTS AND DISCUSSION

The crystalline aluminoscilicate MCM-41 is characterized by a broad band at low angles in the XRD spectrum and a narrow distribution of pore size centered at ~3.5 nm (4, 5). In Fig. 1 the XRD spectra (1a) and pore size distribution (1b) of the synthesized samples are given,

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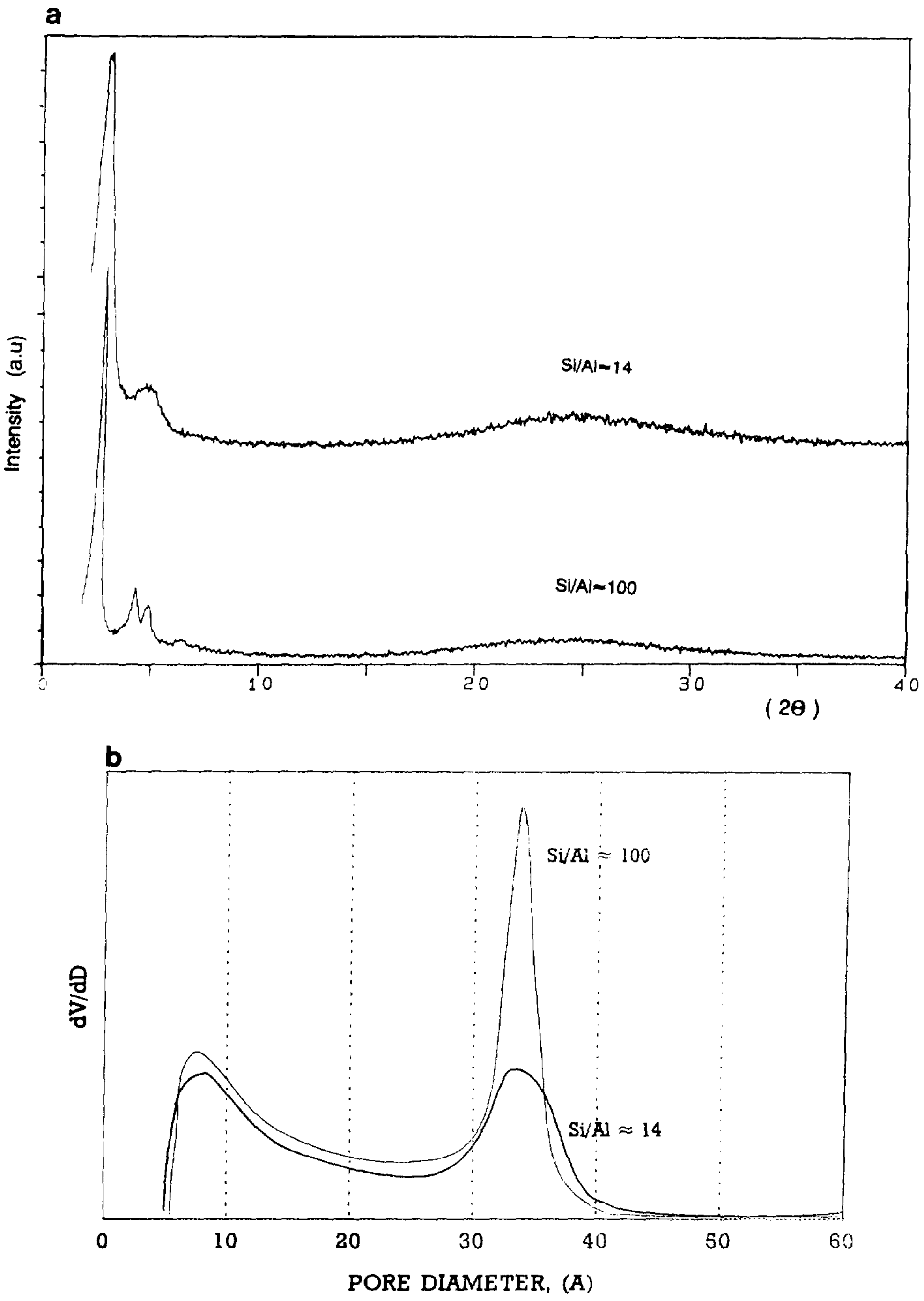

FIG. 1. XRD spectra (a) and pore size distribution (b) of MCM-41.

and from this we can conclude that they correspond to the MCM-41 material. Sample S2 shows a well defined hexagonal phase, while in sample S1 the hexagonal phase is less structured and no improvement is observed when changing the OH/SiO_2 ratio in the synthesis. These results are consistent with those corresponding to the adsorption of Ar (Fig. 1b). Indeed, while both samples give pores at ~3.5 nm, a larger pore volume is found for sample S2. These results seem to indicate that it becomes difficult to incorporate relatively high amounts of Al if alkaline ions are not present during the synthesis. Thus, sodium aluminate is probably a better Al source to use when MCM-41 samples with low Si/Al ratios are to be obtained (9).

