

Adsorption of Methanol on Brønsted Acid Sites in Zeolite H-ZSM-5 Investigated by Multinuclear Solid-State NMR Spectroscopy

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Abstract: Adsorbate complexes formed by adsorption of methanol on zeolite H-ZSM-5 have been investigated by ^1H , ^2H , ^{13}C , and ^{27}Al NMR spectroscopy at temperatures between $T = 425\text{ K}$ and $T = 85\text{ K}$. The data derived were explained by hydrogen-bonded neutral methanol molecules and partially protonated methanol clusters consisting of one and three methanol molecules per SiOHAl group, respectively. At $T \geq 295\text{ K}$, the hydroxyl protons of adsorbate complexes formed by one methanol molecule per SiOHAl group exhibit a high mobility and undergo a rapid chemical exchange. The ^1H MAS NMR shifts ($\delta_{\text{1H}} = 4.1$ and 14.2 ppm) of the OH groups after adsorption of CD_3OH and the ^2H quadrupole coupling constants (QCC = 230 and 140 kHz) of the OD groups after adsorption of CH_3OD , obtained at $T \leq 153\text{ K}$, correspond to those of rigid and hydrogen-bonded molecules. The ^{27}Al quadrupole coupling constants of AlO_4 tetrahedra involved in the local structure of bridging OH groups interacting with one and three methanol molecules (QCC = 8.0 and 2.5 MHz , respectively) depend on the number of adsorbate molecules and indicate a partial deprotonation of SiOHAl groups in the complexes formed by three methanol molecules per SiOHAl group.

Introduction

Brønsted acid sites at the internal surface of zeolites and their interaction with reactant molecules are of utmost importance for the role of these materials in heterogeneous catalysis. Hydroxyl groups in aluminosilicates and silicoaluminophosphates which act as acid sites are located on oxygen bridges connecting tetrahedrally coordinated framework silicon and aluminum atoms. The protons of these bridging OH groups (SiOHAl) compensate for the negative framework charges introduced by the tetrahedrally coordinated aluminum atom. Since the acidic zeolite H-ZSM-5 is applied as catalyst for the conversion of methanol into hydrocarbons, great effort has been invested to develop the understanding of this reaction and to investigate adsorbate complexes formed by methanol and bridging OH groups in zeolites.^{1,2}

Recently, adsorbate complexes formed by methanol molecules bonded on model clusters of bridging OH groups were theoretically investigated by Haase and Sauer,^{3,4} Gale,⁵ and Nusterer et al.⁶ These studies suggest that physisorption of methanol on bridging OH groups via two hydrogen bonds is the most stable binding geometry (complex I in Figure 1), while a methoxonium cation bonded to the deprotonated fragments (complex II in Figure 1) was found to be a transition state.^{3,4} In a number of NMR spectroscopic studies the chemical interactions of bridging OH groups with probe molecules have been studied (for reviews see refs 7 and 8). Anderson et al.⁸

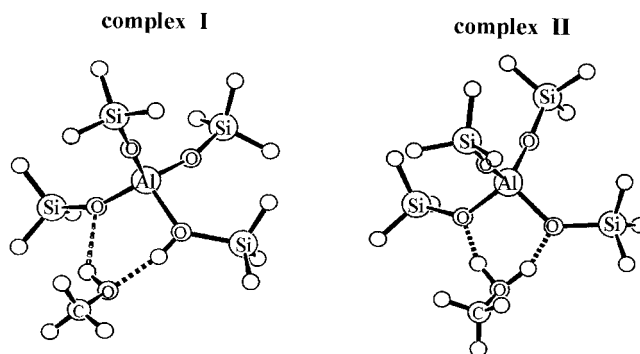


Figure 1. Adsorbate complexes formed by methanol molecules interacting with model clusters of bridging OH groups derived by quantum chemical calculations. Reprinted with permission from ref 4. Copyright 1995 American Chemical Society. In complex I a methanol molecule is physisorbed via two hydrogen bonds while complex II (ion-pair structure) consists of a methoxonium ion hydrogen bonded at the negatively charged model cluster.

explained the ^1H MAS NMR spectra of zeolite H-ZSM-5, loaded with more than one methanol molecule per bridging OH group and recorded at room temperature, by formation of protonated adsorbate complexes. FTIR studies, carried out by Mirth et al.,⁹ indicated a formation of methoxonium ions in zeolite H-ZSM-5 also for low methanol coverages. According to Thursfield and Anderson,¹⁰ an increase of the methanol coverage gives rise to the formation of large methanol clusters. The ^1H MAS NMR shifts, observed for hydroxyl protons contributing to these clusters, were discussed in connection with weak chemical bonds between the zeolite framework and these clusters. ^{13}C MAS NMR shifts, observed at ambient temperature for low coverages of methanol molecules on zeolite

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(1) Chang, C. D. *Hydrocarbons from Methanol*; Marcel Dekker: New York, 1983.

(2) Chen, N. Y.; Garwood, W. E.; Dwyer, F. G. *Shape Selective Catalysis in Industrial Application*; Marcel Dekker: New York, 1989.

(3) Haase, F.; Sauer, J. J. *Phys. Chem.* **1994**, *98*, 3083.

(4) Haase, F.; Sauer, J. J. *Am. Chem. Soc.* **1995**, *117*, 3780.

(5) Gale, J. D.; Catlow, C. R. A.; Carruthers, J. R. *Chem. Phys. Lett.* **1993**, *216*, 155.

(6) Nusterer, E.; Boechl, P. E.; Schwarz, K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 175.

(7) Hunger, M. *Solid State Nucl. Magn. Reson.* **1996**, *6*, 1.

(8) Anderson, M. W.; Barrie, P. J.; Klinowski, J. J. *Phys. Chem.* **1991**, *95*, 235.

(9) Mirth, G.; Lercher, J. A.; Anderson, M. W.; Klinowski, J. J. *Chem. Soc., Faraday Trans. 1* **1990**, *86*, 3039.

(10) Thursfield, A.; Anderson, M. W. *J. Phys. Chem.* **1996**, *100*, 6698.

