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Interaction between CD_3OH and a H-mordenite studied by ^1H NMR, broad-line at 4 K and MAS at 300 K

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The simulation of 4 K ^1H broad-line NMR spectra of CD_3OH interacting with the acidic OH groups of H-mordenite zeolite shows no $CD_3OH_2^+$ ions but hydrogen-bonded complexes. For high CD_3OH concentrations, clusters of hydrogen-bonded methanol molecules are formed, also hydrogen-bonded to Brønsted acid sites of the zeolite. The 300 K ^1H MAS spectra prove that the desorbed H-mordenite sample contains also silanol groups in electrostatic interaction with the framework; these silanols do not interact with methanol under our experimental conditions.

Keywords: H-mordenite, CD_3OH, broad-line ^1H NMR, ^1H MAS NMR

1. Introduction

Some H-form zeolites are used to convert methanol into hydrocarbons [1–16]. The nature of the first interaction is not yet clear: strong hydrogen bond formation between OH groups belonging to zeolite Brønsted acid sites and alcohol has been postulated [4,9], as well as proton transfer from Brønsted sites to methanol [9,12–16]. Most IR studies favour the ionic interpretation [12,15–17]. Theoretical calculations [18–26] are either equivocal or favour the hydrogen-bonded complex [23,25]. However, they show that: (i) both species, methoxonium ions (MIO) and hydrogen-bonded complexes (HBC), would be stabilized by hydrogen bonding to the zeolite framework O atoms; (ii) the internal H–H distance in a $CD_3OH_2^+$ ion would be 149–158 pm [26,27], which is much smaller than in HBC (about 192 pm) (fig. 1).

^1H high-resolution MAS NMR results have been published by several authors. Ernst et al. [28,29] performed a two-dimensional study of the reaction between methanol and H-ZSM-5, the samples being switched from room temperature to 500–600 K by means of a laser beam. The other studies were carried out at room temperature. Also on H-ZSM-5, Klinowski et al. [11–13] observed two signals, at 4.1 and about 9.5 ppm, that they attributed to CH_3 and OH groups, respectively, because they observed only the second signal when CH_3OH is replaced by CD_3OH. The large chemical shift of this second signal depends on the alcohol concentration and is assumed to be due either to HBC or to MIO. Since all protons are equivalent on the NMR time scale, the authors proposed that a "cluster" was formed of up to five hydrogen-bonded methanol molecules, one of them being also hydrogen-bonded to a Brønsted acid site. Luz and Vega [30] reported, on a H-rho zeolite, a shift of 10–12 ppm when the methanol concentration per Brønsted acid site (denoted CH_3OH/bas) was 1; they attributed this shift to H atoms chemically exchanging between different positions at the acid site.

We have already shown that ^1H broad-line NMR in "rigid lattice conditions" can identify some groups of near neighbour H atoms and their relative distances [30–32]. Therefore, based on the quantum-chemical results, ^1H broad-line NMR should answer the question: are methoxonium ions stable or not? This is the purpose of this contribution, performed with the help of the ^1H MAS NMR technique.

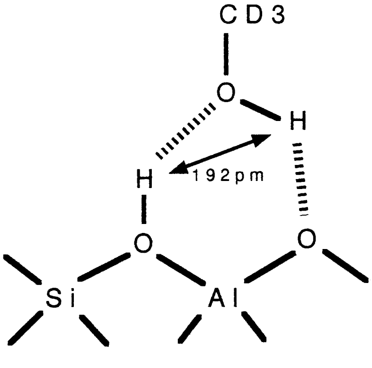

Fig. 1. Hydrogen-bonded complex (HBC) of methanol on H-ZSM-5 on Brønsted acid sites (bas) [23,26,27].