The ^{27}Al NMR MAS spectra of the noncalcined S1 and S2 samples (Fig. 2) show only a 4-coordinated (Al^{IV}) peak at 50–52 ppm, whose intensities are in reasonable

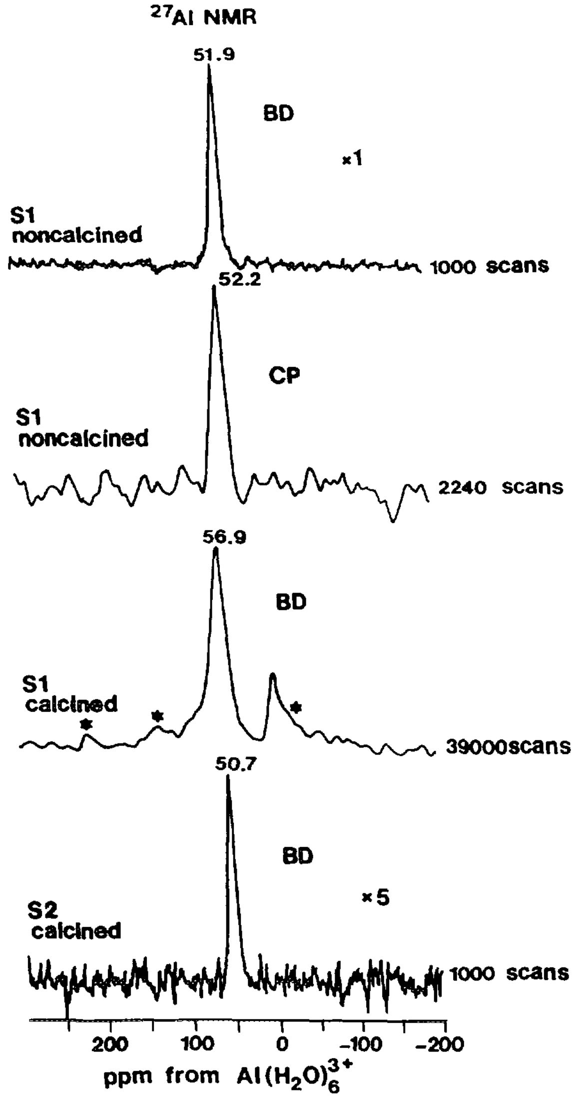

FIG. 2. ^{27}Al MAS NMR spectra of MCM-41. Note different intensity scaling factors for the BD spectra of the noncalcined samples. Asterisks denote spinning sidebands.

agreement with its Si/Al ratio obtained from the chemical analysis (see Ref. (8)). In the as-synthesized sample the 6-coordinated Al (Al^{VI}) signal assigned to extraframework Al (EFAL) is not detected. After calcination, the spectrum of S1 sample shows that the intensity of the Al^{IV} signal strongly decreases while a new signal at 3 ppm appears, indicating that a partial framework dealumination is taking place. For the S2 sample we did not detect the appearance of Al^{VI} signal probably due to the very low amount of Al present in the starting sample.

Infrared Spectroscopy and Acidity Measurements

The IR spectrum of the calcined S1 sample, in the hydroxyl range (Fig. 3a) shows a very intense band at 3740 cm^{-1} corresponding to external silanol groups. The spectra of the S2 sample in the hydroxyl range is not shown because its intensity is out of the range of the infrared apparatus. This result seems to indicate that S2 presents a lower crystal size (higher external surface), as has been confirmed by electron microscopy (results not shown). The calcination procedure partially dealuminates the sample, as was deduced from NMR results, and consequently the IR spectra in Fig. 3a correspond to a partially dealuminated S1 sample. The dealumination produced during calcination results in a sample with a small amount of Brønsted and Lewis acid sites, as measured by pyridine adsorption (bands at 1540 cm^{-1} (B) and 1450 (L) cm^{-1}, respectively), in Fig. 3b. Moreover, after pyridine desorption at 423 and 523 K in vacuum, practically all the pyridine associated to protons has been desorbed, indicating that the Brønsted acid sites generated on the MCM-41 are of medium strength.

