

Solid-State NMR Studies of Adsorption Complexes and Surface Methoxy Groups on Methanol-Sorbed Microporous Materials

Fathollah Salehirad and Michael W. Anderson

Department of Chemistry, UMIST, PO Box 88, Manchester M60 1QD, United Kingdom

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Multinuclear solid-state NMR has been used to study the structure of surface-bonded methanol structures before and after reaction on zeolite H-ZSM-5 and zeolite H-SAPO-34. The results reveal that at low loadings, up to one methanol per acid site, the methanol is adsorbed in two hydrogen bonded configurations. At higher coverages the results suggest methanol clustering with the involvement of one methoxonium ion. After reaction at ca 500 K a variety of surface methoxy groups are observed on both catalysts. NMR is able to differentiate at least four methoxy groups on H-ZSM-5 and the motion of these species is discussed. © 1998 Academic Press

INTRODUCTION

Since the discovery of ZSM-5 (1), a high-silica zeolite which converts methanol to gasoline (MTG), an extensive research effort (2–5) has been invested in studying this conversion reaction. The MTG and other relevant processes (6–13), such as methylation of benzene, toluene, and phenol, consume methanol as a primary reactant. All these processes are catalysed by bridging hydroxyl groups, which are acknowledged (14) to be the focus of Brønsted acidity of zeolites. Hence, to provide a deeper insight into the chemistry of such processes, the elucidation of the reactant/zeolite Brønsted acid site interaction before and after the reaction (at mild temperatures) seems to be of great importance.

Bulk spectroscopic techniques, such as Fourier transform infrared (FTIR) and solid-state magic-angle spinning (MAS) NMR are required to probe the state of the reactant before and after thermal treatment over the catalyst. Recent solid-state NMR (15–17), FTIR (18–23), and theoretical calculation (24–27) studies of methanol and water over zeolite-active sites suggest either a hydrogen-bonded structure or an oxonium structure (as a transient or stable state) of the guest molecule.

Previous studies (28–37) of both methyl iodide on Na-ZSM-5 and methanol over acidic zeolites concluded that surface methoxy species formed as bonded methyls to SiOAl bridging oxygens of the microporous materials at different temperatures.

In this work the use of ^1H , ^2H , and ^{13}C solid-state NMR to investigate the state of methanol on H-ZSM-5 and H-SAPO-34 at room and mild temperatures, i.e., below 543 K, is described. We have briefly reported previously (5) on the formation of surface methoxy groups on a zeolite SAPO-34. Here, the complexation of methanol over a SAPO material, as well as ZSM-5, are discussed in detail.

EXPERIMENTAL

The two microporous materials used in this investigation were characterised by X-ray diffraction, scanning electron microscopy, and by ^{27}Al , ^{29}Si , and ^{31}P MAS NMR. The results (not shown) verified their high quality. The acidic form of ZSM-5¹ (different Si/Al ratios) was prepared by ion-exchanging sodium with ammonium, followed by calcination (17). H-SAPO-34 was obtained by direct calcination of as-synthesised SAPO-34, which was prepared according to literature (38). ^2H and ^{13}C NMR spectra were recorded on samples sealed in glass ampoules as described previously (16). For ^2H NMR experiments approximately 0.40 g of catalyst was used. After dehydration (723 K overnight under high vacuum), the sample was exposed to a certain volume and pressure of CD_3OH or CH_3OD corresponding to one molecule per acid site at room temperature. Methylation of the catalyst for ^2H and ^1H NMR experiments was carried out at 493–533 K for 15 min, followed by evacuation of the sample at the same methylation temperature for 1 h. D-SAPO-34 was prepared by three D_2O exchanges of the catalyst at 363 K for 3 h, followed by dehydration at 723 K overnight. Samples for ^1H MAS NMR experiments were prepared by introducing methanol (CH_3OH , CD_3OD , and CH_3OD 99% enriched, as supplied by Aldrich) over each dehydrated sample to give loadings of 1–3 molecules per Brønsted acid site and then sealing (apart from those for the methylation reaction) in glass tubes. Each tube was transferred to a glove box under an argon atmosphere where the sample was removed from the ampoule and packed in a Bruker 4-mm air tight rotor.

¹ Na-ZSM-5 used in this study was supplied by BP and other research groups.

Spinning speeds of ca 0.8–5 and 8–10 kHz were employed for recording ^{13}C and ^1H MAS NMR spectra, respectively. The number of transients recorded for each individual sample varied in the range 150–42500 scans and depended on the type of nucleus being examined. The samples analysed for direct comparison were recorded with the same number of scans as prepared under the same conditions.

All spectra were recorded using a Bruker MSL400 spectrometer with static, 4-mm Bruker double-bearing and 7-mm Chemagnetics pencil probes. ^1H MAS NMR spectra were recorded using a Hahn-echo (unless stated otherwise) pulse sequence, $\pi/2 - \tau - \pi - \tau$, with $\pi/2$ pulse length of $5.6 \mu\text{s}$ and $\tau = 2\pi/\omega_{\text{rot}}$, where ω_{rot} is the sample rotation frequency. Repetition time of 5–10 s was used. The static wide-line ^2H spectra were recorded using the composite pulse sequence described by Siminovitch *et al.* (39) to give an even broadband excitation, the pulses were set up using *p*-xylene- d_4 adsorbed on H-ZSM-5.

^{29}Si MAS NMR spectra of dehydrated, 1:1 methanol loaded, and methylated H-ZSM-5 were recorded using a single pulse Bloch decay. The quad-echo pulse sequence was employed to record ^{27}Al MAS NMR spectra of dehydrated, 1:1 methanol loaded, and methylated H-ZSM-5, whereas for the as-prepared H-ZSM-5 a Bloch decay was applied.

RESULTS

In order to investigate the nature of surface complexes in an acidic, microporous material/methanol system, several experiments were carried out over zeolites and zeotype listed in Table 1 using different methanol isotopomers. ^{13}C static/MAS, ^2H static, and ^1H static/MAS NMR were employed during the course of this study.