2. Experimental

The framework Si/Al ratio of the H-form mordenite is 8.4. The ^{27}Al high-speed MAS NMR spectrum of the fully hydrated sample at 500 MHz contains only the signal of tetracoordinated Al atoms. The sample is "shallow-bed" evacuated and pretreated to 400°C [30,32] (denoted then "anhydrous", it is not dehydroxylated but dehydrated) before CD_3OH adsorption. The methanol methyl group is deuterium enriched to 99.6%. The gas is adsorbed at 300 K, in steps (about 3 kPa/step), to the final pressure. The amount of adsorbed methanol is gravimetrically controlled. After adsorption the samples are sealed; they are not thermally homogenized but shaken and kept at least 48 h at room temperature before the experiments. The same sealed sample is used for both MAS and broad-line ^{1}H NMR experiments.

The ^{1}H NMR conditions have already been described in detail [31–33]. MAS NMR is performed at room temperature with a Bruker 400 MHz apparatus [34,35]; the home-made probe allows the samples to be rotated at 4 kHz; the delay between successive pulses is from 5 s for methanol containing samples to 20 s for "anhydrous" ones. A special pulse sequence for $^1H\{^{27}Al\}$ dipolar dephasing has been used by Beck [36] and Freude et al. [37,38] for H-ZSM-5 and H-Y samples; it consists of an ^{1}H echo sequence at integer MAS rotation periods of the sample, with various durations of ^{27}Al irradiation before and after the ^{1}H inversion. It is used to differentiate those H atoms which are near Al atoms (for which ^{1}H–^{27}Al coupling reduces the signal intensity) from those far from ^{27}Al (for which the signal is only slightly reduced). Broad-line experiments are performed at 60 MHz on samples quenched at 4 K, using a modified Varian DP 60, with accumulation of the spectra. These spectra are unchanged if helium at low pressure has been introduced into the samples before sealing in order to enhance the thermal conductivity. All conditions are selected so that the spectra are not modified by artefacts. Spectra are recorded as derivatives of the absorption relative to the magnetic field versus the magnetic field. Only half of the centrosymmetric spectra are shown in the figures. For both ^{1}H NMR types the empty probe signal is subtracted from the rough experimental spectra. As broad-line spectrum simulation is very simple in the case of this study, it will be explained in section 3.

3. Results

3.1. ^{1}H MAS NMR

The "anhydrous" mordenite sample contains the following signals (fig. 2) [34,35]; (i) 4.0 ± 0.2 ppm due to 5.0 (±5%) acid SiO(H)Al protons per uc (denoted ZOH); (ii) 2.0 ± 0.2 ppm, silanol H atoms, denoted silanol$_1$, whose contribution is negligible; (iii) 6.6 ± 0.2 ppm, silanol H, denoted silanol$_2$ [37,38], whose contribution, 1.2 (±40%) is not very reproducible. Several types of H atom of "anhydrous" zeolite resonate between 6 and 7 ppm [37–39]: ZOH type 2 and/or silanol$_2$, which are in strong electrostatic interaction with the framework. The presence of ZOH type 2 has been shown in mordenites and in H-ZSM-5 samples [33,36,38,39]; the corresponding signal, which is relatively wide at room temperature, is narrowed by lowering the temperature to 123 K [40]. The $^1H\{^{27}Al\}$ dipolar dephasing experiment on the "anhydrous" mordenite only slightly affects the 6.6 ppm signal, in contrast to the 4 ppm one (fig. 3). According to Freude [36], the 6.6 ppm signal must therefore be attributed to silanol$_2$ H atoms. Their concentration is 1.2/uc ± 40%. Other arguments agree with this attribution of the 6.6 ppm signal: (i) it is always narrow; (ii) it cannot be simulated using a Lorentzian curve [37].

