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Nature and acidity of aluminum species in AlMCM-41 with a high aluminum content (Si/Al = 1.25)

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Abstract

A series of low-silica (Si/Al = 1.25) [H,Na]AlMCM-41 with H/Na ratios comprised between 0 and 1 has been obtained by ionic exchange with ammonium nitrate followed by calcination. Standard procedures starting from a calcined [Na]-precursor could not be applied; some of the Na^+ species were not accessible and treatments in water led to a significant dealumination and to a gradual collapse of the structure. By contrast, Na^+ ions could be exchanged along with surfactant molecules in alcoholic solutions without damaging the structure, and the corresponding [NH_4,Na] solids possess exclusively tetrahedral aluminum. Calcination leads to a significant dealumination, as evidenced by ^{27}Al and ^{29}Si NMR. The fraction of residual tetrahedral aluminum in the solids, which can be correlated with the H/Na ratio, decreases with the level of exchange down to a limit of $\approx$0.25. Despite a high extent of dealumination in completely exchanged compounds, solids remain highly ordered and retain the textural properties of the directly calcined [Na]AlMCM-41. Both the Lewis and Brönsted acidity increase with the proton concentration. The Lewis acidity is relatively weak up to a level of exchange of 90%, but hugely increases for the completely exchanged solid.

Keywords: MCM-41; Mesoporous solids; Aluminum; Coordination; Ion exchange; Acidity

1. Introduction

Incorporation of aluminum in the neutral silica network of MCM-41 provides materials with interesting properties in catalysis [1–6]. It has been widely reported that [H] AlMCM-41materials, obtained by calcination of a sodium-containing precursor followed by exchange with NH_4^+ ions, possess a moderate acidity similar to that of disordered amorphous silica–alumina co-gels. Although the acidity is not as high as that of crystalline microporous zeolites having the same Al content, it is sufficient to catalyze reactions like cracking and hydrocracking of bulky molecules, oligomerization of olefins or alkylation of aromatics [7–11].

The acidity of MCM-41 directly depends on the nature and amount of aluminum species in the silica walls. Since Bronsted acid sites result from the presence of isolated, tetrahedrally coordinated aluminum atoms, it is reasonable to believe that the acidity of [H]AlMCM-41 will increase with the amount of aluminum in the framework. However, many experimental reports show that the acidity of Al-rich MCM-41 is not as high as expected, because calcination of the NH_4^+ exchanged solid is accompanied by a severe dealumination [12–15].

Up to date, studies on the nature and acidity of Al species in solids with Si/Al ratios below 5 are scarce, which drastically differs from low-silica zeolites, for which many studies have been reported. One of the reasons is that the preparation of highly ordered, low-silica MCM-41 is difficult. Indeed, the long range ordering typical of purely siliceous MCM-41 generally diminishes with the Al content, as evidenced by the decrease and broadening of XRD reflections and most of Al-rich compounds are disordered [14–17]. Moreover, even solids with a highly ordered mesoscopic structure tend to collapse partially upon

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calcination at high temperature [17]. Finally, the exchange capacity of MCM-41 is relatively low, some of the Na^+ cations being occluded inside the aluminosilicate walls and hardly accessible to NH_4^+ cations [18].

Recently, Janicke et al. have prepared MCM-41 materials with Si/Al ratios close to 1 that remain highly ordered after calcination of the precursors [19]. We have already reported that such solids are not stable in water after calcination and that standard procedures in aqueous media could not be applied to exchange Na^+ cations [20]. Exchanging cations in alcoholic solutions helped to circumvent this problem; both surfactant and Na^+ cations could be exchanged without extracting aluminum and without damaging the long-range ordering of the structure. In the particular case of NH_4^+ cations, surfactant molecules were rapidly expelled from the mesopores, which offered the possibility to obtain organic-free mesoporous aluminosilicates without turning to calcination [21,22].

In the present paper, the above procedure has been used to prepare $[NH_4,Na]$AlMCM-41 with Si/Al = 1.25 and NH_4/Na molar ratios ranging from 0 to 1. After calcination, the corresponding [H,Na]AlMCM-41 materials were characterized by XRD, nitrogen adsorption and solid-state NMR. ^{27}Al and ^{29}Si MAS NMR allowed us to study the evolution of the nature and concentration of the various types of aluminum species with the level of exchange. The acidity of the corresponding materials was evaluated by adsorption of pyridine followed by infrared spectroscopy.

