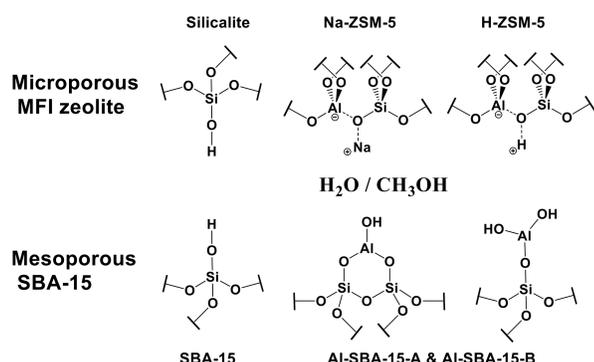


Abstract



Adsorption and desorption of water as well as methanol on porous solids have been investigated by ^1H MAS NMR spectroscopy and thermogravimetric analysis (TGA). For microporous MFI zeolites, aluminum, cations and acidic OH groups (H^+) strongly increase the adsorption capacity of water by a factor of 9, while these sites have little effect on the methanol adsorption. Similarly, on mesoporous SBA-15, the adsorption capacity of water raises with increasing aluminium content. However, the aluminium modification leads to lower adsorption of methanol on SBA-15. After a 30-minute room-temperature desorption, the ^1H MAS NMR spectra changed remarkably. Signals of hydronium ions and complexes of water at cations become visible. On microporous materials, the nature of water species is more diverse than on mesoporous materials.

Results and Discussion

Microporous MFI Zeolite

Adsorption Capacity of Water and Methanol on MFI Zeolite

Table 1. Amounts of H_2O adsorbed on MFI zeolites

Sample	evaluation result (mmol / g)	
	NMR	TGA
Silicalite	0.4	0.5
Na-ZSM-5	3.6	4.4
H-ZSM-5	4	4.5

Table 2. Amounts of CD_3OH adsorbed on MFI zeolites

Sample	evaluation result (mmol / g)	
	NMR	TGA
Silicalite	2.3	1.4
Na-ZSM-5	1.5	2.1
H-ZSM-5	2.2	2.6

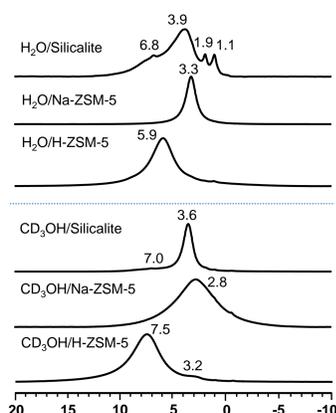


Figure 1. ^1H MAS NMR spectra of MFI zeolites loaded with H_2O or CD_3OH

Both NMR and TGA indicate that aluminum and Na^+/H^+ species affect the total amount of water adsorbed from the vapor phase. But these species have a smaller effect on the methanol adsorption. Different water states cause different ^1H MAS NMR signals.

Desorption at Room Temperature for 30 min

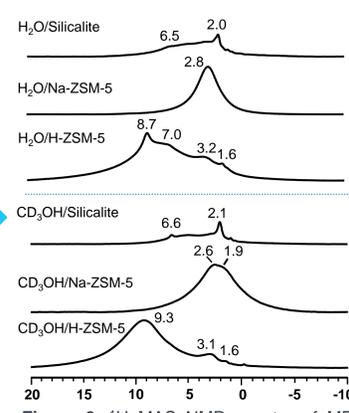


Figure 2. ^1H MAS NMR spectra of MFI zeolites after room-temperature desorption of H_2O or CD_3OH for 30 minutes

After room-temperature evacuation for 30 minutes, less than 5% water or methanol remain on silicalite, whereas much more adsorbates remain on Na-ZSM-5 (H_2O 33%; CD_3OH 48%) and H-ZSM-5 (H_2O 24%; CD_3OH 28%).

Mesoporous SBA-15

Adsorption Capacity of Water and Methanol on SBA-15

Table 3. Amounts of water adsorbed on SBA-15

Sample	evaluation result (mmol / g)	
	NMR	TGA
SBA-15	2.0	2.9
Al-SBA-15-A	2.6	3.3
Al-SBA-15-B	6.6	7.8

Table 4. Amounts of methanol adsorbed on SBA-15

Sample	evaluation result (mmol / g)	
	NMR	TGA
SBA-15	10.9	3.0*
Al-SBA-15-A	9.5	2.9*
Al-SBA-15-B	8.3	8.0*

*: Need to be repeated

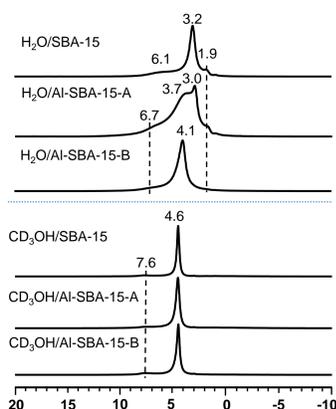


Figure 3. ^1H MAS NMR spectra of SBA-15 loaded with H_2O or CD_3OH

Aluminum modification influences both adsorption of H_2O and CD_3OH on SBA-15. More aluminum causes higher water adsorption but less methanol adsorption in tendency. On the other hand, SBA-15 can hold much more methanol than MFI zeolites due to large volume of pores.

Desorption at Room Temperature for 30 min

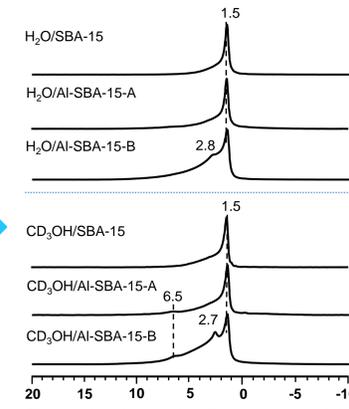


Figure 4. ^1H MAS NMR spectra of SBA-15 after room-temperature desorption of H_2O or CD_3OH for 30 minutes

After room-temperature evacuation for 30 minutes, more than 95% of water and methanol desorb from SBA-15 and Al-SBA-15-A, while about 17% of water and 9% of methanol still remain on Al-SBA-15-B due to the higher aluminum content of the latter material.

Experimental Methods

Modification of SBA-15 was performed in a conical flask containing the mixture of AlCl_3 and SBA-15 with a mass ratio of 1:5. The conical flask was placed in a furnace and heated with a rate of 2 K/min up to 393 K under a nitrogen flow, keeping this temperature for 2 h, and then heated at 423 K for 36 h. All the materials were activated at a vacuum line at 673 K for 12 h. The adsorption of H_2O was performed by equilibrating the sample in a desiccator over saturated $\text{Ca}(\text{NO}_3)_2$ solution, while the adsorption of CD_3OH was achieved under N_2 atmosphere saturated with CD_3OH vapor by using a glass tube wherein sample and CD_3OH were on different sides. Desorption of molecules from samples for NMR measurement was carried out at a vacuum line below 0.4 mbar at room temperature. Thermogravimetric analysis (TGA) data were collected using NETZSCH STA 449 Thermogravimetric Analyzer with a temperature program ranging from room temperature to 473 K. A heating ramp of 5 K/min is applied and intermediately equilibrated for 30 minutes at room temperature, 323 K, 348 K, 373 K, 423 K, and 473 K respectively. ^1H MAS NMR experiments were performed using a resonance frequency of 400.13 MHz on a Bruker AVANVEIII 400 WB spectrometer using a 4 mm MAS NMR Bruker probe and with a spinning rate of 8 kHz.

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