H-ZSM-5, were explained by rigidly bonded protonated adsorbate complexes. In contrast to these results, ^2H NMR investigations and ^1H MAS NMR spin-echo experiments on adsorbate complexes consisting of one methanol molecule per bridging OH group in zeolite H-ZSM-5 indicated a high mobility of hydroxyl protons at $T = 295\text{ K}$.^{11,12} Therefore, the experimentally derived ^1H NMR shifts may be influenced by a rapid chemical exchange of hydroxyl protons between SiOHAl groups and hydrogen-bonded neutral and/or protonated adsorbate complexes.¹² In addition, multinuclear solid-state NMR investigations have shown that the adsorption of methanol molecules on zeolite H-ZSM-5 leads to a variation in the local structure of SiOHAl groups.^{11,12}

The aim of the present study is the characterization of complexes formed by adsorption of up to three methanol molecules per SiOHAl group in zeolite H-ZSM-5. By application of a new *in situ* adsorption technique^{13,14} and of multinuclear NMR spectroscopy at variable temperatures the chemical bonding and mobility of hydroxyl protons and deuterons contributing to adsorbate complexes and the influence of methanol adsorption on the local SiOHAl structure have been investigated.

Experimental Section

The synthesis of zeolite ZSM-5 was carried out without a template according to ref 15. By ^{27}Al MAS NMR spectroscopy all aluminum atoms were found at tetrahedrally coordinated framework positions. The ammonium exchange of the parent sample was carried out by 4-fold ion exchange in a 1 N aqueous solution of NH_4NO_3 for 12 h at 353 K. From the bulk chemical analysis using atomic-emission spectroscopy with inductively coupled plasma (AES-ICP) an $n_{\text{Si}}/n_{\text{Al}}$ ratio of 22 and an ion exchange degree of 96% were derived. The zeolite H-ZSM-5 was prepared by calcination of the ammonium-exchanged sample in vacuum (below 10^{-2} Pa) for 12 h at 673 K. The *ex situ* prepared samples were loaded with CH_3OH (Fluka), CD_3OD (99.95 atom % D, Th. Geyer), CD_3OH (99.0 atom % D, Th. Geyer), and CH_3OD (99.0 atom % D, Deutero GmbH) using a vacuum line. The number of adsorbed molecules was adjusted volumetrically to one or three methanol molecules per bridging OH group. The numbers of adsorbed CH_3OH and CH_3OD molecules were proved by a comparison of the ^1H MAS NMR intensities of the unloaded and loaded samples.

The NMR spectroscopic investigations were carried out on a Bruker MSL 400 spectrometer with resonance frequencies of 100.6 MHz for ^{13}C , 104.3 MHz for ^{27}Al , 61.4 MHz for ^2H , and 400.13 MHz for ^1H NMR. ^2H and ^{27}Al NMR spectra were recorded on static samples (without MAS) as described in ref 16 applying a phase-cycled quadrupole-echo sequence. ^{13}C and ^1H MAS NMR measurements were carried out with 7 and 4 mm MAS NMR Bruker probes and rotation frequencies of 4 and 10 kHz, respectively. The pulse delay τ of the rotation-synchronized ^1H MAS NMR spin-echo sequence ($\pi/2 - \tau - \pi - \tau$ -acquisition) was adjusted to multiples of the MAS period $\tau_{\text{rot}} = 100\text{ }\mu\text{s}$.¹⁷ For the *in situ* adsorption of methanol on zeolite H-ZSM-5 the injection equipment described in refs 13 and 14 was applied. During these experiments nitrogen gas, loaded with CD_3OH , was injected into a commercial 7 mm MAS NMR Bruker rotor via an axially placed glass tube. This glass tube was inserted into the rotor through an axial

adsorption of CD_3OH on zeolite H-ZSM-5:

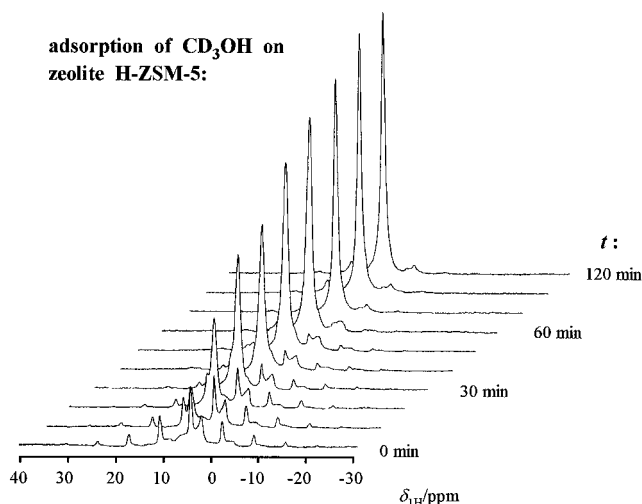


Figure 2. ^1H MAS NMR spectra of dehydrated zeolite H-ZSM-5 recorded during *in situ* adsorption of CD_3OH at $T = 295\text{ K}$.

hole in the rotor cap. In a saturator the nitrogen gas was loaded with methanol having a partial pressure of $6 \times 10^3\text{ Pa}$ at $T = 283\text{ K}$. The chemical shifts are referenced to external standards of a 0.1 N aqueous solution of $\text{Al}(\text{NO}_3)_3$ for ^{27}Al , tetramethylsilane for ^{13}C and ^1H , and D_2O for ^2H NMR spectroscopy. The PC program WIN-FIT (Bruker software) was used for decomposition and simulation of NMR spectra.

Results and Discussion

A. *In Situ* NMR Investigations of Methanol Adsorption on Zeolite H-ZSM-5. In the present study a new technique for the injection of gaseous molecules into the MAS rotor was applied which allows *in situ* NMR spectroscopic investigations of adsorption on zeolites. The dehydrated zeolite H-ZSM-5, filled in the *in situ* MAS rotor,^{13,14} is flushed during the measurements with nitrogen gas. Prior to the injection of the carrier gas into the MAS rotor, it is loaded in a saturator with CD_3OH (partial pressure of $6 \times 10^3\text{ Pa}$). Figure 2 shows a stacked plot of ^1H MAS NMR spectra of zeolite H-ZSM-5 recorded immediately before ($t = 0\text{ min}$) and after ($t > 0\text{ min}$) the *in situ* adsorption of CD_3OH at $T = 295\text{ K}$ was started. The ^1H MAS NMR spectrum obtained at $t = 0\text{ min}$ consists of a signal at 1.8 ppm due to terminal silanol groups and a superposition of two signals at ca. 4.2 ppm caused by free bridging OH groups in 10-ring channels (narrow component) and perturbed bridging OH groups (broad component).^{7,18,19} The peaks at ca. 17, 11, -3, and -9 ppm are due to MAS sidebands ($\nu_{\text{rot}} = 2.5$). After the adsorption of CD_3OH is started, a low-field signal appears at ca. 9.5 ppm which is caused by hydroxyl protons of adsorbate complexes. With running adsorption time the intensity of the low-field signal increases while the line of bridging OH groups at 4.2 ppm decreases. The fact that the ^1H MAS NMR signal of silanol groups remains at the position of 1.8 ppm is a hint for the low affinity of these hydroxyl groups to interact with methanol molecules. Since no signal of methyl groups appears at 3.6 ppm, the occurrence of an isotopic H/D exchange between zeolitic OH groups and deuterated methyl groups can be excluded.^{7,11}

