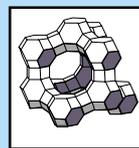


Local structure of framework aluminum in zeolite H-ZSM-5 during conversion of methanol investigated by *in situ* MAS NMR spectroscopy



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Summary

In situ MAS NMR spectroscopy under continuous flow (CF) conditions and spin-echo NMR experiments [1,2] were applied to investigate the local structure of framework aluminum in zeolite H-ZSM-5. ^1H CF MAS NMR spectra recorded during conversion of methanol on zeolite H-ZSM-5 gave signals due to methanol and dimethyl ether, simultaneously ^{27}Al CF MAS NMR spectra show a strong decrease of the signal of framework aluminum at 54 ppm after raising the temperature. To investigate the local geometry of framework aluminum, ^{27}Al spin-echo NMR experiments were performed on dehydrated zeolite H-ZSM-5 in the unloaded state and after adsorption of reactants. While methanol decreases the ^{27}Al quadrupolar coupling constant, dimethyl ether complexes formed at bridging OH groups cause a strong increase of the ^{27}Al quadrupolar interactions.

Introduction

In zeolites, the tetrahedrally coordinated framework aluminum contributes to the local structure of acidic hydroxyl groups formed at oxygen bridges between silicon and aluminum atoms (SiOHAl). Due to the electric quadrupole moment of the ^{27}Al nuclei, the shape of the ^{27}Al NMR signals depends strongly on the z-component of the electric field gradient which is caused by the charge distribution in the local structure of the AlO_4 tetrahedra. In dehydrated zeolites as well as after adsorption of benzene, the framework AlO_4 tetrahedra have only a low symmetry which leads to strong quadrupolar interaction and large quadrupole coupling constants. On the other hand, the interaction of adsorbate molecules such as water, ammonia or pyridine with SiOHAl groups via proton transfer increases the symmetry of the framework AlO_4 tetrahedra leading to a weak quadrupolar interaction and, therefore, to small quadrupole coupling constants [3]. For comparing the influence of adsorbate complexes caused by methanol and dimethyl ether (dme) on zeolite H-ZSM-5, *in situ* ^{27}Al CF MAS NMR and ^{27}Al spin-echo NMR experiments were made.

Experimental Section

The MAS NMR investigations were performed on a Bruker MSL 400 spectrometer at resonance frequencies of 400.1 MHz and 104.3 MHz for ^1H and ^{27}Al nuclei, respectively. *In situ* ^1H and ^{27}Al MAS NMR experiments under continuous flow (CF) were performed with a sample spinning rate of ca. 2 kHz using a modified DSI-740 7 mm STD MAS NB NMR probe, Doty Scientific Instruments, Texas, USA.

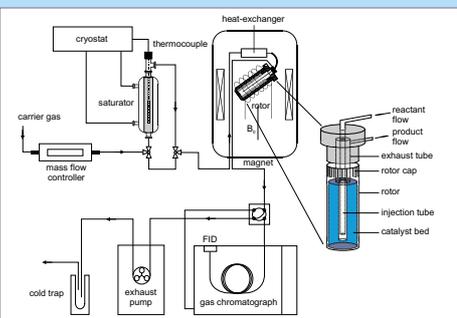


Fig. 1: Scheme of the equipment applied for simultaneous *in situ* MAS NMR spectroscopy and *on-line* gas chromatography and the design of the modified MAS NMR rotor with axially placed tubes for the injection of reactant molecules and the exhaust of reaction products.

^1H and ^{27}Al CF MAS NMR spectra were recorded after excitation with $\pi/2$ and $\pi/6$ pulses and with repetition times of 5 s and 500 ms, respectively. ^{27}Al spin-echo NMR spectra were recorded applying a phase-cycled spin-echo sequence ($\pi/2 - 20 \mu\text{s} - \pi - 20 \mu\text{s} - \text{echo}$) with a repetition time of 500 ms. During the *in situ* CF MAS NMR experiments, dry nitrogen loaded with CH_3OH , according to a modified residence time of $W/F_m = 25$ gh/mol, were injected into the 7 mm MAS NMR rotor [4].

Results and Discussion

^1H and ^{27}Al CF MAS NMR during injection of methanol

- The ^1H MAS NMR spectrum of dehydrated zeolite H-ZSM-5 recorded at 295 K consists of signals due to SiOHAl groups at 4.1 ppm and SiOH groups at 1.9 ppm while no signal can be observed in the ^{27}Al MAS NMR spectrum indicating strong quadrupolar interactions (Fig. 2a).
- During injection of methanol at temperatures of 295 to 473 K, ^1H MAS NMR signals of methanol and dme appear at 3.7 and 2.8 ppm, respectively (Fig. 2b-d, left). At 473 K, the ^1H MAS NMR signal at 8.0 ppm, caused by hydroxyl protons contributing to hydrogen bound methanol complexes, shifts to 10.5 ppm.

Simultaneously, the ^{27}Al CF MAS NMR signal of framework aluminum at 54 ppm is strongly decreased indicating a conversion of the methanol complexes formed at the SiOHAl groups. The absence of a ^1H MAS NMR sideband pattern in the spectrum recorded at 573 K (Fig. 2e, left), in comparison with the spectrum obtained at 295 K, indicate a high thermal mobility of the hydroxyl protons. However, this proton mobility does not improve the local symmetry of the AlO_4 tetrahedra as shown by the broad background signal in the ^{27}Al MAS NMR spectrum.

