Preparation of Strong Brønsted Acid Sites on MCM-41 by Treatment with $AlCl_3$

M. Xu, M. Hunger
Institute of Chemical Technology, University of Stuttgart, D-70550 Stuttgart, Germany

Summary

Strong Brønsted acid sites were prepared on mesoporous MCM-41 materials by a modification of siliceous MCM-41 with aluminum chloride in vacuum at 403 K. The modified MCM-41 material was characterized by X-ray diffraction, N_2 adsorption/desorption and multi-nuclear solid-state NMR spectroscopy. A model for the local structure of acid sites is proposed. According to this model, hydroxychloroaluminum species are formed containing strongly acidic bridging OH groups.

Introduction

- Although MCM-41 materials found wide attention because of their uniform mesopores, the weak acidity of these materials limits their valuable application in catalysis.
- Different methods have been proposed to introduce strong acid sites in MCM-41 material such as vapor phase alumination under atmospheric pressure at 634 K and impregnation of MCM-41 with aluminum chloride in benzene at room temperature. Strong Brønsted acid sites, however, were still not unequivocally identified [1, 2].
- In the present work, a method is introduced which is based on a modification of siliceous MCM-41 with sublimated aluminum chloride in vacuum at 403 K.

Results and Discussion

XRD and nitrogen adsorption:

- Long range order still remained after modification with $AlCl_3$, as evidenced by the XRD patterns (Fig. 1).
- N_2 adsorption/desorption experiments showed a slight decrease of the BET surface area from 1351 $m^2 g^{-1}$ to 1088 $m^2 g^{-1}$ and a decrease of the pore diameter from 2.5 nm to 1.9 nm for the conditioned MCM-41 and $AlCl_3$/MCM-41, respectively.

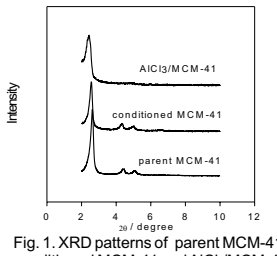


Fig. 1. XRD patterns of parent MCM-41, conditioned MCM-41 and $AlCl_3$/MCM-41.

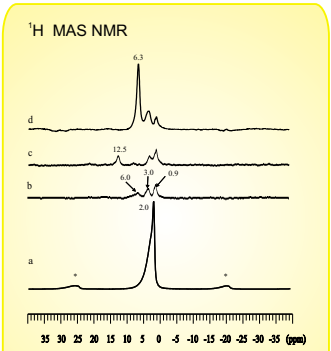


Fig. 2. ^1H MAS NMR spectra of conditioned MCM-41 (a), $AlCl_3$/MCM-41 (b), d_5-pyridine (c) and ammonia loaded $AlCl_3$/MCM-41 (d).

^1H MAS NMR studies:

- Silanol groups (signal at 2.0 ppm) were strongly reduced by modification with $AlCl_3$ (Figs. 2a and 2b).
- Signals at 0.9 ppm and 3.0 ppm are due to AlOH and related hydrogen-bonded OH groups, respectively (Fig. 2b).
- Acidic protons were identified by the adsorption of d_5-pyridine, which induced a new signal of pyridinium ions at 12.5 ppm accompanied by a disappearance of the signal at 6.0 ppm (Fig. 2c).
- The number of acid sites (0.10 mmol/g) was determined by adsorption of ammonia inducing a signal at 6.3 ppm due to the formation of ammonium ions.

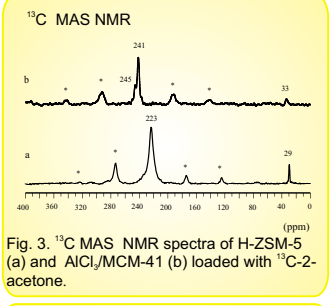


Fig. 3. ^{13}C MAS NMR spectra of H-ZSM-5 (a) and $AlCl_3$/MCM-41 (b) loaded with ^{13}C-2-acetone.

^{13}C MAS NMR studies:

- The ^{13}C MAS NMR spectrum of $AlCl_3$/MCM-41 loaded with 0.15 mmol/g of ^{13}C-2-acetone consists of two signals at 241 and 245 ppm due to carbonyl atoms of acetone molecules interacting with acid sites (Fig. 3b).
- Comparison with ^{13}C-2-acetone molecules adsorbed on H-ZSM-5 (Fig. 3a), which have a chemical shift of 223 ppm only, indicates that $AlCl_3$/MCM-41is a much stronger solid acid.