In Figure 3a the uptake of CD_3OH , given in numbers, $n_{\text{CD}_3\text{OH}}$, of molecules per SiOHAl group in zeolite H-ZSM-5, is depicted as a function of the adsorption time t . This uptake curve was derived using the unloaded sample, recorded at time $t = 0\text{ min}$, as intensity standard. After adsorption of four molecules of CD_3OH per SiOHAl group ($t = 120\text{ min}$) the experiment was

(11) Hunger, M.; Horvath, T.; Engelhardt, G.; Karge, H. G. In *Catalysis by Microporous Materials, Studies in Surface Science and Catalysis*; Beyer, H. K., Karge, H. G., Kiricsi, I., Nagy, J. B., Eds.; Elsevier: Amsterdam, 1995; Vol. 94, p 756.

(12) Hunger, M.; Horvath, T. *Ber. Bunsen-Ges. Phys. Chem.* **1995**, 99, 1316.

(13) Hunger, M.; Horvath, T. *J. Chem. Soc., Chem. Commun.* **1995**, 1423.

(14) Hunger, M.; Horvath, T.; Weitkamp, J. *Proceedings of the 11th International Zeolite Conference*, Seoul, Korea, 1996, in press.

(15) Schwiager, W.; Bergk, K.-H.; Freude, D.; Hunger, M.; Pfeifer, H. *ACS Symp. Ser.* **1989**, 398, 274.

(16) Freude, D.; Ernst, H.; Wolf, I. *Solid State Nucl. Magn. Reson.* **1994**, 3, 271.

(17) Hunger, M.; Freude, D.; Pfeifer, H. *J. Chem. Soc., Faraday Trans.* **1991**, 87, 657.

(18) Beck, L. W.; White, J. L.; Haw, J. F. *J. Am. Chem. Soc.* **1994**, 116, 9657.

(19) Brunner, E. *J. Mol. Struct.* **1995**, 355, 61.

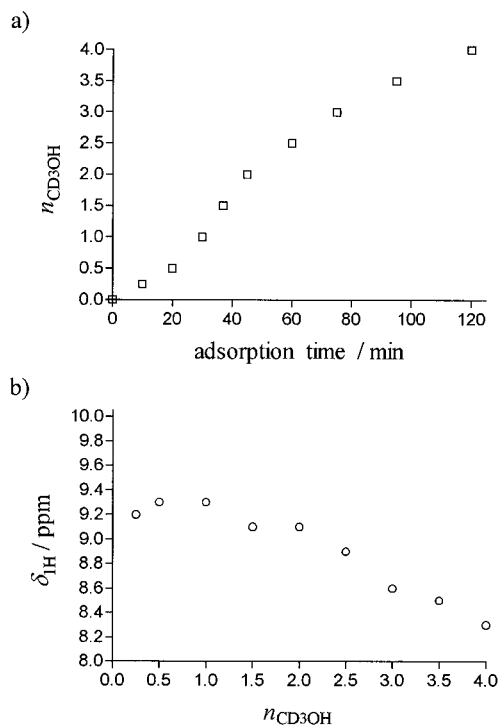


Figure 3. Uptake of CD₃OH given in numbers, $n_{\text{CD}_3\text{OH}}$, of molecules per SiOHAl group in zeolite H-ZSM-5 depicted as a function of the adsorption time t (a) and ¹H MAS NMR shifts, δ_{H} , of the hydroxyl protons involved in adsorption complexes depicted as a function of $n_{\text{CD}_3\text{OH}}$ (b). The values $n_{\text{CD}_3\text{OH}}$ and δ_{H} were derived by an evaluation of the spectra in Figure 2.

stopped. Figure 3b shows the ¹H MAS NMR shifts, δ_{H} , of the hydroxyl protons involved in adsorption complexes depicted as a function of $n_{\text{CD}_3\text{OH}}$. While for coverages of up to one methanol molecule per SiOHAl group the ¹H MAS NMR shifts are constant at ca. 9.3 ppm, a further increase of the methanol coverage leads to a decrease of the shift values (for an explanation see below). Using the same *in situ* MAS NMR technique, the conversion of alcohols under continuous-flow conditions was investigated.^{13,14}

B. ¹H and ¹³C MAS NMR Investigations of Zeolite H-ZSM-5 Loaded with One and Three Methanol Molecules per Bridging OH Group. For the investigation of the chemical bonding of bridging OH groups with different methanol isotopomers, dehydrated zeolite H-ZSM-5 was *ex situ* loaded with CD₃OH and CD₃OD. As observed in the spectrum shown in Figure 2 ($t = 0$ min), the ¹H MAS NMR spectrum of the dehydrated zeolite H-ZSM-5 recorded with an MAS frequency of $\nu_{\text{rot}} = 10$ kHz (Figure 4a) consists of signals of SiOH and SiOHAl groups at 1.8 and 4.2 ppm, respectively. After adsorption of one CD₃OH molecule per SiOHAl group or one CD₃OD molecule per SiOHAl group the low-field signal appears at 9.5 ppm (Figure 4b,c). It is important to note that the resonance position of this low-field signal is equal for zeolite H-ZSM-5 loaded with CD₃OH and CD₃OD. This behavior indicates a rapid H/D exchange between the zeolitic SiOHAl groups and the methanol OD groups and agrees with the results of theoretical investigations.^{3,4} Haase and Sauer⁴ proposed the formation of two symmetry-equivalent neutral adsorbate complexes which are 2-fold hydrogen bonded (compare complex I in Figure 1). The above-mentioned H/D exchange corresponds to a transition between these symmetry-equivalent adsorbate complexes I and has an energy barrier of only 12 kJ/mol.⁴

After adsorption of three CD₃OH or CD₃OD molecules per SiOHAl group, low-field signals at the resonance position of 8.5 ppm were found (Figure 4e,f). Hence, there is a good

