Generation and Identification of Strong Acid Sites in AlMCM-41 Prepared by Gel Equilibrium Adjustment Method

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AlMCM-41 materials with SiO_2/Al_2O_3 ratio 46 (in gel) were prepared by varying the chain length of the template from C_{10}-C_{16} in the main chain of alkyltrimethyl ammonium halide and by adjusting the gel pH to 11.00. Thus obtained H-AlMCM-41 materials possess strong acid sites which are characterized by improved ammonia TPD technique using mass detector and co-adsorbed water. An almost good agreement in number was observed between desorbed NH_3 molecules and Al atoms in H-AlMCM-41.

Researchers at Mobil Oil Corporation discovered the ordered mesoporous materials, designated as M41S.[1,2] MCM-41 with unidimensional hexagonal mesopores is the representative of this family. Generation of strong acid sites in these materials is an important aspect with respect to their potential application in the petrochemical industry. Many reports were appeared in literature dealing with the generation of acid sites in MCM-41 materials which resulted mesoporous materials with mild acid sites.[3-5] Ryoo et al.[6] reported the preparation of mesoporous materials by adjusting the gel pH at 11.00 during the synthesis. They found the adjustment of gel pH improves the thermal and hydrothermal stability of final mesoporous materials. Recently, Kim et al.[7] studied the catalytic activity of AlMCM-41 materials prepared using gel pH adjustment method. In this communication we report the preparation of AlMCM-41 materials by varying the template chain length from C_{10}-C_{16} in the main chain of alkyltrimethyl ammonium halide and by adjusting the gel pH to 11.00. Thus obtained H-AlMCM-41 materials were thoroughly characterized by improved ammonia TPD technique.

We prepared the AlMCM-41 samples similar to the procedure reported by Ryoo et al.[6] except the following changes: (a) Solution-B was prepared by mixing 0.75 g of 28 wt.% aqueous ammonia and 50 g, 52.54 g, 48.04 g or 43.67 g of 25 wt.% hexadecyltrimethyl ammonium chloride, tetradecyltrimethyl ammonium bromide, dodecyltrimethyl ammonium bromide or decyltrimethyl ammonium bromide solution, respectively and (b) the procedure of adjustment of gel pH was repeated four times. The final gel composition of AlMCM-41 materials was
$46SiO_2{:}Al_2O_3{:}11.5\ Na_2O{:}7.7\ ATMAH{:}2.3\ NH_4OH{:}1687\ H_2O$
where ATMAH is alkyltrimethyl ammonium halide.

The final white crystallized product was filtered, washed with hot deionized water (3 L) and dried at 100 °C. As-synthesized sample was calcined at 530 °C (ramp rate 2 °C/min) in nitrogen. After 1 h at 530 °C, the carrier gas was switched to oxygen and increased the temperature to 550 °C, then continued for 10 h. 1 g of calcined AlMCM-41 and 100 ml of 1 M ammonium nitrate solution was stirred for 2 days at room temperature for ammonium-exchange. To avoid/minimize the removal of Al from framework positions, the pH of ammonium nitrate solution was adjusted to 7-8 (neutral) using aqueous ammonia. The final NH_4^+-form AlMCM-41 sample was calcined at 500 °C (ramp rate 5 °C/min) for 5 h to get H-form.

Temperature programmed desorption (TPD) of ammonia is widely used to characterize the acidic property of solid materials. Recently, Bagnasco[8] developed a technique to improve the selectivity of ammonia TPD by adding the water to the system after ammonia adsorption. Katada et al.[9] applied this method to analyze the amount of acid sites in H-Y zeolite by selectively removing the lower temperature ammonia desorption peak which complicates overall TPD profile. Experimental procedure for ammonia TPD is follows. The detailed description of apparatus described elsewhere.[10] Here we used mass spectrometer (MS) detector instead of thermal conductivity detector (TCD) to monitor the desorbed gases. About 100 mg of H-AlMCM-41 (pellets) was evacuated at 400 °C for 1 h. The sample was equilibrated with ammonia (100 Torr, 1 Torr = 133.3 Pa) at 100 °C for 30 min and then evacuated for 30 min. Water vapor (12-14 Torr) was introduced into the system for 30 min and then evacuated for 30 min. The latter step, water vapor treatment was repeated two times totally. 16 m/e was used for ammonia and the peak area of NH_3 was calibrated by injecting known amount of NH_3. The acid amount was calculated from the desorbed ammonia peak area.