The IR spectra of the adsorbed pyridine in sample S2, which was synthesized with a higher framework Si/Al

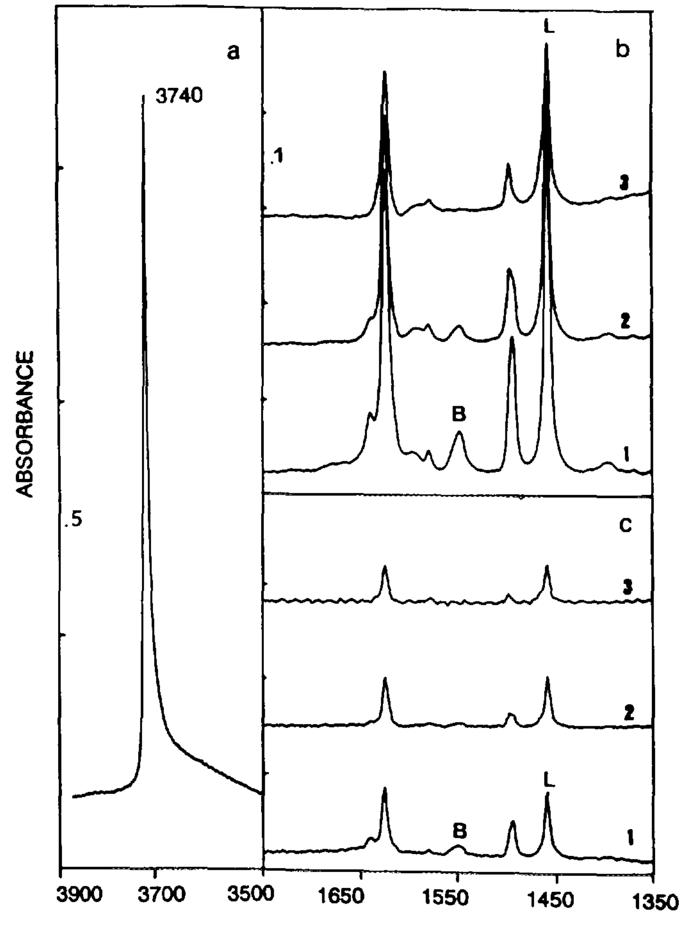

FIG. 3. IR spectra of MCM-41 samples: (a) Hydroxyl range. (b) and (c) Pyridine adsorbed on S1(b) and S2(c) samples and desorbed in vacuum at different temperatures: (1) 423 K; (2) 523 K; (3) 623 K.

ratio, shows, as expected, a very low amount of acid sites (Brønsted and Lewis) (Fig. 3c). The remaining acidity is also of medium strength, indicating that in the range studied here, the Si/Al ratio has no significant influence on the acid strength of the zeolite.

As a reference, we have compared the more acidic S1 sample with an ultrastable Y zeolite (USY) with a framework Si/Al ~ 100 (Fig. 4). The pyridine spectra shows that a USY, even with a Si/Al ~ 100, has a higher amount of Brønsted acid sites than MCM-41 zeolite, indicating that, at least in the sample prepared from Catapal, a high degree of dealumination has taking place upon calcination. It may however occur that in the case of a better sample, and/or a sample produced using sodium aluminate as the aluminum source, the stability is higher and a smaller dealumination is produced. When the pyridine adsorption spectra of the calcined S1 and an amorphous silica–alumina containing 25 wt% of Al_2O_3 are compared (see Fig. 5), it can be deduced that a similar amount of Brønsted acid sites are detected on the two samples at 150°C. However, when the desorption temperature is increased, the amorphous silica–alumina presents a higher amount of pyridinium ions than sample S1. This is an indication that a higher proportion of Brønsted sites with stronger acidity are present in amorphous silica–alumina than on our calcined MCM-41 sample. Finally, the IR spectra show that the calcined S1 sample has a higher amount of Lewis acid sites than amorphous silica–alumina, corresponding to a higher dispersion of the EFAL formed over the MCM-41 sample, upon calcination.