H-ZSM-5

^{13}C CP static NMR spectra of samples with a loading of 1:1 methanol molecule per Brønsted acid site, with and without evacuation of the samples, show a broad pattern, convoluted with a symmetrical signal. The deconvolution of the spectra clearly shows these two resonances,

a nearly isotropic peak and a powder pattern (Figs. 1 and 2, top spectra). As the coverage increases the nearly isotropic resonance becomes narrower. The differences which arise between the samples with different Si/Al ratio (40 in Fig. 1, 27.6 in Fig. 2) may either be associated with extra-framework aluminium in the former sample or the difference in Si/Al ratio. Note that H-ZSM-5 with Si/Al ratio of 27.6 is free from extra-framework aluminium. Line simulation was employed to find the principal elements σ_{11} , σ_{22} , and σ_{33} of the shielding anisotropy, the asymmetry parameter η_{CS} and the anisotropy parameter δ_{CS} of surface adsorbed methanol (Table 2).

Figure 3 is the static ^1H NMR spectrum of CD_3OH adsorbed on active sites of the catalyst (Si/Al = 27.6). This can, due to the homonuclear (H–H) dipolar interactions involved, be informative about the state of CD_3OH molecules adsorbed on Brønsted acid sites. The spectrum is deconvoluted into two resonances: one nearly isotropic signal superimposed with the second resonance, a Pake doublet powder pattern (Fig. 3) with splitting of the perpendicular component $\Delta\nu_{\perp} = 15930.2$ Hz. Resonances resulting from silanol groups and mainly background (3 and 4) are also shown in the deconvoluted spectra. The ^1H MAS NMR spectra of the bare and CD_3OD or CH_3OH adsorbed on three different H-ZSM-5 samples are summarized in Table 3. Some of these spectra are also shown in Fig. 4. Two Brønsted acid sites can be seen at 4.2 and ca 6 ppm (40–42) by deconvoluting the ^1H NMR spectrum of the bare catalyst (Fig. 4h, resonances 4 and 5). These two resonances move downfield to higher chemical shift values as the methanol coverage increases (up to 3:1). The silanol group protons (ca 1.7–1.9 ppm) remain unchanged while the peak at 2.8 ppm (resonance 3) corresponding to $-\text{AlOH}$ starts moving downfield after the adsorption of three methanol molecules per acid site. The peak labelled by 1 (centred at ca 1 ppm) in the spectra corresponding to bare H-ZSM-5 and a sample at a 3:1 coverage (Figs. 4h and 4g) may be assigned to the probe background and also water vapour around the coil. Peaks 3 and 4 in the 3:1 spectrum (Fig. 4g) could be assigned to AlOH and perturbed AlOH of extra-framework aluminium in this zeolite. The resonance at ca 3.6 ppm in Table 3 (the last row, column 4) results from the methyl protons.

Surface Methoxy on H-ZSM-5

Methanol can begin methylating acidic zeolites at very mild temperatures before the onset of hydrocarbon products. To verify this the zeolite was initially dehydrated at 723 K, followed by lowering the temperature to 293 K in order to enable the adsorption of ^{13}C -enriched methanol (1:1) onto the dehydrated zeolite. This sample was treated with methanol at 533 K and then allowed to be vigorously evacuated at the same temperature for 1 h. The prolonged evacuation was found to be enough to remove any physisorbed species since the initial high vacuum was

TABLE 1

Summary of Catalyst Characterization Data

Microporous material	Si/Al	EFA ^a
H-ZSM-5	40	15%
H-ZSM-5	35.5	No
H-ZSM-5	27.6	No
H-SAPO-34	0.17	
D-SAPO-34	0.17	

^a EFA = extra-framework aluminium.