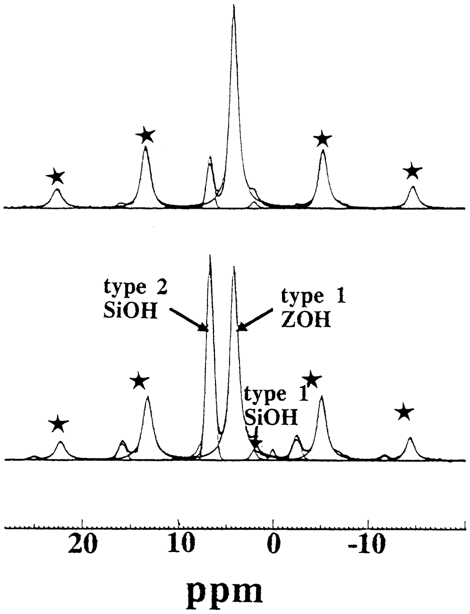

Fig. 2. ^{1}H MAS NMR spectra at 300 K (experimental, simulated and partial contributions of different types of H atom) in the "anhydrous" H-mordenite sample. Asterisks denote spinning side bands.

After CD_3OH adsorption at whatever concentration, the two signals at 2 and 6.6 ppm are unchanged. The 4 ppm signal intensity decreases with increasing CD_3OH concentration per Brønsted acid site, denoted adsCD_3OH/bas, and totally disappears only for adsCD_3OH/bas = 5. A new signal, at 8.6 ppm, is visible for adsCD_3OH/bas = 0.32; its chemical shift and width increase to 9.9 ppm and 2.7 kHz, respectively, for adsCD_3OH/bas = 1. For larger values of adsCD_3OH/bas, both the chemical shift and width decrease (9.5 ppm and 1 kHz, respectively, for adsCD_3OH/bas = 2.8). This signal is attributed to exchange between H atoms of methanol and ZOH groups.

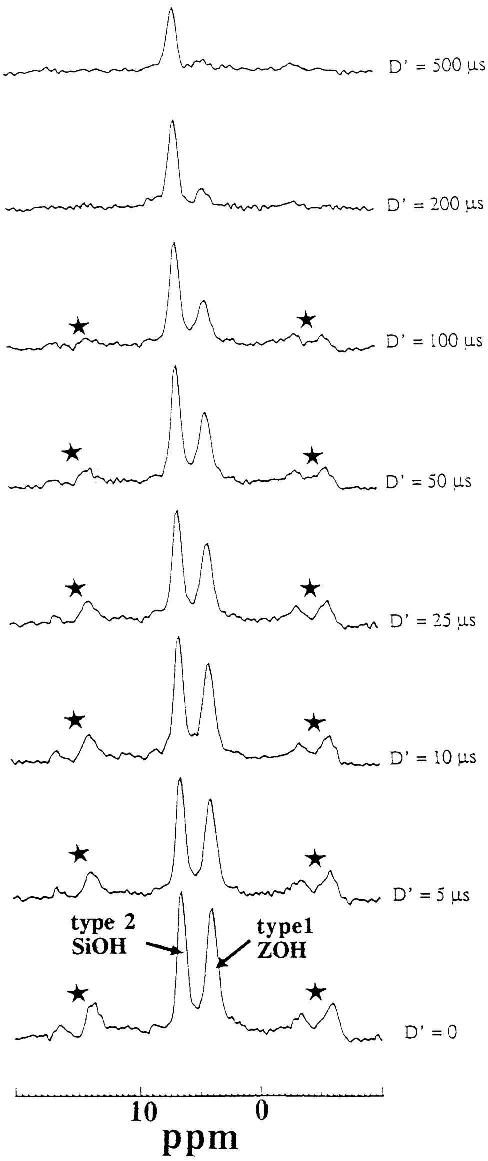

Fig. 3. ^1H MAS NMR spectra, at 300 K, of the "anhydrous" H-mordenite with $^1H\{^{27}Al\}$ dipolar dephasing spin-echo for various durations (D') of ^{27}Al irradiation. Asterisks denote spinning side bands.