All these conclusions are supported by the NH_3 TPD results given in Fig. 6. Indeed, the total amount of NH_3 adsorbed (Brønsted + Lewis acid sites) is higher on amorphous silica—alumina (10.5 $cm^3 g^{-1}$) than on calcined S1 sample (7.5 $cm^3 g^{-1}$) or USY (5.7 $cm^3 g^{-1}$). However, the shift of the maximum in the desorption curve with temperature indicates the order of the acid strength is S1 $\leq$ amorphous silica–alumina $\ll$ USY.

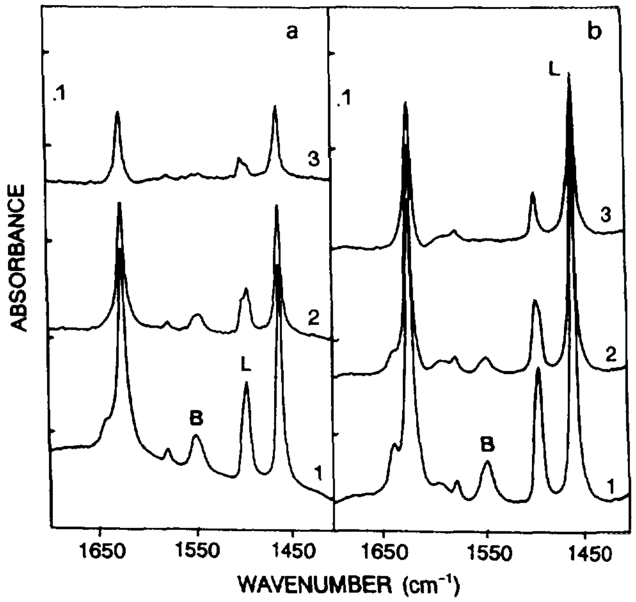

FIG. 5. IR spectra of pyridine adsorbed on (a) amorphous silica–alumina and (b) S1 sample of MCM-41 after different desorption treatments, as in Fig. 3.

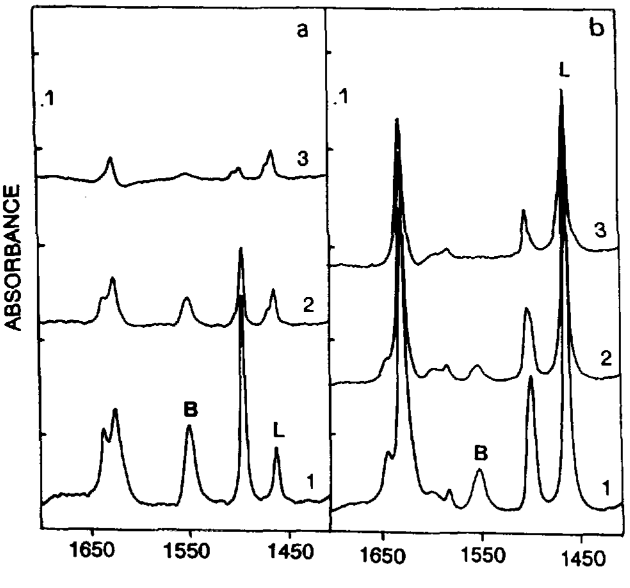

FIG. 4. IR spectra of the pyridine adsorbed on USY (a) and MCM-41 (b) at different desorption temperatures as in Fig. 3.

Influence of the Activation Conditions of MCM-41 Zeolites on the Textural and Acid Properties

It was shown above that during the activation of MCM-41, framework dealumination occurs. Dealumination can be due to the combination of the high local temperatures

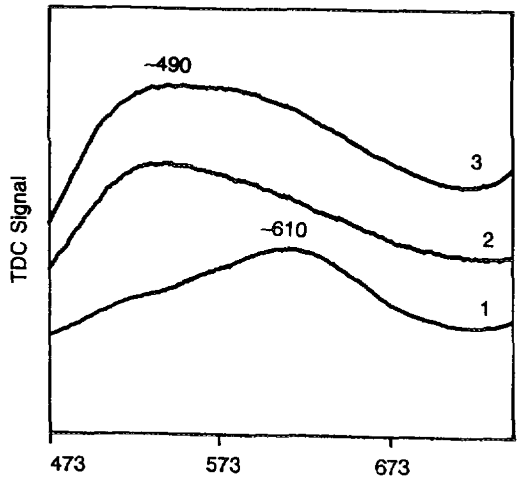

FIG. 6. TPD NH_3 spectra of USY (1), calcined S1 sample (2), and amorphous silica alumina (3).