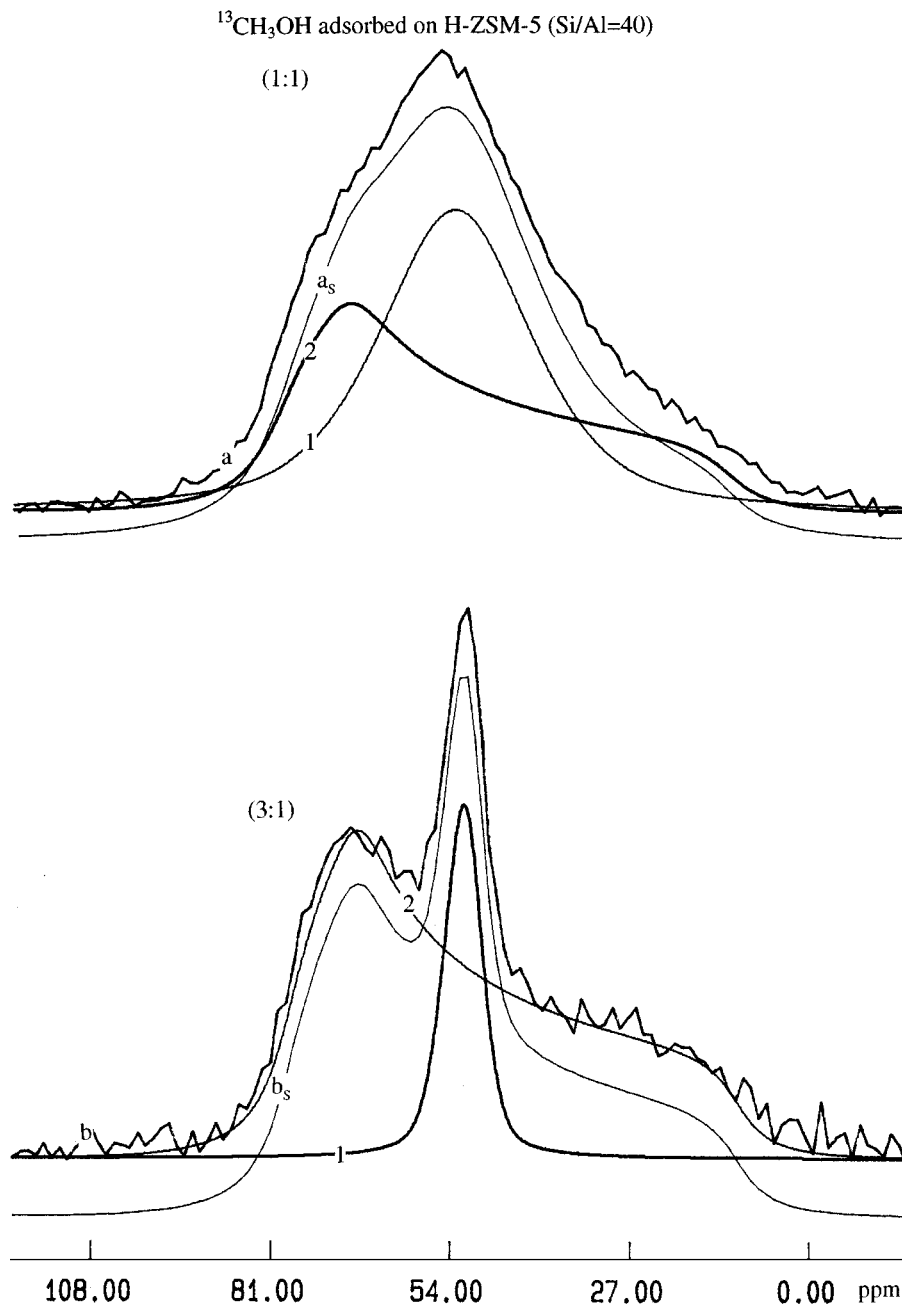


FIG. 1. ^{13}C CP static NMR spectra of $^{13}\text{CH}_3\text{OH}$ adsorbed on H-ZSM-5 (Si/Al=40) at room temperature with (a) 1:1 (13269 transients) and (b) 3:1 methanol molecules per acid site (10857 transients). Both simulated spectra (a_s) and (b_s), comprise (1) a nearly isotropic component and (2) a powder pattern.

quickly restored after the exposure. Both $^{13}\text{C}\{\text{H}\}$ (^{13}C proton decoupled) and ^{13}C CP MAS NMR of the sample were recorded. The resulting spectra show at least four resonances at chemical shifts, ranging from 53–65.5 ppm (Fig. 5). The shifts 53–59 ppm, as reported (30), arise from surface methoxy groups. The ^1H MAS NMR spectrum of a similarly prepared sample (normal methanol used instead of carbon-enriched methanol) shows two main resonances at ca 2 and 3.9 ppm with a broad shoulder centred at ca

7.3 ppm (Fig. 6a). In order to assign these resonances, a further methylated sample prepared under identical conditions using CD_3OH as a reactant was run for ^1H MAS NMR (Fig. 6b). The spectrum shows $-\text{SiOH}$, $-\text{AlOH}$, a small peak from unreacted Brønsted acid sites and the broad shoulder centred at ca 7.3 ppm. In conjunction with the signal at ca 2 ppm ^1H MAS NMR spectra of the bare and methylated silicalite-1 (equal masses) were performed under the same conditions (Table 4). These results exhibit

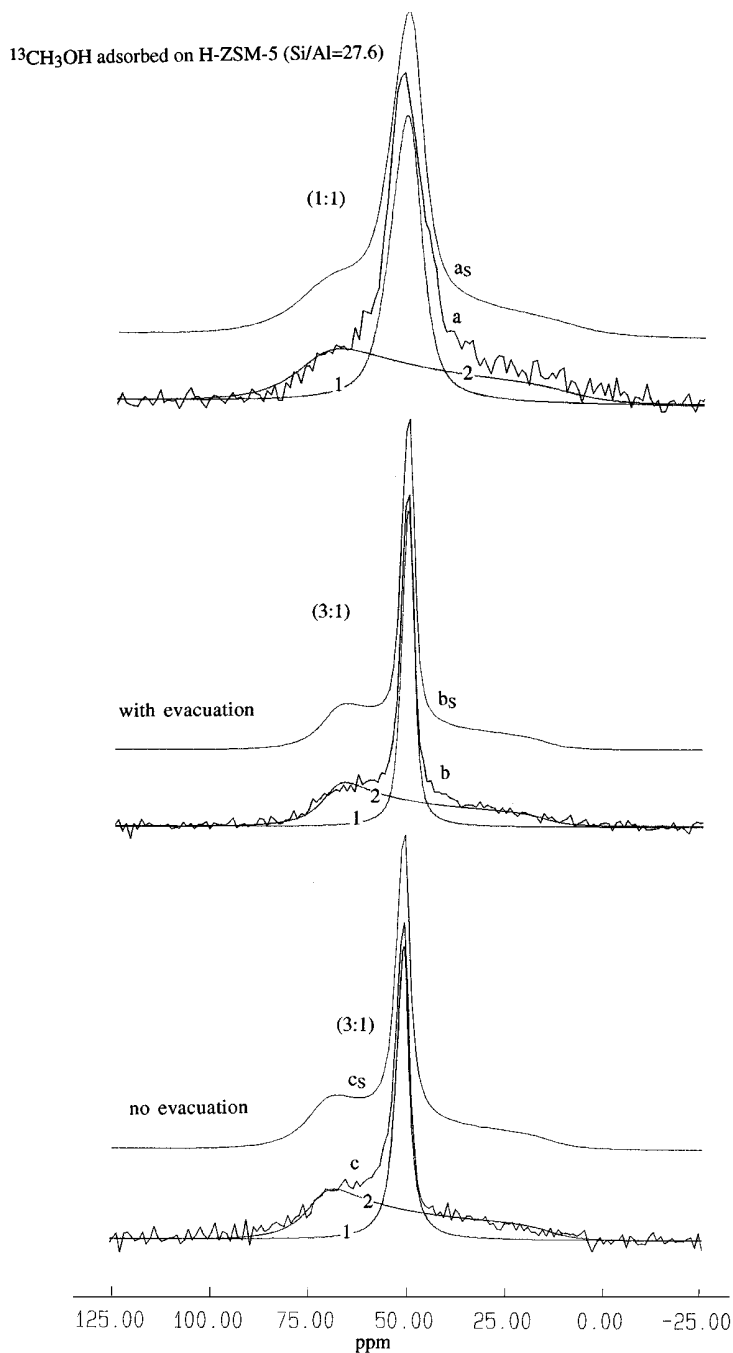


FIG. 2. ^{13}C CP static NMR spectra of $^{13}\text{CH}_3\text{OH}$ adsorbed on H-ZSM-5 (Si/Al = 27.6) at room temperature with (a) 1:1, (b) 3:1, and (c) 3:1 loadings (not evacuated). All simulated spectra (a_s), (b_s), and (c_s) comprise (1) a nearly isotropic component and (2) a powder pattern.

three resonances at chemical shifts of 4.3, 3.7, and 2 ppm. A ^{13}C CP MAS NMR experiment of the similarly methylated (^{13}C) silicalite-1 was also performed (Table 4). The spectrum (see Table 4) shows only one resonance at 48.1 ppm which is assigned to methylated silanol groups.