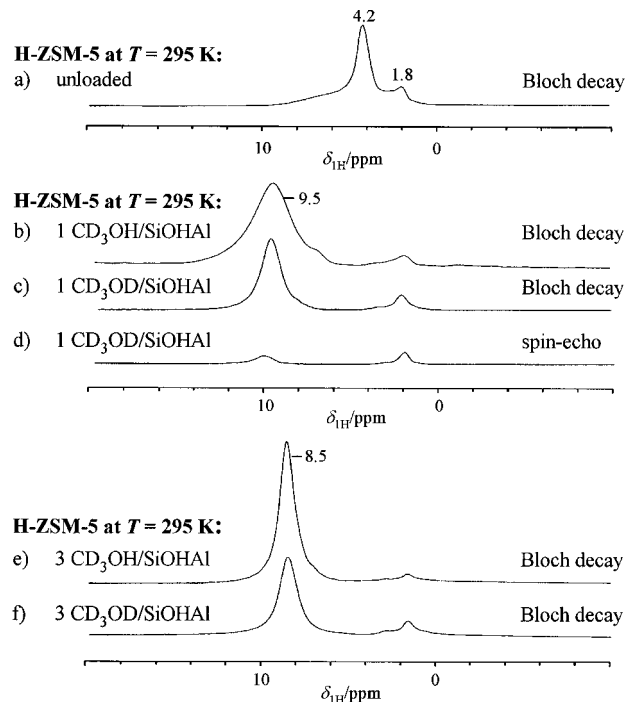


Figure 4. ¹H MAS NMR spectra of dehydrated zeolite H-ZSM-5 recorded at $T = 295$ K before (a) and after adsorption of one CD₃OH molecule per SiOHAl group (b), one CD₃OD molecule per SiOHAl group (c, d), three CD₃OH molecules per SiOHAl group (e), and three CD₃OD molecules per SiOHAl group (f). The pulse delay τ of the rotation-synchronized ¹H MAS NMR spin-echo experiment applied to obtain the spectrum in (d) amounts to $\tau = 0.4$ ms.

agreement of the ¹H MAS NMR shifts observed for *in situ* and *ex situ* prepared samples.

In previous ¹H MAS NMR investigations of partially rehydrated zeolite HY²⁰ and zeolites HY and H-ZSM-5 loaded with pyridine¹¹ a rotation-synchronized Hahn-echo sequence was applied. By this technique, signals due to mobile and rigid nuclei could be distinguished. If the thermal correlation time, τ_c , of mobile nuclei is small in comparison with the pulse delay, τ , of the pulse sequence, the corresponding signal is suppressed in the echo. Figure 4d shows the ¹H MAS NMR spectrum of zeolite H-ZSM-5 loaded with one CD₃OD molecule per SiOHAl group and recorded using the Hahn-echo sequence with a pulse delay of $\tau = 0.4$ ms. The significant decrease of the low-field signal at 9.5 ppm points to a high mobility of the corresponding hydroxyl protons. Therefore, the continual variation of the ¹H MAS NMR shift of the hydroxyl protons caused by an increase of the methanol coverage during the *in situ* adsorption experiment (see Figures 2 and 3b) can be explained by a rapid chemical exchange. This rapid chemical exchange may occur between hydroxyl protons of bridging OH groups and of methanol molecules in the physisorbed (2-fold hydrogen-bonded) and/or chemisorbed (methoxonium) state. A suitable way to slow this rapid exchange are measurements at low temperatures.

Figure 5 shows ¹H MAS NMR spectra of zeolite H-ZSM-5 loaded with different methanol isotopomers and recorded at $T = 153$ K. Generally, the decrease of the temperature results in a strong broadening of the ¹H MAS NMR signals. The existence of MAS sideband patterns indicates that the thermal correlation times, τ_c , of these hydroxyl protons are large in comparison with the period, $\tau_{\text{rot}} = 1/\nu_{\text{rot}}$, of the MAS frequency, ν_{rot} .^{7,21} Parts a and b of Figure 5 show the low-temperature ¹H

(20) Hunger, M.; Freude, D.; Pfeifer, H. J. Chem. Soc., Faraday Trans. 1991, 87, 657.

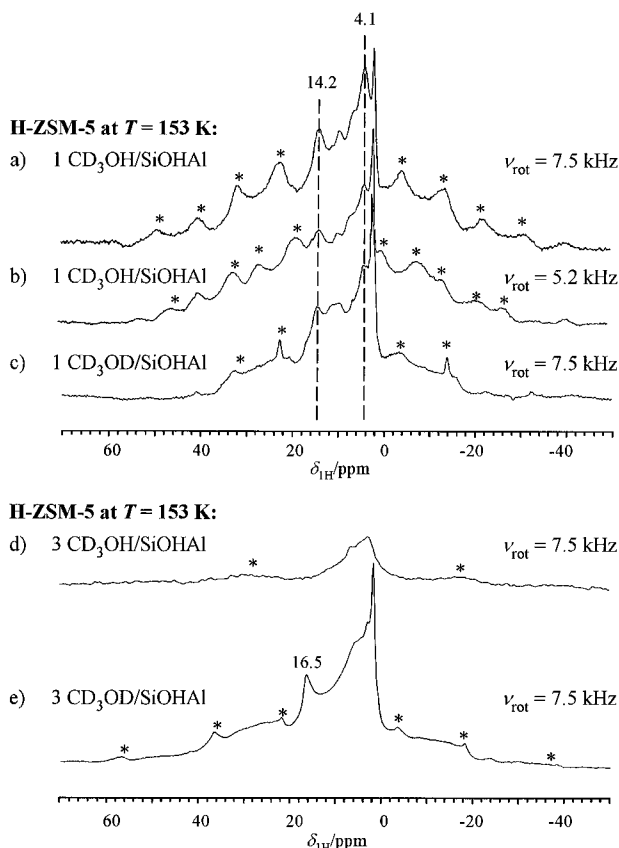


Figure 5. Low-temperature ($T = 153$ K) ^1H MAS NMR spectra of dehydrated zeolite H-ZSM-5 loaded with one CD_3OH molecule per SiOHAl group (a, b), one CD_3OD molecule per SiOHAl group (c), three CD_3OH molecules per SiOHAl group (d), and three CD_3OD molecules per SiOHAl group (e) (asterisk indicates MAS sidebands).