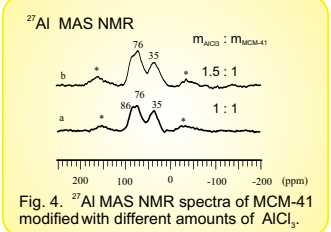


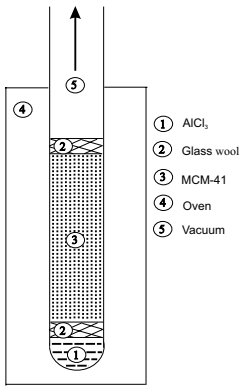
Fig. 4. ^{27}Al MAS NMR spectra of MCM-41 modified with different amounts of $AlCl_3$.

^{27}Al MAS NMR studies:

- Based on literature [5], the signal at 35 ppm is assigned to hydroxychloro-aluminum species (Fig. 4).
- Broad signals at 76 and 86 ppm, occurring in the spectrum of $AlCl_3$/MCM-41, are tentatively ascribed to tetrahedral aluminum species with different numbers of chlorine atoms (Fig. 4).

Experimental Section

- Siliceous MCM-41 was synthesized without addition of sodium aluminate and conditioned with H_2O_2 as described in References [3] and [4], respectively.
- Modification with aluminum chloride was performed in vacuum (< 10^{-2} mbar) using the set-up shown in Scheme 1. When heated at 403 K, aluminum chloride was sublimated into the vapor phase. It slowly diffused upwards and reacted with the surface sites of the siliceous MCM-41. The product was denoted $AlCl_3$/MCM-41.
- The NMR spectroscopic investigations were performed on an NMR spectrometer MSL 400 at resonance frequencies of 400.1 MHz for ^1H, 104.2 MHz for ^{27}Al, 79.5 MHz for ^{29}Si MAS NMR and 100.4 MHz for ^{13}C MAS NMR spectroscopy. All spectra were recorded using samples in the dehydrated state (as-modified).



Scheme 1. Set-up for the modification of MCM-41 with $AlCl_3$.

Results and Discussion

^{29}Si MAS NMR studies:

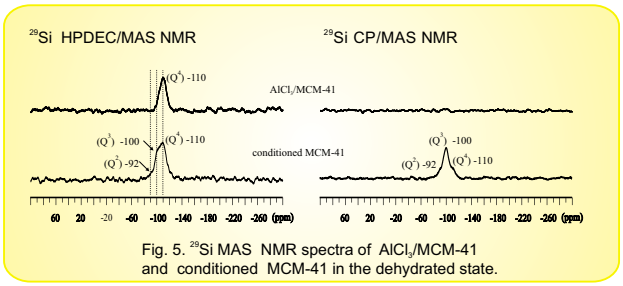
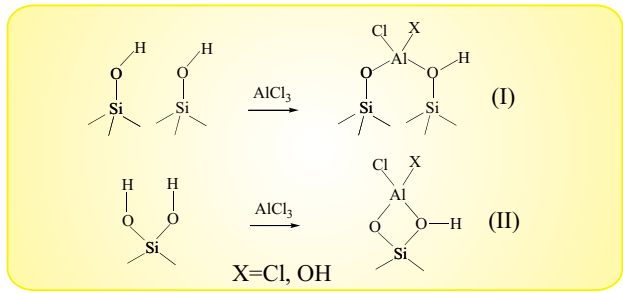


Fig. 5. ^{29}Si MAS NMR spectra of $AlCl_3$/MCM-41 and conditioned MCM-41 in the dehydrated state.

- Pretreatment of MCM-41 with H_2O_2 before modification with $AlCl_3$ is very important since this step increases the amount of the silanol groups from 2.3 mmol/g to 3.4 mmol/g.
- After modification with $AlCl_3$, the SiOH groups (Q^2, Q^3) were almost removed as evidenced by the ^{29}Si MAS NMR spectra shown in Fig. 5. This agrees with the ^1H MAS NMR spectra shown in Figs. 2a and 2b, in which a strong decrease of the signal of SiOH groups at 2.0 ppm from 3.4 mmol/g to 0 mmol/g was observed.
- Models (I) and (II) with X=Cl were proposed by Drago et al. to explain strong Brønsted acid sites formed by modification of silica gel with $AlCl_3$ [5]. In the present study of modified MCM-41, model (I) dominates (see Fig. 5).



Conclusion

Low temperature modification of siliceous MCM-41 with sublimated $AlCl_3$ leads to the formation of Brønsted acid sites with an acid strength higher than that of H-ZSM-5.

References

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Acknowlegements

Financial support by the German Science Foundation (DFG), Max-Buchner-Forschungsstiftung and Fonds der Chemischen Industrie is gratefully acknowledged.