The static wide-line ^2H NMR spectrum of methylated (d_3) H-ZSM-5 is shown in Fig. 7a. This illustrates a nearly

isotropic signal on two Pake doublets with widths of ca 4.9 and 38 kHz. The Pake doublets indicate that the surface species are different in their restricted motion, whereas the isotropic resonance results from rapid isotropic motion on the NMR time scale. In order to differentiate between physisorbed and chemisorbed surface species, we performed ^{29}Si and ^{27}Al NMR of the dehydrated, methanol loaded (1:1), and methylated H-ZSM-5. ^{29}Si MAS NMR spectra (Fig. 8) of the three samples (Si/Al = 40) reveal a small change in the chemical shift of a broad shoulder on the left side of the main signal due to the methylation process. This shoulder is assigned to Si(1Al) groupings of the framework; however, the possible contribution from defect $-\text{SiOH}$ sites is not rejected. Figure 9 shows a marked difference in the ^{27}Al MAS NMR of these three samples (Si/Al = 27.6).

H-SAPO-34

^{13}C CP static NMR spectra for the samples with loadings of 0.25, 1, and 2 $^{13}\text{CH}_3\text{OH}$ molecules per acid site, followed by evacuation (with the exception of the latter sample) at room temperature for 1 h are shown in Fig. 10. Deconvolution of these spectra indicates two types of NMR signal, similar to those of H-ZSM-5, a nearly isotropic and a powder pattern with chemical shift anisotropy principal elements shown in Table 2. Figure 10c has been recorded from a sample with the 1:1 loading not followed by

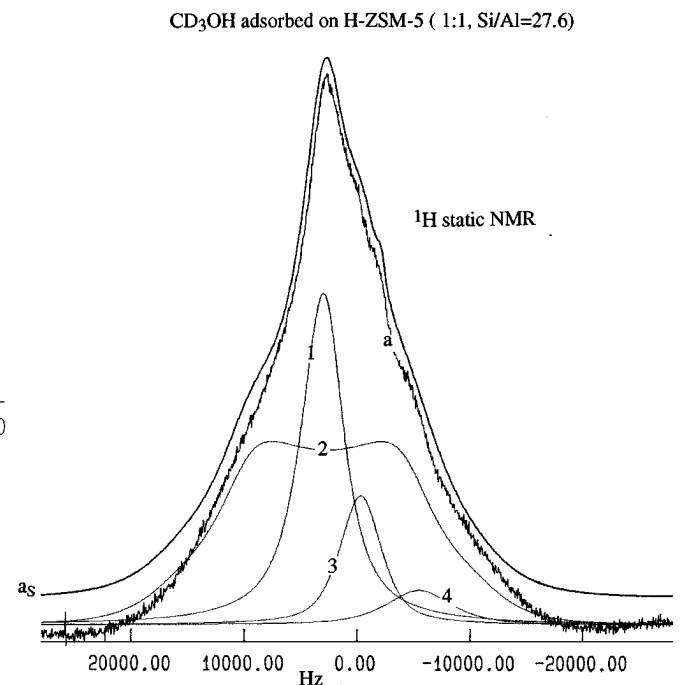


FIG. 3. ^1H static NMR spectrum of CD_3OH adsorbed on H-ZSM-5 (1:1) at room temperature, showing (a_s) the simulated signal comprising (1) an isotropic component and (2) a Pake doublet, and (a) the experimental signal. The other signals result to a greater extent from probe background and to a lesser extent from silanol groups.

TABLE 2
Chemical Shift Anisotropy Tensor Components and Isotropic Shift Values of Both Adsorbed $^{13}\text{CH}_3\text{OH}/\text{CD}_3\text{OH}$ and a Surface Methoxy Group

Molecular sieve	MeOH/acid site	σ_{11}	σ_{22}	σ_{33}	δ_{av}	δ_{CS}	η_{CS}	Motion	Area percentage
H-ZSM-5 (Si/Al = 40)	1	79.7	69.7	12	53.80	-41.7	0.24	Anisotropic	53
	1	—	—	—	53.70	—	—	Isotropic	47
	3	78	68	11	52.50	-41.7	0.24	Anisotropic	82
	3	—	—	—	52.35	—	—	Isotropic	18
H-ZSM-5 (Si/Al = 27.6)	1	72	71	7	52.80	-43	0.01	Anisotropic	44
	1	—	—	—	52.80	—	—	Isotropic	56
	3	72	72	15	52.70	-39	0.009	Anisotropic	52
	3	—	—	—	51.60	—	—	Isotropic	48
	1	—	—	—	7.7 ^b	—	—	Dipolar int.	47
	1	—	—	—	8.4 ^b	—	—	Isotropic	38
H-SAPO-34	0.25	81	69	9	52.81	-44.1	0.27	Anisotropic	56
	0.25	—	—	—	51.02	—	—	Isotropic	44
	1	80.6	69	9	52.81	-41.1	0.26	Anisotropic	55
	1	—	—	—	49.35	—	—	Isotropic	45
	2	75	65	10	49.80	-40.2	0.26	Anisotropic	63
	2	—	—	—	49.80	—	—	Isotropic	37
$\text{AlOCH}_3\text{Si}^{\text{a,c}}$	1	91.8	67.7	11.4	57	-46.6	0.23	Anisotropic	—
$\text{AlOCH}_3\text{Si}^{\text{d}}$	1	85.3	74.7	11.3	57	-45.7	0.24	Anisotropic	—

^a Methoxy groups of SAPO-34.