MAS NMR spectra of zeolite H-ZSM-5 loaded with one $\text{CD}_3\text{-OH}$ molecule per SiOHAl group. By a comparison of the spectra recorded with MAS frequencies of $\nu_{\text{rot}} = 7.5$ kHz and $\nu_{\text{rot}} = 5.2$ kHz, MAS NMR central lines at 1.8, 4.1, 9.6, and 14.2 ppm were identified. The signal at 1.8 ppm is due to terminal SiOH and SiOHAl groups.^{7,18,19} The broad signal at ca. 9.6 ppm corresponds to a residual amount of mobile hydroxyl protons as observed at $T = 295$ K (compare Figure 4b,c). The remaining two signals at 4.1 and 14.2 ppm (marked by dashed lines) are due to hydroxyl protons of adsorbate complexes. The strong MAS sideband patterns of the signals at 4.1 and 14.2 ppm indicate that these hydroxyl protons (spin $I = 1/2$) are involved in a strong dipolar interaction with neighboring hydroxyl protons and framework aluminum atoms (spin $I = 5/2$) which is characteristic for hydroxyl protons in adsorbate complexes and SiOHAl groups. Furthermore, the splitting of the spectrum into two ^1H MAS NMR patterns shows that the transitions between the above-mentioned two symmetry-equivalent adsorbate complexes I are frozen at $T = 153$ K.

Figure 5c shows the ^1H MAS NMR spectrum of zeolite H-ZSM-5 loaded with one CD_3OD molecule per SiOHAl group recorded at $T = 153$ K. The fact that also this spectrum consists of two signals at 4.1 and 14.2 ppm can be explained by the rapid isotopic H/D exchange between the zeolitic SiOHAl groups and the methanol OD groups after the preparation of the sample.

The ^1H MAS NMR spectrum of zeolite H-ZSM-5 recorded at $T = 153$ K after adsorption of three CD_3OH molecules per SiOHAl group (Figure 5d) consists of a broad background and

only weak signals at chemical shifts in the range of 1.8 to ca. 4 ppm. The background may be explained by a strong broadening of the ^1H MAS NMR signals due to a homonuclear dipolar interaction of hydroxyl protons contributing to large methanol clusters. As expected, the spectrum of the same sample recorded at $T = 295$ K consists of a narrow line at 8.5 ppm (compare with Figure 4e). At this temperature, the above-mentioned homonuclear dipolar broadening is averaged by an isotropic reorientation of the methanol clusters. The low-temperature ^1H MAS NMR spectrum recorded of zeolite H-ZSM-5 after adsorption of three CD_3OD molecules per SiOHAl group (Figure 5e) is similar to that in Figure 5c. Because of the small concentration of hydroxyl protons in this sample—the same concentration as in the parent zeolite H-ZSM-5—no homonuclear dipolar broadening occurs. However, in contrast to zeolite H-ZSM-5 loaded with one CD_3OD molecule per SiOHAl group (low-field line at 14.2 ppm), the adsorption of three CD_3OD molecules per SiOHAl group results in a resonance position of the low-field signal at 16.5 ppm (Figure 5e).

Application of ^{13}C MAS NMR spectroscopy allows the study of the chemical state of molecules adsorbed on zeolites.²² The protonation of methanol molecules in a superacidic medium leads to a low-field shift of the ^{13}C MAS NMR signal from ca. 49 ppm¹⁰ to 61 ppm.²³ Therefore, also the protonation of adsorbate complexes formed by adsorption of methanol molecules on zeolite H-ZSM-5 should cause a low-field shift of the ^{13}C MAS NMR signal. However, after adsorption of one and even of three methanol molecules per SiOHAl group, ^{13}C MAS NMR signals at shifts of 50.5 ± 0.5 ppm were found. Hence, the low-field shift described by Thursfield and Anderson¹⁰ seems to be caused by methanol molecules adsorbed on the considerable amount of extra-framework aluminum species (15% Al^{ex} , ref 10) of the zeolite H-ZSM-5 used in that study.

C. Mobility and State of Hydroxyl Deuterons in Adsorbate Complexes Consisting of One and Three Methanol Molecules Studied by ^2H NMR. A suitable way to investigate the mobility of deuterons contributing to the OD groups of the methanol complexes in zeolite H-ZSM-5 is the application of variable-temperature ^2H NMR spectroscopy. Since the ^2H nuclei have a nuclear spin of $I = 1$, the dominating line-broadening mechanism is the interaction of the electric quadrupole moment, eQ , of the ^2H nuclei with the z -component of the electric field gradient, $V_{zz} = eq$, at the site of the nuclei. The strength of this quadrupole interaction is described by the quadrupole coupling constant, $\text{QCC} = e^2qQ/h$, which can be derived by a simulation of the NMR line shape.²⁴ The ^2H NMR spectra of rigid hydroxyl deuterons consist of quadrupolar patterns with an edge splitting in the range of 100–200 kHz.^{25–27} Denoting τ_c as the thermal correlation time of an isotropic molecular reorientation, the line width, $\Delta\nu_{1/2}$, in the fast-exchange regime is given by²⁸

$$\Delta\nu_{1/2} = \frac{3\pi}{20} \left(\frac{e^2qQ}{h} \right)^2 \left(3\tau_c + \frac{5\tau_c}{1 + (\omega_o\tau_c)^2} + \frac{2\tau_c}{1 + 4(\omega_o\tau_c)^2} \right) \quad (1)$$

(22) Pfeifer, H.; Ernst, H. *Annu. Rep. NMR Spectrosc.* **1994**, 28, 91.

(23) Olah, G.-A.; White, A. M. *J. Am. Chem. Soc.* **1969**, 91, 5801.

(24) Freude, D.; Haase, J. In *NMR, Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin, 1993; Vol. 29, p 1.

(25) Berglund, Bo; Vaughan, R. W. *J. Chem. Phys.* **1980**, 73, 2037.

(26) Luz, Z.; Vega, A. J. *J. Phys. Chem.* **1987**, 91, 374.

(27) Stepanov, A. G.; Zamaraev, K. I.; Thomas, J. M. *Catal. Lett.* **1992**, 13, 407.

(28) Spiess, H. W. In *NMR, Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin, 1978; Vol. 15, p 55.