achieved during the combustion of the template, and also to the presence of steam generated during the combustion of the organic in the presence of O_2. If this is so, the negative effect of calcination should be diminished if the sample is first calcined in a N_2 atmsophere and then calcined in the presence of air. In this way the pyrolysis produces the endothermic decomposition of the organic, probably giving $(CH_3)_3N$, $C_{16}H_{32}$, H_2O, and carbonaceous compounds formed by consecutive reactions of the organic products. Then, when calcined in the presence of air the carbonaceous products, with a low H/C ratio, are burned off with a very small formation of water, and a relatively lower heat of combustion is also generated. This activation in two steps should result in a smaller dealumination and consequently in a lower damage than when the sample was directly calcined in the presence of air. Results given in Table 1 indicate that in the sample calcined first in N_2 (S1N) the pore volume corresponding to the 3.5-nm structural pores is almost twice that of the sample calcined directly in air, and that surface area is also higher for the former. With respect to acidity, Table 1 clearly shows that activation under N_2 leads to samples with a higher amount of Brønsted and Lewis acid sites.

All these results indicate that in the presence of air, the calcination produces samples with a higher degree of dealumination and a higher level of structural damage than in the case where a previous heating in the presence of N_2 was carried out. The much higher amount of Lewis acid sites on S1N sample can be due to the fact that the EFAL formed has a lower degree of polymerization in this sample, as a consequence of the lower local temperatures and much lower amount of water formed during the two-step activation of the MCM-41 sample.

In Situ IR Study of the Template Thermal Desorption

The as-synthesized sample S1 was treated at increasing temperatures under vacuum, and the IR spectra of hydroxyl groups (Fig. 7) and adsorbed template molecules (Fig. 8) were registered at room temperature. Treatment at 373 K and vacuum for 2 h removes the hydration water as can be monitored by the band at ~1640 cm^{-1} (spectrum not shown) and, consequently, all the IR bands appearing in the spectra taken at higher temperatures must correspond exclusively to template molecules or hydroxyl groups.

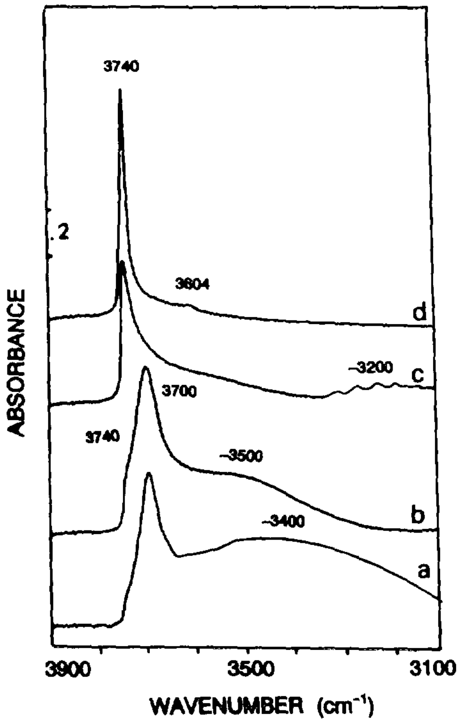

FIG. 7. IR spectra in the hydroxyl range of S1 sample after different thermal treatments: calcination in vacuum 1 h at 473 K (a), 573 K (b), 673 K (c), and 773 K (d).

TABLE 1

Textural and Acidic Properties of MCM-41 Samples Calcined in Air (A) and Nitrogen (N)

Sample	Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Acidity (μmol py)[a] Brønsted 423			Lewis 423	523	623
			423	523	623	423	523	623
S1A	750	0.25	14	5	—	37	29	21
S1N	900	0.5	25	14	<5	105	80	52
S2N	1112	0.5	5	—	—	20	15	13

[a] From extinction coef. by Hughes and White (11).