^b Proton chemical shift of adsorbed methanol(d_3) on H-ZSM-5.

^c Experimental values for shielding tensor components.

^d Simulated values for shielding tensor components.

evacuation after the adsorption. This is slightly different from that of the evacuated sample (Fig. 10b), indicating the effect of weakly adsorbed methanol. Such an effect is more pronounced in the sample with 2 : 1 loading.

In connection with mobility of CD_3OH adsorbed onto H-SAPO-34, ^2H static NMR of such a sample was carried out. The resulting spectrum (Fig. 7b) shows two resonances, a nearly isotropic signal on a Pake pattern with a width of ca 35.2 kHz.

The H-SAPO-34 used in this study has a ^1H MAS NMR spectrum with a main resonance at 3.7 ppm, on the left side of which are three small shoulders at 0.7, 1.8, and 2.7 ppm (Fig. 11a). There is also a small broad signal at 7.3 ppm. This is not due to ammonium ions since the H-SAPO-34 was prepared by direct calcination of the as-synthesised sample. This resonance, along with the peak at 3.7 ppm, is attributed to the Brønsted acid sites (23). The lines at 1.8 and 2.7 ppm correspond to $-\text{SiOH}$ or $-\text{POH}$ and $-\text{AlOH}$, respectively.

TABLE 3
Summary of ^1H MAS NMR Spectra Resulting from the Adsorption of Different Methanol Isotopomers on H-ZSM-5

Sample	Adsorbate	Loading(M : B.A.)	B.A.C.S./ppm	EFA ^1H C.S./ppm	Silanol ^1H C.S./ppm
H-ZSM-5(Si/Al = 40)	—	—	4.2, \approx 6	2.7–3	1.8–2
	CD_3OD	0.5	4.2, \approx 6.5	—	—
		1	Broad shoulder (5–9)	—	—
		3	\approx 9	\approx 5	—
H-ZSM-5(Si/Al = 27.6)	—	—	4.2, \approx 6	—	1.8–2
	CD_3OD	0.5	4.2, 6.6–7.5	—	—
		1	7, 9.1	—	—
H-ZSM-5(Si/Al = 35.5)	—	—	4.2, \approx 6	—	1.8–2
	CD_3OD	1	7, 9.1	—	—
		3 (evacuated)	9.3, 7.2	—	—
			1	7, 9.1, \approx 3.6	—

Note. B.A. = Brønsted acid; M : B.A. = methanol per Brønsted acid; EFA = extra-framework Al; B.A.C.S. = Brønsted acid chemical shift.

The very small signal at ca 0.7 ppm could be from both the probe background and water vapour around the coil. Adsorption of 0.5, 1, and 3 CD₃OD molecules per acid site of H-SAPO-34 have different effects on the chemical shift of the Brønsted protons, compared to that observed for H-ZSM-5. As the coverage increases (1:1) the resonance at 3.7 ppm moves downfield to a higher chemical shift value (8 ppm). Additional adsorption of two methanol molecules per acid site (i.e., 3:1), however, shifts the resonance back to ca 6.8 ppm while leaving a small shoulder at the same chemical shift (ca 8 ppm). The silanol groups have not been perturbed, indicating no interaction with methanol at these coverages. The line at 2.7 ppm is shifted downfield as the coverage increases to 1:1. The trend, however, does not continue at the higher coverage (3:1, Fig. 11, spectra b and c).

Surface Methoxy on H-SAPO-34

The ¹H MAS NMR spectrum of methylated H-SAPO-34 shows a main signal at 3.9 ppm with a shoulder at 3.7 ppm. This shoulder results from the unreacted Brønsted acid sites, presumably due to insufficient methanol for a complete methylation (Fig. 12, spectra c and b). There is no line at ca 10–16.5 ppm assigned to methoxonium ions (16, 43). For the assignment of the resonance at 3.9 ppm, a similarly prepared sample from the reaction of CH₃OD with D-SAPO-34 was used for ¹H MAS NMR. The spectrum again shows the same peak at 3.9 ppm (Fig. 12a).

²H static NMR of methylated (d₃) H-SAPO-34 illustrates a Pake doublet pattern with a splitting of ca 35.5 kHz (Fig. 7c). Such a pattern would be expected for methyl groups with only motion about the C–O bond. The ¹³C CP MAS NMR spectrum of another methylated sample (¹³CH₃OH as methylating agent) shows a main signal at 56.9 ppm. Three small shoulders, two on the right and one on the left (Fig. 13a), with the total percentage area less than 24% (deconvoluted spectrum not given) are also present in this spectrum. The ¹³C CP MAS NMR spectrum

TABLE 4

Summary of ¹H and ¹³C CP MAS NMR Spectra Resulting from the Reaction of Methanol with Silicalite-1

Sample	Reactant	Reaction-temperature/ K	Chemical shift/ppm ¹ H	Chemical shift/ppm ¹³ C
Silicalite-1/ bare	—	—	≈0.8–3.8	—
Silicalite-1/ methylated	CH ₃ OH	Methylation/533	≈0.8–4.3	—
Methylated silicalite-1 ^a			≈2, 3.7, 4.3	—
Silicalite-1/ methylated	¹³ CH ₃ OH	Methylation/533	—	≈48.1

^a After subtraction of spectra of the above two samples.