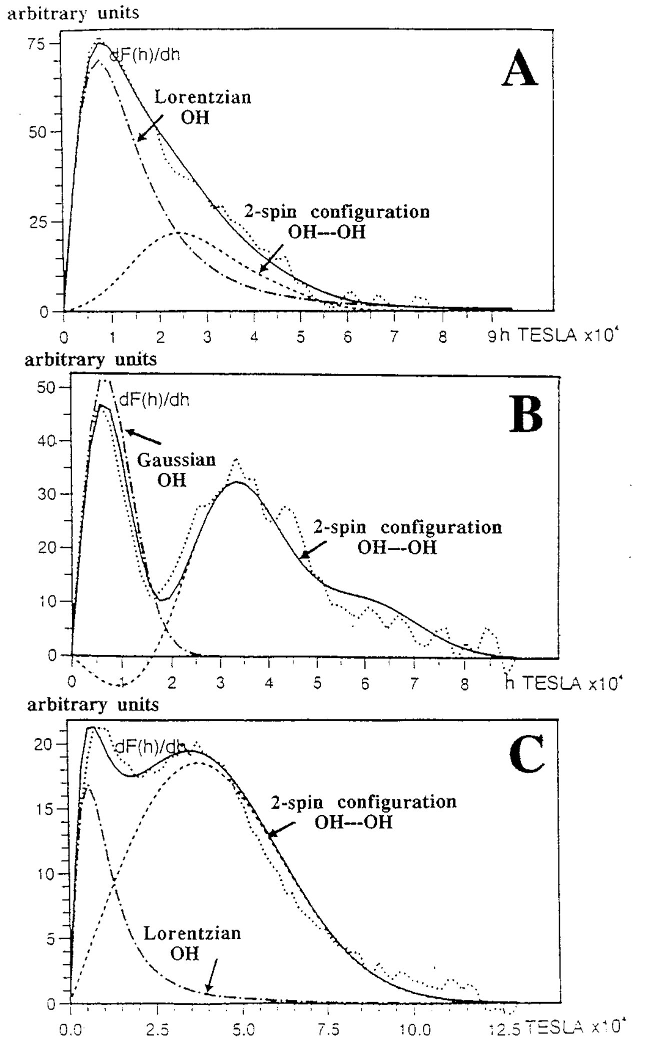

Fig. 4. ^1H broad-line NMR spectra of H-mordenite after adsorption of CD_3OH: (small dots) experimental spectrum; (continuous line) simulated spectrum; (- - -) two-spin contribution; (–· –) Lorentzian or Gaussian absorption. (A), (B) and (C) refer to adsCD_3OH/bas = 0.32, 1.0 and 1.76, respectively.

3.2. ^1H broad-line NMR

All the broad-line spectra are noisy (fig. 4) because the samples contain few H atoms: one per zeolite ZOH, one per silanol$_2$ group, and one per adsorbed CD_3OH.

The spectrum of the "anhydrous" mordenite (not shown) corresponds to a Lorentzian absorption (parameter 1.35×10^{-4} T); it is typical of the absence of hydrogenated adsorbed species. It contains no contribution for $h \geqslant 6 \times 10^{-4}$ T, where h is the difference between the applied magnetic field and the Zeeman resonance field.

When CD_3OH is adsorbed, the experimental spectra can be simulated with only two distinct contributions. These contributions correspond to: (i) pairs of r-distant H atoms which are simulated using a two-spin magnetic configuration calculated by Pake [41]; (ii) protons without any particular near-neighbour H, for which the absorption is either Lorentzian (L) or Gaussian (G) and considered as "free H atoms". Their concentration and that of species containing H-pairs are given in table 1, with the distance or typical parameters of the configurations, for different values of adsCD_3OH/bas. It can be concluded that:

(i) For adsCD_3OH/bas$\leqslant 1$, almost all CD_3OH interact with ZOH. The r distance is between 200 and 193 pm when adsCD_3OH/bas increases from 0.32 to 2.