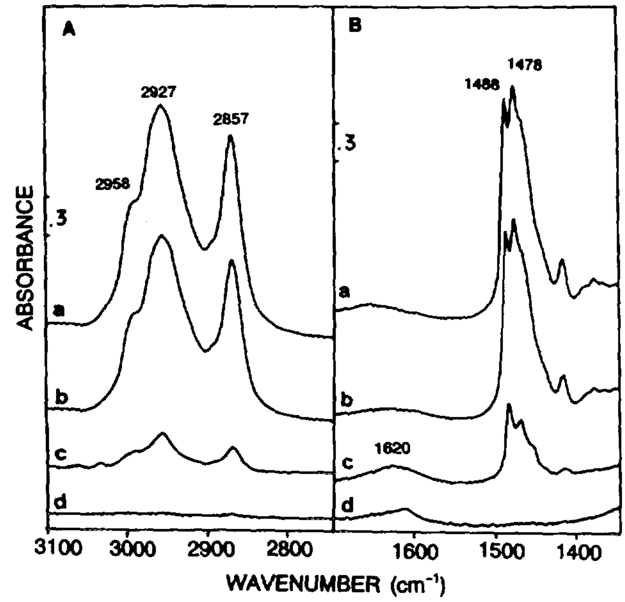

FIG. 8. IR spectra of template molecules adsorbed on S1 sample after different thermal treatments, as in Fig. 7.

Figure 7 shows the IR spectra of the S1 sample heated between 473 and 773 K, in the hydroxyl range (3900–3100 cm^{-1}). In this figure we can see that at low temperature (Fig. 7a) only two bands are clearly visible: a broad one centered at ~3400 cm^{-1} and a sharp one at ~3700 cm^{-1}. Both bands can be assigned to silanol groups, the first one being shifted to lower wavenumber and enlarged due to strong interaction with template molecules located at the channels. In fact, when a part of the template molecules is removed by increasing the temperature of desorption (Fig. 7b) the 3400 cm^{-1} band decreases its intensity and shifts to higher wavenumber indicating a decrease in the interaction of the silanol groups with template molecules. Simultaneously a shoulder appears at 3740 cm^{-1}, corresponding to noninteracting external silanol groups. The behavior of the band located at 3700 cm^{-1} is in agreement with its assignation to silanols at defects or located at mesopores of low diameter (10, 12, 13), because its intensity does not depend on the amount of template molecules (see Figs. 7a and b).

After treatment at 673 K (Fig. 7c), only a band due to free external silanol groups remains in the spectrum, indicating that silanol interactions have practically disappeared. It must be noted that the intensity of this band is much lower than the equivalent in the sample calcined in air or N_2, indicating also a lower damage of the structure. Some deformation of the band in the low wavenumber range shows that a small amount of interacting silanols are still present. Finally, at 773 K the template has been removed (as can be seen in Fig. 8d) and the hydroxyl spectrum shows a very intense and narrow silanol band, while a small one at 3604 cm^{-1} indicates the presence of "bonded" SiOHAl hydroxyls probably responsible for the acidity of the sample. This band is not visible in the sample calcined in air probably due to the fact that strong dealumination occurred during that treatment.

The spectra of the zeolite template (Fig. 8) shows the presence of bands corresponding to CH stretching (2958 cm^{-1}, CH_3; 2927 cm^{-1}, CH_2; 2857 cm^{-1}, CH_2 + CH_3) and CH bending (1488 cm^{-1}, CH_3; 1478 cm^{-1}, CH_2) (14). Heating between 473 and 573 K (Figs. 8a and b) slightly decreases its intensity, and after treatment at 673 K (Fig. 8c) an important part of the template molecules has been removed. Moreover, at this temperature of treatment we can detect a change in the relative intensity of CH_3 (1488 cm^{-1}) and CH_2 (1478 cm^{-1}) bending vibrations, indicating that part of the cetyl branch of the ammonium cation has been cracked and removed from the sample. It is worth noting the appearance, at this temperature, of bands at ~1620 cm^{-1} (Fig. 8c) and ~3200 cm^{-1} (Fig. 7c) assigned to the $R{-}NH_3^+$ group of a protonated amine, showing that decomposition of template alkylammonium molecules occurs through a Hoffmann reaction, as proposed by Parker *et al.* (15). Finally, heating at 773 K totally removes the template (see Fig. 8d).

CONCLUSIONS

The MCM-41 appears as an ordered silica–alumina with uniform mesoporosity possessing some acid sites of medium acid strength. The as-synthesized sample has the totality of aluminum in framework tetrahedral position. However, a direct calcination in air dealuminates the sample, decreasing its potential Brønsted acidity but increasing the Lewis acidity due to the EFAL formed. A previous calcination under N_2 produces catalysts with higher acidity and better textural properties than those activated directly in air. Using Catapal as the Al source, it becomes difficult to incorporate high amounts of aluminum while obtaining well structured materials. It appears that, at least in these cases, a sodium aluminate source could be more adequate. If this is so, it may happen that samples with higher thermal stability and therefore higher residual acidity could be prepared using alkalines during the synthesis.

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