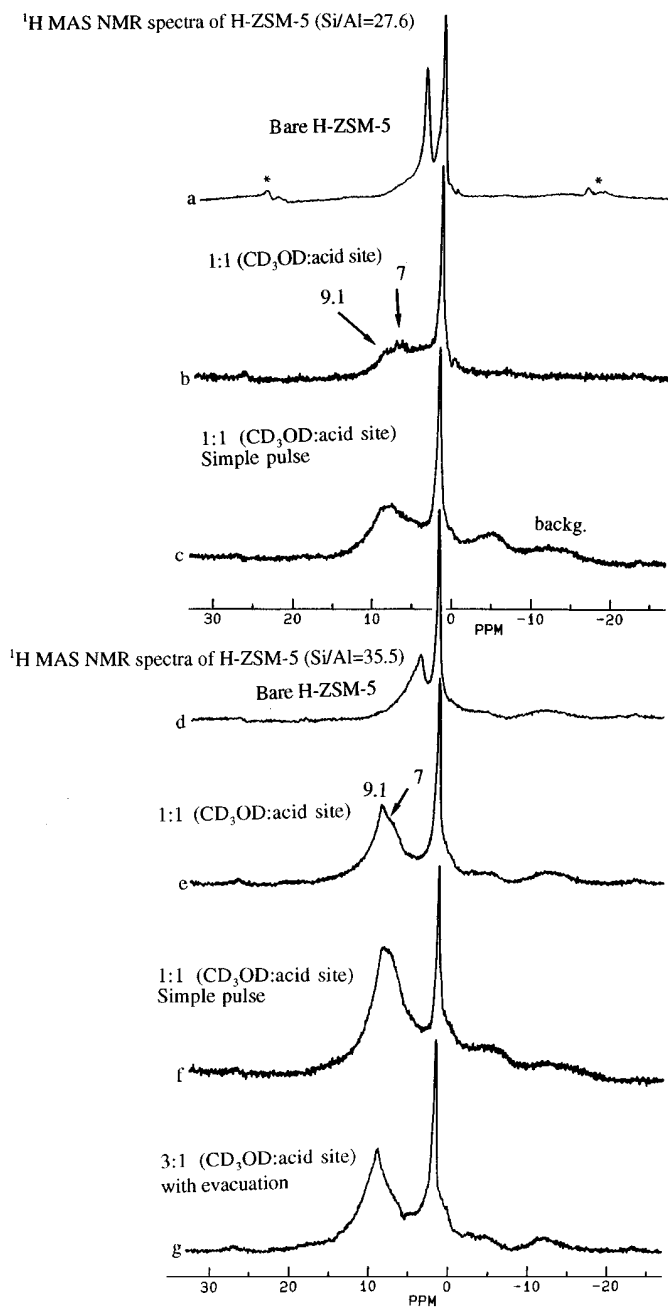


FIG. 4. ¹H MAS NMR spectra of (a), (d), and (h) bare H-ZSM-5 (Si/Al=27.6, 35.5, and 40, respectively) and (b), (c), (e)–(g), and (i) CD₃OD loaded H-ZSM-5. All spectra, with the exception of (c) and (f), which were recorded using a Bloch decay (a simple pulse excitation), are recorded using a Hahn-echo pulse sequence. Asterisks denote spinning sidebands. The simulated spectra are labelled by *h*_S and *i*_S.

of the same sample, recorded at a low spinning rate of ca 940 Hz (Fig. 13c), was used to measure the principal tensor elements of the shift anisotropy of surface methoxy groups using the graphical method reported by Herzfeld and Berger (44). The ¹³C CP static NMR spectrum of the sample gives approximately the same values for the tensor components using the Bruker Win-NMR package for line

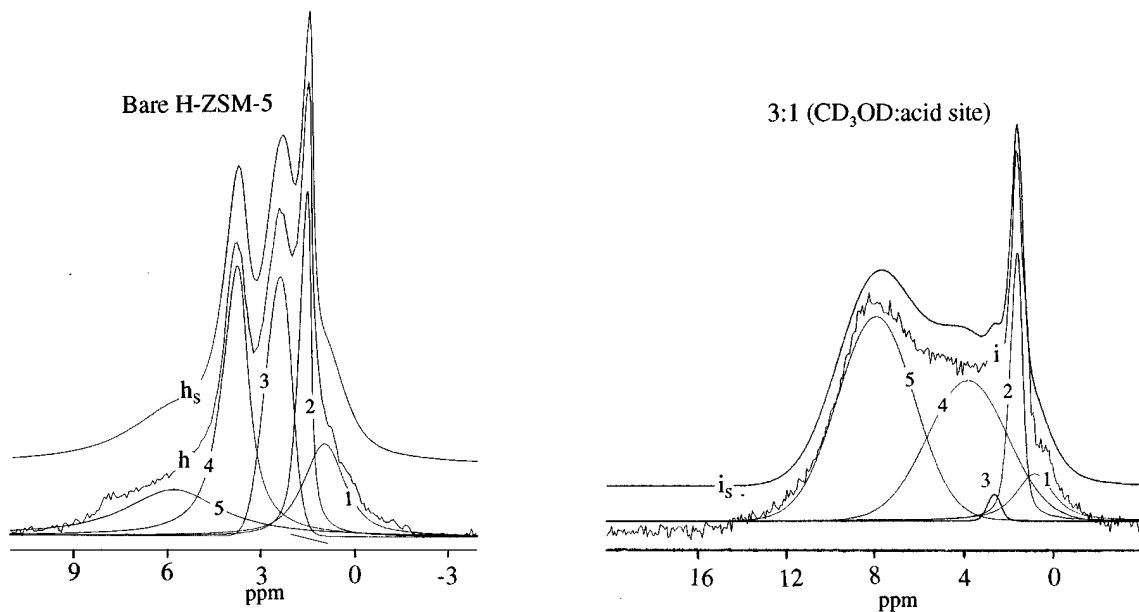
^1H MAS NMR spectra of H-ZSM-5 (Si/Al=40)

FIG. 4—Continued

simulation (Fig. 13, spectra b and b_s). Such a line simulation was also employed to simulate the experimental ^{13}C spectra obtained with magic angle at frequencies of ca 940 and 3000 Hz (Fig. 13, spectra c, c_s , a, and a_s). The shielding tensor components used for these simulations were the same tensor elements found in the previous simulation (Fig. 13b).

Finally, to investigate whether there is any interaction between surface methoxy protons and methanol hydroxyl groups, CH_3OD was adsorbed onto pre-methylated H-SAPO-34 and the sample was run for ^2H static NMR. A Pake doublet with a splitting of 113.8 kHz can be clearly seen in the spectrum (Fig. 7d). For the assignment of this Pake doublet, the ^2H static NMR spectrum of D-SAPO-34 was recorded. The spectrum comprises an isotropic line on a Pake doublet with a splitting of 178.7 kHz or with a quadrupolar coupling constant (QCC) of ca 238 kHz (Fig. 7e). These two signals are assigned to the mobile groups such as silanol ($-\text{SiOD}$) and framework bridging OD groups ($-\text{AlODSi}-$), respectively. The large width of the Pake doublet pattern indicates that the bridging hydroxyl deuterons are almost static. The second Pake doublet seems to be present within the first one. This is presumably associated either with relatively mobile Brønsted acid or with $-\text{AlOD}$ groups, the motion freedom of which is somewhat restricted. The exact assignment of the splitting, however, remains undetermined.