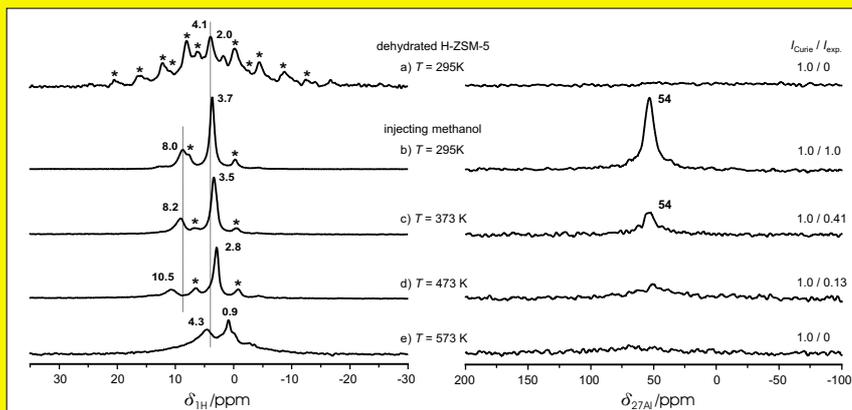


Fig. 2: *In situ* ^1H CF MAS NMR spectra (left) and ^{27}Al CF MAS NMR spectra (right) recorded during injection of methanol on H-ZSM-5 with a modified residence time of $W/F_m = 25$ gh/mol at $T = 295$ to 573 K.

^{27}Al spin-echo NMR of dehydrated H-ZSM-5 and after loading with methanol and dme

- The spectrum in Fig. 3a consists of a broad quadrupolar pattern (QP) due to framework aluminum atoms in the local structure of SiOHAl groups and a narrow quadrupolar line (QL) caused by aluminum atoms adjacent to cationic species.
- The increase of the temperature to 573 K (Fig. 3b) led only to a weak narrowing of the signal QP. This finding indicates that the highly mobile hydroxyl protons do not jump between all four oxygen positions of the AlO_4 tetrahedra averaging their electric field gradient.
- After adsorption of methanol (Fig. 3c), the ^{27}Al NMR spectrum consists of a single signal corresponding to a quadrupole coupling constant of 4.4 MHz (Tab. 1).
- The adsorption of dme leads to a significant broadening of this signal (Fig. 3d) according to a quadrupole coupling constant of 11.1 MHz. This strong quadrupolar interaction hinders the observation of framework aluminum by MAS NMR spectroscopy (Fig. 2d, right).

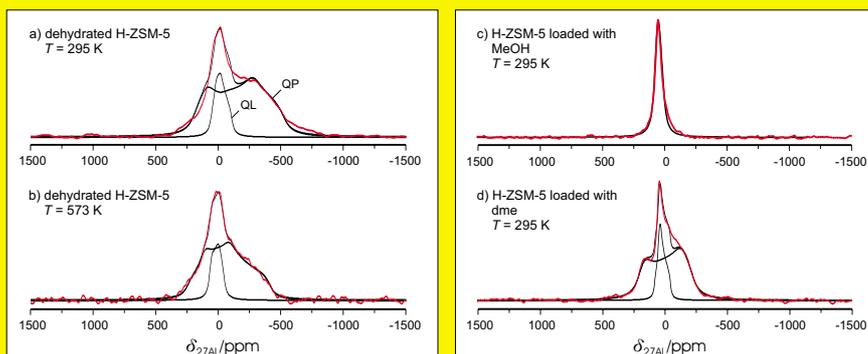


Fig. 3: ^{27}Al spin-echo NMR spectra of a) dehydrated zeolite H-ZSM-5 at $T = 295$ K, b) dehydrated zeolite H-ZSM-5 at $T = 573$ K, c) zeolite H-ZSM-5 loaded with methanol and d) zeolite H-ZSM-5 loaded with dme.

Tab. 1: Data of framework aluminum in zeolite H-ZSM-5 obtained by simulations of the ^{27}Al spin-echo NMR spectra.

Sample	Signal	Intensity	QCC	η
H-ZSM-5 at 295 K	QL	100 %	4.4 MHz	0.90
+ 1 $\text{CH}_3\text{OH} / \text{SiOHAl}$	QL	22 %	4.9 MHz	0.90
+ 1 dme / SiOHAl	QP	78 %	11.1 MHz	0.20
H-ZSM-5 at 295 K	QL	20 %	5.9 MHz	0.70
	QP	80 %	13.7 MHz	0.35
H-ZSM-5 at 573 K	QL	18 %	5.6 MHz	0.50
	QP	82 %	12.4 MHz	0.60

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Conclusions

- The strong quadrupolar interaction of framework aluminum atoms in zeolite H-ZSM-5 during conversion of methanol at elevated temperatures hinders their observation by ^{27}Al MAS NMR spectroscopy.
- By application of a ^{27}Al spin-echo NMR sequence could be shown that the adsorption of the reaction product dimethyl ether on zeolite H-ZSM-5 causes a strong increase of the ^{27}Al quadrupole coupling constant from 4.4 MHz (adsorption of methanol) to 11.1 MHz.
- The high mobility of hydroxyl protons at elevated temperatures has no significant influence on the local symmetry of framework AlO_4 tetrahedra.