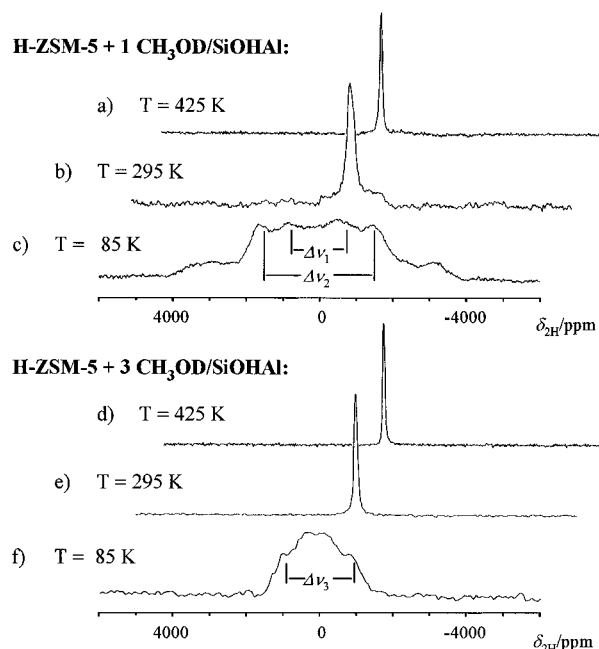


Figure 6. ^2H NMR spectra of dehydrated zeolite H-ZSM-5 loaded with one CH_3OD molecule per SiOHAl group (a–c) and three CH_3OD molecules per SiOHAl group (d–f), recorded with a quadrupole-echo sequence at temperatures of $T = 425$ K (a, d), $T = 295$ K (b, e), and $T = 85$ K (c, f).

where $\omega_0 = 2\pi\nu_0$ is the resonance frequency. An important prerequisite for the application of eq 1 to obtain information about the thermal correlation time is the knowledge of the quadrupole coupling constant of the quadrupolar pattern of rigid nuclei.

Figure 6 shows the ^2H NMR spectra of zeolite H-ZSM-5 loaded with one CH_3OD molecule per SiOHAl group (a–c) and three CH_3OD molecules per SiOHAl group (d–f) recorded at temperatures of $T = 425$, 295, and 85 K. The spectra recorded at $T = 295$ K and $T = 425$ K (Figures 6a,b,d,e) are dominated by narrow signals indicating an isotropic reorientation of the OD groups. At $T = 425$ K, the centers of gravity of the isotropic lines appear at the chemical shift of 10 ± 2 ppm which agrees very well with the ^1H MAS NMR shift value obtained at $T = 295$ K. The ^2H NMR spectrum of zeolite H-ZSM-5 loaded with one CH_3OD molecule per SiOHAl group and recorded at $T = 295$ K (top of Figure 6b) shows an isotropic signal with a line width of about 15 kHz. The quadrupolar patterns observed in the ^2H NMR spectra at $T = 85$ K (Figure 6c,f) indicate a strong slowing of the molecular motions. The spectrum of zeolite H-ZSM-5 loaded with one CH_3OD molecule per SiOHAl group (Figure 6c) consists of two quadrupolar patterns with edge splittings of about $\Delta\nu_2 = 175 \pm 10$ kHz and $\Delta\nu_1 = 105 \pm 10$ kHz. According to $\text{QCC} = (4/3)\Delta\nu$,²⁹ the quadrupolar coupling constant of the former pattern ($\Delta\nu_2$) amounts to ca. 230 kHz which corresponds to free or weakly bonded SiODAl groups^{26,27} or weakly bonded OD groups of molecular compounds.²⁵ The quadrupolar coupling constant of the latter pattern ($\Delta\nu_1$) of ca. 140 kHz is influenced by the chemical interaction of hydroxyl deuterons of methanol complexes. According to eq 1 and to the ^2H quadrupole coupling constant $\text{QCC} = 140$ kHz of the rigid (at $T = 85$ K) deuterons in methanol complexes formed by one CH_3OD molecule per SiOHAl group, the ^2H NMR linewidth of $\Delta\nu_{1/2} = 15$ kHz observed at $T = 295$ K corresponds to an isotropic reorientation of the OD bonds with a thermal correlation time, τ_c , of ca. 0.5

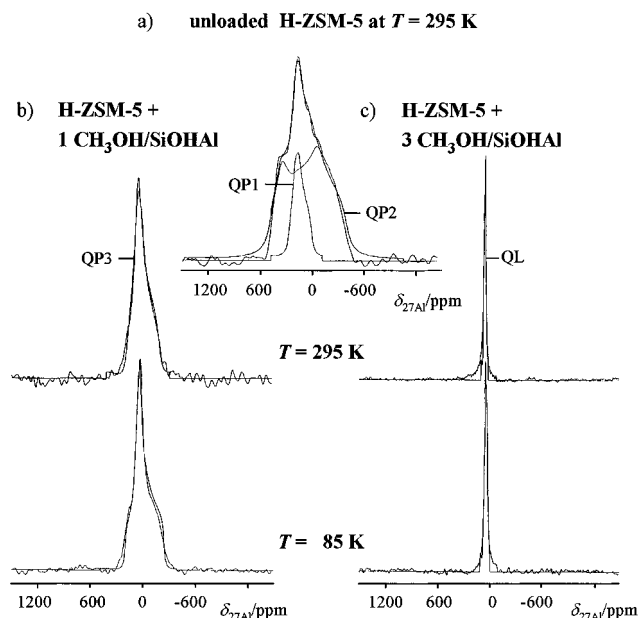


Figure 7. ^{27}Al NMR spectra of dehydrated zeolite H-ZSM-5, unloaded (a) and loaded with one CH_3OH molecule per SiOHAl group (b) and three CH_3OH molecules per SiOHAl group (c). All samples were recorded with the quadrupole-echo sequence described in ref 16 at temperatures of $T = 295$ K (b and c, top) and $T = 85$ K (b and c, bottom).

μs . The low-temperature ^2H NMR spectrum of the adsorbate complex formed by three CH_3OD molecules per SiOHAl group (Figure 6f) consists of at least one quadrupolar pattern with an edge splitting of $\Delta\nu_3 = 115 \pm 5$ kHz corresponding to a quadrupole coupling constant of $\text{QCC} = 153$ kHz. However, this pattern seems to be overlapped by an additional isotropic component.