DISCUSSION

The ^{13}C static NMR spectra of methanol adsorbed on the surface of the microporous materials studied clearly

reflect the degree of its mobility, which ranges from highly mobile to almost rigid. This feature of the spectra enables the elucidation of structural aspects of the surface adsorbed molecules. Such information is lost when the chemical shift anisotropy is averaged into isotropic chemical shift by fast spinning of a sample at the magic angle.

Methanol over H-ZSM-5 at 1:1 Loading

^{13}C CP static NMR spectra of strongly adsorbed methanol onto the catalyst surface clearly reveal two superimposed resonances, one with a chemical shift anisotropy powder pattern and the other with a nearly isotropic shape. Deconvolution and line simulation analysis were employed to separate these resonances in order to determine their approximate contribution relative to each other (N.B. spectra recorded with CP are not absolutely quantitative) and the CSA tensor components of the anisotropic portion of the spectra. The marked difference in shapes of the two resonances implies that methanol/zeolite complexes are differently restricted in their motion. Such restriction in motion must be correlated to the way of methanol complexation with zeolite active sites; this will be discussed later.

In order to determine the importance of extra-framework aluminium in forming a complex by interacting with methanol, we compared two samples, with and without extra-framework aluminium, using ^{13}C CP static NMR. Two resonances, one nearly isotropic and the other anisotropic, appear in the ^{13}C spectra corresponding to these two samples. The anisotropic resonances in the spectra are similar and are consequently not associated with extra-framework

H-ZSM-5 (Si/Al=40) reacted with $^{13}\text{C}_3\text{H}_7\text{OH}$ (1:1) at 533 K

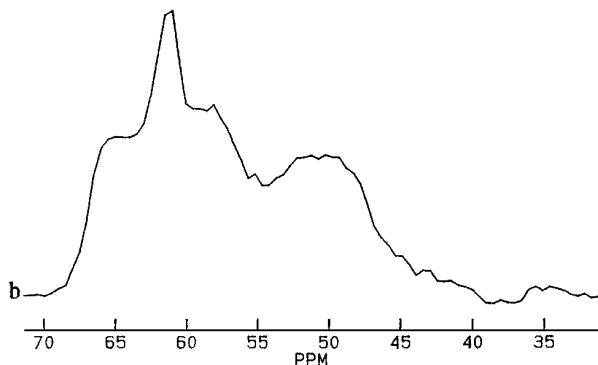
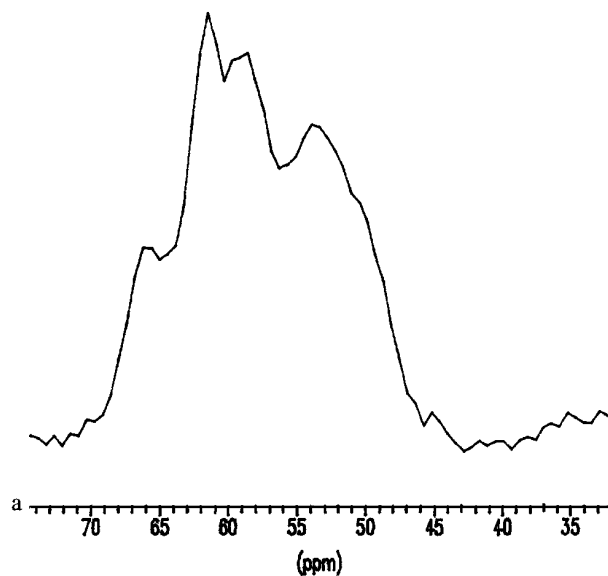
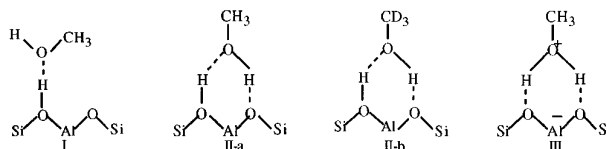


FIG. 5. ^{13}C MAS NMR spectra of methylated H-ZSM-5 (Si/Al = 40), showing (a) CP (7812 transients) and (b) $^{13}\text{C}\{\text{H}\}$ (8390 transients).

aluminium. However, the approximately isotropic resonances have a substantially different line width and therefore might be at least partially associated with extra-framework aluminium. Three possible complexes are expected from the adsorption of methanol (II shows as both CH_3OH and CD_3OH) over the zeolite. One structure frequently reported is a complex in which methanol is doubly hydrogen bonded to the Brønsted acid site and an adjacent bridging oxygen (see complex II). Another possibility is a singly hydrogen-bonded structure with the involvement of the Brønsted acid site (see complex I). Based on the experimental findings of this study, we conclude that both complexes (I and II) form on adsorbing methanol

over H-ZSM-5 (complex III is ruled out; see below). However, as reported previously (45), complex I structure is less stable than complex II by 3 kcal/mol. The approximately isotropic signal with a chemical shift of ca 52 ppm results from a simple adsorption, i.e. the singly hydrogen-bonded methanol molecules either at acid sites (complex I) or on extra-framework aluminium. Complex I allows the methanol molecule to have a nearly isotropic motion on the surface of the catalyst. The methanol hydroxyl proton can also be either free or weakly hydrogen bonded to the more distant bridging oxygen of the framework. Such an isotropic motion is also expected from a methanol molecule interacting with extra-framework aluminium:



A complex comprising a methanol molecule doubly hydrogen bonded to the surface, i.e., complex II, allows only the restricted rotation of the CH_3 group about an axis along the C–O bond. The powder pattern portion of the ^{13}C spectra can be characteristic of such a methyl rotor in complex II. The appearance of both the shift anisotropy pattern and the quasi-isotropic signal in the ^{13}C CP spectra indicate that motion frequencies of methanol (complexes I and II) are low enough to allow energy transfer on the basis of dipolar coupling interactions. Further support for these assignments is derived from the static ^1H NMR spectra of CD_3OH adsorbed on an H-ZSM-5 sample without extra-framework aluminium at room temperature. Deconvolution and line simulation of the spectrum clearly show that there are two types of signals. The narrow isotropic signal is again indicative of the simple adsorption of methanol molecules (I) with a motional freedom similar to that in the liquid. The Pake doublet of the powder pattern of the spectra is characteristic of a system of two spin-1/2 nuclei as shown in complex II-b.