2. Experimental

2.1. Synthesis

The low-silica [Na]AlMCM-41 was synthesized with Si/Al = 1 in the gel following a recipe adapted from that reported by Janicke et al. [19]. In a typical preparation, 8.511 g $Al(O^iPr)_3$ were dissolved in a solution containing 7.252 g NaOH in 90 mL H_2O. 941 mL water was then added and the resulting mixture was stirred for about 30 min. Then, 32.345 g of cetyltrimethylammonium bromide (CTMABr) were added and the temperature was increased to ≈25 °C to dissolve completely the surfactant. 8.685 g tetraethylorthosilicate (TEOS) were then added and the gel, with the following composition:

$$Al(O^iPr)_3{:}SiO_2{:}4.32NaOH{:}2.13CTMABr{:}1250H_2O$$

was stirred for 2 h. Concentrated HCl (37 wt%) was then added dropwise to decrease the pH value to 12. After 4 h more, additional HCl was added to decrease the pH to 11. Stirring was then maintained for 12 h at room temperature. The solid was recovered by filtration, washed with distilled water and air-dried at room temperature.

After drying, a portion of mesoporous solid was calcined to remove the organics. The compound was slowly heated to 520 °C in air and the temperature was maintained for ≈16 h. The solid was then rehydrated in a saturator (>75% humidity) for 3 days before characterization.

2.2. Exchanges

2.2.1. Standard procedure

One gram of calcined [Na]AlMCM-41 was dispersed in 150 mL of an aqueous solution of NH_4NO_3 and heated at 60 °C for 30 min under stirring. The solid was then recovered, washed with distilled water and dried at room temperature. A series of experiments have been done using different concentrations in ammonium nitrate, corresponding to theoretical levels of exchange NH_4/Na between 0.2 and 2 (Na is the amount of sodium contained in 1 g of calcined solid).

2.2.2. Exchanges in alcohol

Exchange experiments were also carried out using alcoholic solutions of ammonium nitrate as reported in previous papers [20–22]. In a typical experiment, 1 g as-made [Na]AlMCM-41 was dispersed in 150 mL of a solution containing NH_4NO_3 in ethyl alcohol at 60 °C. The concentration of the solution corresponded to a NH_4/CTMA cation to surfactant ratio of 1.5/1. After stirring for 15 min at 60 °C, the solid was recovered by filtration and washed three times with cold ethanol. The above procedure could be repeated up to seven times. After exchange, solids were dried at room temperature and calcined in air at 520 °C.

As for the directly calcined compound, exchanged solids were rehydrated for 3 days before characterization.

2.3. Characterization

X-ray diffraction powder patterns were recorded between 1° and 10° (2θ) on a Bruker (Siemens) D 5005 diffractometer using $CuK\alpha_2$ radiation with steps of 0.02° and 10 s per step.

N_2 adsorption/desorption isotherms for BET surface area and pore size distribution measurements were collected at −196 °C using a Micromeretics ASAP 2010 apparatus. Before the measurement, ≈50 mg of the sample was dehydrated under vacuum at 300 °C overnight.

The evolution of the amount of surfactant in the solids during exchange experiments was evaluated by thermal analysis. Data were collected on a SETERAM TGDSC 111 apparatus connected to a mass spectrometer. Compounds were heated in air from 25 to 750 °C at a heating rate of 5 °C/min.

The aluminum and sodium contents in the various materials were determined by ICP after solids had been dissolved in HF:HCl solutions.

TEM pictures were taken on a JEOL 2010 microscope with an accelerating voltage of 200 kV. Samples were embedded in an epoxy resin and sectioned on an ultramicrotome.

Solid-state NMR spectra were collected on a Bruker DSX-400 spectrometer. Magic Angle Spinning (MAS) experiments were conducted at 10 kHz using a double bearing probe head with 4 mm zirconia rotors. ^{29}Si and ^{27}Al NMR chemical shifts were referenced to tetramethylsilane