D. Influence of Methanol Adsorption on the Local Structure of Bridging OH Groups Studied by ^{27}Al NMR Spectroscopy. Similar to the above-mentioned ^2H nuclei (spin $I = 1$), also the ^{27}Al nuclei (spin $I = 5/2$) are involved in quadrupole interactions with the electric field gradients at their sites. Quadrupole coupling constants of framework aluminum atoms in dehydrated H-form zeolites (faujasite, ZSM-5, mordenite) of 11–16 MHz were derived by application of a phase-cycled quadrupole-echo sequence and the simulation of the quadrupole patterns recorded without application of MAS.^{11,12,30,31} In addition, a strong influence of adsorbate molecules on the ^{27}Al quadrupolar parameters of framework aluminum atoms contributing to the local structure of bridging OH groups was found.^{11,12} Figure 7 shows the ^{27}Al NMR spectra of zeolite H-ZSM-5 before (a) and after adsorption of one (b) and three (c) CH_3OH molecules per SiOHAl group recorded at temperatures of $T = 295$ K (top) and $T = 85$ K (bottom). Decomposition and simulation of the ^{27}Al NMR spectrum shown in Figure 7a yield two quadrupolar patterns corresponding to quadrupole coupling constants of $\text{QCC} = 7.5 \pm 0.5$ MHz (QP1) and $\text{QCC} = 15.5 \pm 0.5$ MHz (QP2). As shown in Figure 7b,c, adsorption of methanol results in a significant narrowing of the quadrupolar patterns. The ^{27}Al NMR spectra of zeolite H-ZSM-5, loaded with one (Figure 7b) and three (Figure 7c) CH_3OH molecules per SiOHAl group consist of only one component which corresponds to a quadrupolar pattern with $\text{QCC} = 8.0 \pm 0.5$

(30) Freude, D.; Klinowski, J.; Hamdan, H. *Chem. Phys. Lett.* **1988**, *149*, 355.

(31) Ernst, H.; Freude, D.; Wolf, I. In *Zeolites and Related Microporous Materials: State of the Art 1994, Studies in Surface Science and Catalysis*; Weitkamp, J., Karge, H. G., Pfeifer, H., Hölderich, W., Eds.; Elsevier: Amsterdam, 1994; Vol. 84, p 381.

(29) Barnes, R. G. *Adv. Nucl. Quadrupole Reson.* **1974**, *1*, 335.

MHz (QP3) and to a narrow quadrupolar line with $QCC = 2.5 \pm 0.5$ kHz (QL), respectively. The decrease of the temperature from $T = 295$ K (Figure 7b,c, top) to $T = 85$ K (Figure 7b,c, bottom) does not lead to a variation of the ^{27}Al NMR spectra and, therefore, of the quadrupole coupling constants.

E. Chemical State of Methanol Molecules Adsorbed on Bridging OH Groups in Zeolite H-ZSM-5. (1) Adsorbate Complexes Formed by One Methanol Molecule per SiOHAl Group. Recently, Haase and Sauer⁴ published quantum chemical *ab initio* calculations on adsorbate complexes formed by one methanol molecule per bridging OH group. The ^1H NMR shifts of hydroxyl protons in these model clusters were calculated to be 10.8 ppm for the neutral 2-fold hydrogen-bonded adsorbate complex and 17.4 ppm for the ion-pair structure.⁴ In the ion-pair structure both hydroxyl protons bonded at the methoxonium ion have the same ^1H NMR shift (17.4 ppm).⁴ The ^1H NMR shift of the hydroxyl protons in neutral adsorbate complexes of 10.8 ppm is a mean shift value of the hydrogen-bonded hydroxyl protons of the methanol molecule ($\text{CH}_3\text{OH}\cdots\text{O}$, 7.0 ppm)⁴ and of the bridging OH group ($\text{SiAlOH}\cdots\text{O}$, 14.6 ppm)⁴. The ^1H MAS NMR spin-echo experiment (Figure 4d) and ^2H NMR investigations carried out at $T = 295$ K indicate a high mobility of the hydroxyl protons and deuterons (τ_c of ca. 0.5 μs), perhaps coupled with a rapid exchange. The mean ^1H and ^2H NMR shifts of hydroxyl protons and deuterons in adsorbate complexes formed by one methanol molecule per SiOHAl group of 9–10 ppm agree very well with the mean shift value of 10.8 ppm, theoretically derived for the neutral 2-fold hydrogen-bonded complex.⁴

The strong line-broadening and MAS sideband patterns in ^1H MAS NMR spectra recorded at $T = 153$ K and the quadrupolar patterns in the ^2H NMR spectra obtained at $T = 85$ K are a hint for rigidly bonded adsorbate complexes at these temperatures. The low-temperature ^1H MAS NMR spectrum of zeolite H-ZSM-5 loaded with one CD_3OH molecule per SiOHAl group consists of two signals at 4.1 and 14.2 ppm which are due to hydroxyl protons of the adsorbate complexes. Considering the theoretically derived ^1H NMR shifts (*vide supra*),⁴ the lines at 4.1 and 14.2 ppm may be explained by hydrogen-bonded hydroxyl protons of methanol molecules and SiOHAl groups, respectively, contributing to the neutral adsorbate complexes. The splitting of these two signals, observed at $T = 153$ K, indicates that the transitions between the two symmetry-equivalent states of the neutral adsorbate complexes are frozen.

The low-temperature ^2H NMR spectrum of zeolite H-ZSM-5 loaded with one CH_3OD molecule per SiOHAl group consists of two patterns corresponding to quadrupole coupling constants of $QCC = 230$ kHz and $QCC = 140$ kHz. In a review on ^2H NMR parameters of deuterons in $\text{OD}\cdots\text{O}$ bonds, Berglund and Vaughan²⁵ point to the relationship between the ^2H quadrupole coupling constants, QCC , and the $\text{O}\cdots\text{O}$ distances, $R_{\text{O}\cdots\text{O}}$, of these arrangements (Figure 8). Considering the curve depicted in Figure 8, the ^2H quadrupole coupling constant of $QCC = 140$ kHz corresponds to deuterons in $\text{OD}\cdots\text{O}$ bonds between bridging OH groups ($\text{SiAlOD}\cdots\text{O}$) and adsorbed methanol molecules with $\text{O}\cdots\text{O}$ distances in the range from 0.25 to 0.26 nm. The quadrupolar pattern corresponding to $QCC \approx 230$ kHz may be caused by free hydroxyl deuterons or weakly hydrogen bonded deuterons in arrangements with a $\text{O}\cdots\text{O}$ distance between 0.28 and 0.29 nm (probably $\text{CH}_3\text{OD}\cdots\text{O}$). Hence, also the low-temperature ^2H NMR investigations carried out on zeolite H-ZSM-5 loaded with one methanol molecule per SiOHAl group indicate the existence of hydrogen-bonded adsorbate complexes.