(ii) For adsCD_3OH/bas $\geqslant 1$, the "free" H atom concentration agrees with that of silanol$_2$. All other H atoms are associated as pairs. The pair r-value seems to increase a little from 200 to 205 pm when adsCD_3OH/bas> 2. The shortest interpair distances, X, which are constant for adsCD_3OH/bas$\leqslant 1$, decrease for larger values of adsCD_3OH/bas to a value equal to r.

Table 1
Concentrations of the following species per Brønsted acid site (bas): (column 1) adsorbed methanol molecules on the mordenite sample; (column 2) hydrogen-bonded complex (HBC) plus hydrogen-bonded methanol molecules; (column 5) "isolated" OH groups; (columns 3 and 4) distance parameters (pm) for the two-spin configuration which describes species of column 2; (column 6) nature of the absorption for "isolated" OH groups; (column 7) parameter for the absorption for "isolated" OH groups, in 10^{-4} T for Lorentzian absorption, (column 8) distance (in pm) corresponding to the magnetic field parameter for the Gaussian absorption

1	2	3	4	5	6	7	8
adsCD_3OH/bas $\pm10\%$	(OH. . .OH)/bas			O H/bas			
	number $\pm10\%$	two-spin configuration		number $\pm10\%$	absorption shape	parameter for L ±0.05	X ±8
		$r \pm 5$	$X \pm 5$				
0.32	0.31	200	285	1.01	L	1.40	
0.74	0.74	196	265	0.50	L	1.70	
1.00	1.00	193	273	0.24	G		315
1.06	1.02	196	252	0.24	L	1.20	
1.22	1.11	198	251	0.24	L	0.98	
1.50	1.25	198	240	0.24	L	0.85	
1.76	1.38	200	210	0.24	L	0.99	
2.00	1.49	200	210	0.24	L		280
2.40	1.70	205	205	0.24	G		280
2.80	1.91	205	205	0.24	G		291

4. Discussion

Both NMR results show that silanol$_2$ groups do not interact with methanol. Because their concentration is too low, it is not possible to determine, from our experiments, if type 1 silanols of the zeolite sample interact with CD_3OH.

The observed chemical shift of exchanging H atoms for adsCD_3OH/bas = 1, which is 9.9 ppm, agrees with the one Klinowski observed (9.5 ppm) [11–13] and that calculated by Haase et al. for HBC (10–12 ppm) [23].

The two-spin configuration *r*-value, 193–200 pm, is in acceptable agreement with the results of quantum-chemical calculations for the intra H–H distance in HBC, 191 ± 2 pm [26,27] (fig. 1). However, this experimental value does not agree with the calculated H–H distance in MIO stabilized by hydrogen bonds to the zeolite framework, which is 149–158 pm [26,27]. Therefore, MIO is not a stable product of the initial interaction between methanol and Brønsted acid sites at room temperature.

The fact that *r* increases only a little (from 196 to 205 pm) when adsCD_3OH/bas increases from 1 to the maximum adsCD_3OH/bas value of 2.8 means that the H–H distances resulting from hydrogen bond formation between distinct methanol molecules do not differ much from those between methanol and ZOH. This is confirmed by the small change in the chemical shift for the exchanging H atom, from 9.9 to 9.5 ppm, when adsCD_3OH/bas increases from 1 to 2.8. These results are in qualitative agreement with Klinowski's proposal [11–13] that small clusters of methanol hydrogen-bonded to ZOH are formed.

5. Conclusion

^1H broad-line and MAS NMR results on CD_3OH interacting with a H-mordenite sample show that $CH_3OH_2^+$ ions are not stable species in contrast to hydrogen-bonded ones. The H–H distance of the hydrogen-bonded complex for adsCD_3OH/bas = 1 is a little shorter than that of hydrogen-bonded methanol molecules for larger values of adsCD_3OH/bas.

In the "anhydrous" mordenite sample, there is evidence for silanol groups in strong electrostatic interaction with the framework. They do not interact with methanol.

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