Ammonia TPD profiles of various H-AlMCM-41 samples obtained with water treatment were shown in Figure 1. All the samples show two peaks at about 570 K and 790 K. From the TPD profiles of H-AlMCM-41 it is assumed that these materials consist two types of acid sites; one with weak/moderately strong acid sites and second one with strong acid sites. This is the first report to show the strong acid sites in H-AlMCM-41 materials. Zeolites with strong (mordenite, ZSM-5) or moderately strong acid sites (zeolite ß) show two peaks in TPD profile when no

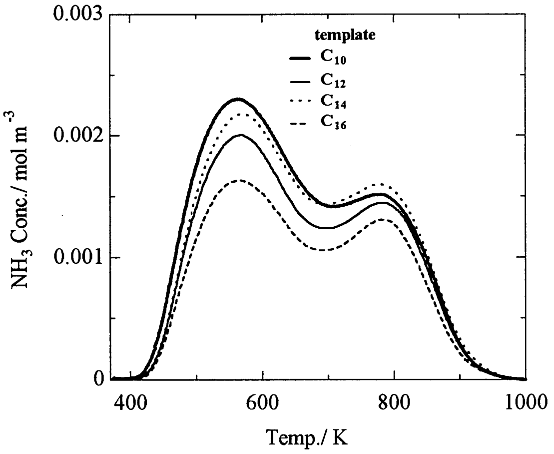

Figure 1. TPD profiles of various H-AlMCM-41 materials with water.

Table 1. Chemical analysis and acid amount of H-AlMCM-41 materials

Template	SiO_2/Al_2O_3 gel	SiO_2/Al_2O_3 product[a]	Al content[a] /mol/kg	Acid amount[b] /mol/kg	NH_3/Al[c] ratio
C_{16}	46	57	0.57	0.33	0.58(0.63)[d]
C_{14}	46	61	0.53	0.43	0.81(0.89)
C_{12}	46	64	0.51	0.40	0.79(0.93)
C_{10}	46	51	0.63	0.45	0.71(0.81)

[a] Al content was analyzed by ICP using H-form samples.

[b] From TPD. [c] The ratio calculated from total Al.

[d] NH_3/Al ratio in parenthesis was calculated from the tetrahedrally coordinated Al (from NMR).

water was added to the system. Upon addition of water, the lower temperature peak in zeolites completely disappears and the high temperature peak remain unchanged;[9] this is due to only one type of acid sites present in zeolites. In case of H-AlMCM-41 samples, no difference was observed in TPD profiles with and without water treatment. The molar ratio of desorbed ammonia per Al was calculated, and the results were presented in Table 1. An almost good agreement was observed between Al content and the desorbed ammonia (Table 1). However, H-AlMCM-41 materials prepared from C_{14} and C_{12} templates show the highest NH_3/Al ratio (≈0.8), and that from C_{16} template shows the least NH3/Al (≈0.6) ratio.

NMR study of AlMCM-41 materials suggest that in all as-synthesized samples all of the Al atoms are in tetrahedral positions, and in all H-form samples about 90% Al atoms are in tetrahedral positions and about 10% Al atoms are in octahedral positions.

In conclusion, H-AlMCM-41 samples show two peaks in TPD profiles even after water treatment during the ammonia adsorption. All H-AlMCM-41 samples contain two types of acid sites which belong to weak/moderately strong acid sites and strong acid sites. This is the first report to identify and quantitatively analyze the strong acid sites in H-AlMCM-41 materials. Further investigations are required in order to elucidate the origin of these two peaks.

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References

1 C.T. Kresge, M.E. Leonowics, W.J. Roth, J.C. Vartuli, and J.S. Beck, *Nature,* **359**, 710 (1992).

2 J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, and J.L. Schlenker, *J. Am. Chem. Soc.*, **114**, 10834 (1992).

3 A. Corma, M.S. Grande, V. Gonzalez-Alfaro, and A.V. Orchilles, *J. Catal.*, **159**, 375 (1996).

4 C-Y. Chen, H-X, Li, and M.E. Davis, *Microporous Mater.*, **2**, 17 (1993).

5 A. Corma, V. Fornes, M.T. Navarro, and J. Perez-Pariente, *J. Catal.*, **148**, 569 (1994).

6 J.M. Kim, J.H. Kwak, S. Jun, and R. Ryoo, *J. Phys. Chem.*, **99**, 16742 (1995).

7 J.H. Kim, M. Tanabe, and M. Niwa, *Microporous Mater.*, 1997 (in press).

8 G. Bagnasco, *J. Catal.*, **159**, 249 (1996).

9 N. Katada, H. Igi, and M. Niwa, To be presented at *Intl. Symp. on Zeolites and Microporous Crystals*, August 24-27, Tokyo (1997) Japan.

10 M. Niwa, N. Katada, M. Sawa, and Y. Murakami, *J. Phys. Chem.*, **99**, 8812 (1995).