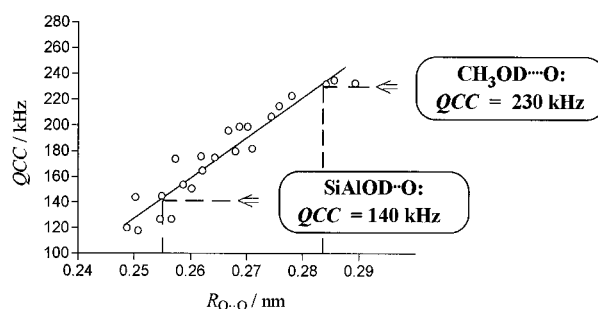


Figure 8. ^2H quadrupole coupling constants, QCC , of deuterons in $\text{OD}\cdots\text{O}$ arrangements depicted as a function of the $\text{O}\cdots\text{O}$ distance, $R_{\text{O}\cdots\text{O}}$.²⁵

(2) Adsorbate Complexes Formed by Three Methanol Molecules per SiOHAl Group. According to Thursfield and Anderson,¹⁰ adsorption of more than one methanol molecule per SiOHAl group leads to the formation of large adsorbate clusters. ^1H MAS NMR and ^2H NMR studies have shown that at temperatures of $T \geq 295$ K the OH and OD groups contributing to these clusters undergo a rapid isotropic reorientation (*vide supra*). The continual decrease in the mean ^1H MAS NMR shift of the OH groups with increasing methanol coverage (Figure 2) indicates a rapid exchange of hydroxyl protons between bridging OH groups and free, hydrogen-bonded and/or protonated methanol molecules. The broadening of the low-temperature ^1H MAS NMR spectrum of zeolite H-ZSM-5 loaded with three CD_3OH molecules per SiOHAl group (see Figure 5d) is a hint for a condensation of the methanol molecules to clusters. The observed strong dipolar broadening is due to the small H–H distances of the hydroxyl protons in these rigid methanol clusters. The ^1H MAS NMR signal observed at 16.5 ppm, after adsorption of three CD_3OD molecules per SiOHAl group, has to be attributed to hydroxyl protons of bridging OH groups interacting with the methanol clusters. The proton resonance position of this signal (16.5 ppm) is significantly larger than that observed after adsorption of one CD_3OD molecule per SiOHAl group (14.2 ppm). This fact indicates a higher proton affinity of large methanol clusters in comparison with small adsorbate complexes. According to Haase and Sauer,⁴ a proton transfer from the bridging OH group to the adsorbed methanol molecule (methoxonium ion) leads to a ^1H NMR signal at 17.4 ppm which agrees qualitatively with the experimentally observed low-field shift of the signal of bridging OH groups interacting with large methanol clusters.

Ghose and Tsang³² pointed to a linear relationship between the ^{27}Al quadrupole coupling constants of AlO_4 tetrahedra in various inorganic solids and the $\text{O}–\text{Al}–\text{O}$ bond angles in these AlO_4 tetrahedra. The authors described the geometry of the AlO_4 tetrahedra by a *shear strain parameter* which is calculated by the differences between the individual $\text{O}–\text{Al}–\text{O}$ bond angles and the ideal bond angle of 109.5° .³² According to the above-mentioned linear relationship, the decrease in the quadrupole coupling constant of the AlO_4 tetrahedra in zeolite H-ZSM-5 as a result of methanol adsorption (from $QCC = 15.5$ MHz to $QCC = 2.5–8.0$ MHz) is due to a decrease of the *shear strain* corresponding to a more symmetric geometry of the AlO_4 tetrahedra. For zeolite H-ZSM-5 loaded with basic probe molecules this variation of the AlO_4 geometry was explained by the deprotonation of the SiOHAl groups.¹² In addition, also a variation of $\text{Al}–\text{O}$ bond lengths has to be considered. *Ab initio* calculations on model-clusters of bridging OH groups interacting with methanol⁴ and water molecules³³ indicated a

(32) Ghose, S.; Tsang, T. *Am. Mineral.* **1973**, *58*, 748.

(33) Krossner, M.; Sauer, J. *J. Phys. Chem.* **1996**, *100*, 6199.

change of O–Al–O bond angles as well as of Al–O bond lengths in the AlO_4 tetrahedra. The variation of the O–Al–O bond angles in AlO_4 tetrahedra contributing to the local structure of SiOHAl groups is nearly the same for neutral 2-fold hydrogen-bonded adsorbate complexes and ion-pair structures.^{4,33} On the other hand, there are significant differences in the Al–O bond lengths of the above-mentioned AlO_4 tetrahedra.^{4,33} For AlO_4 tetrahedra in Si–O–Al bridges contributing to ion-pair structures the Al–O bond length differences are significantly smaller than for AlO_4 tetrahedra of SiOHAl groups contributing to neutral 2-fold hydrogen-bonded adsorbate complexes.^{4,33} This effect may be responsible for the significant smaller ^{27}Al quadrupole coupling constant of AlO_4 tetrahedra in the local structure of bridging OH groups interacting with three methanol molecules (QCC = 2.5 MHz) in comparison with the QCC value of AlO_4 tetrahedra interacting with one methanol molecule (QCC = 8.0 MHz). Hence, the small ^{27}Al quadrupole coupling constant of framework AlO_4 tetrahedra of zeolite H-ZSM-5 loaded with three methanol molecules per SiOHAl group supports the partial protonation of large methanol clusters.

Conclusions

Adsorption of methanol molecules on bridging OH groups in zeolite H-ZSM-5 leads to the formation of neutral 2-fold hydrogen-bonded adsorbate complexes consisting of one methanol molecule per SiOHAl group or partially protonated methanol clusters formed by three methanol molecules per SiOHAl group. The chemical state of hydroxyl protons in adsorbate complexes

formed by one methanol molecule per SiOHAl group has been investigated by variable-temperature ^1H MAS NMR and ^2H NMR spectroscopy. The application of these methods yielded ^1H NMR signals and ^2H quadrupolar patterns which are characteristic for hydrogen-bonded hydroxyl protons and deuterons, respectively. The ^1H MAS NMR shift of hydroxyl protons observed in low-temperature spectra of adsorbate complexes formed by three methanol molecules per SiOHAl group indicated a higher proton affinity of these complexes than observed for complexes consisting of one methanol molecule per SiOHAl group. In addition, a strong association of methanol molecules leading to methanol clusters was found at $T = 153$ K for the zeolite H-ZSM-5 loaded with three methanol molecules per SiOHAl group. The ^{27}Al quadrupole parameters of the AlO_4 tetrahedra contributing to the local structure of SiOHAl groups were found to be sensitive for the interaction of bridging OH groups with methanol molecules. The small ^{27}Al quadrupole coupling constant derived for framework AlO_4 tetrahedra in zeolite H-ZSM-5 loaded with three methanol molecules per SiOHAl group indicated a partial protonation of the methanol molecules.

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