The interaction giving rise to this Pake doublet in such a rigid system arises from the direct dipole–dipole interaction between the two homonuclear spins. There is, however, some effect on the Pake pattern of both the much smaller chemical shift interaction and the smaller dipolar interaction with the framework aluminium. Aluminium decoupling cannot be achieved for static ^1H NMR spectrum of dehydrated H-ZSM-5 (41) due to the large spectral width of ^{27}Al NMR satellite lines, arising from the first-order quadrupolar interaction. Because the 1:1 loading of methanol cannot restore the tetrahedral symmetry of the framework aluminium therefore, ^1H NMR of the sample with aluminium decoupling is not achievable even for central band. The intra-H–H distance, r , is measured by using the Pake doublet spacing of $2\Delta\nu'(1 - 3\cos^2\Theta_{ii})$, where Θ_{ii}

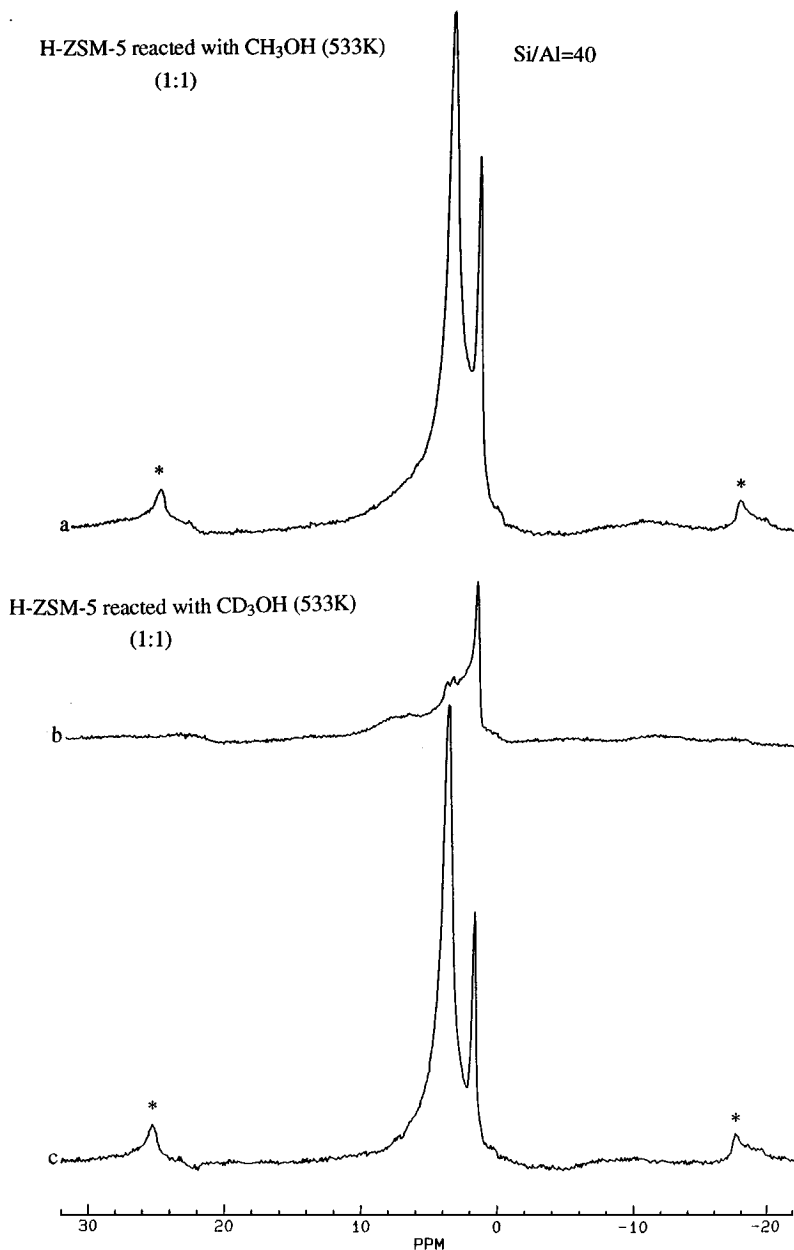


FIG. 6. ^1H MAS NMR spectra of methylated samples using (a) H-ZSM-5 (Si/Al = 40) and CH_3OH and (b) H-ZSM-5 (Si/Al = 40) and CD_3OH . (c) was obtained by subtracting (b) from (a). Asterisks denote spinning sidebands.

is the angle between r and the applied magnetic field direction (z) and the expression $\Delta\nu'$ is given by $3\gamma_i^2 h\mu_o / 64\pi^3 r_{ii}^3$. This value is ca 2.2 Å, which is in the range of values calculated for methanol, hydrogen bonded to Brønsted acid sites. However, the broadening arising from both the small dipolar interaction with aluminium, and the small chemical shift anisotropy could alter this value. The error in dipolar splitting is estimated to be within a range of 3800 Hz which is equivalent to a range of 2.09–2.2 Å for the H–H distance, r . This two spin-1/2 distance range is only slightly longer than the previously reported values 1.93–2 Å (46) for complex

II. However, complex III, the hydrogen-bonded methoxonium is expected to have a H–H distance of 1.49–1.58 Å (46) and can therefore be ruled out.

Methanol over H-SAPO-34 at 1 : 1 Loading

The ^{13}C CP static NMR spectra of adsorbed methanol at room temperature show the same spectral features as those observed for H-ZSM-5. Methanol molecules again strongly interact with the Brønsted acid sites in two different forms, i.e. complexes I and II. This is evidenced by deconvolution

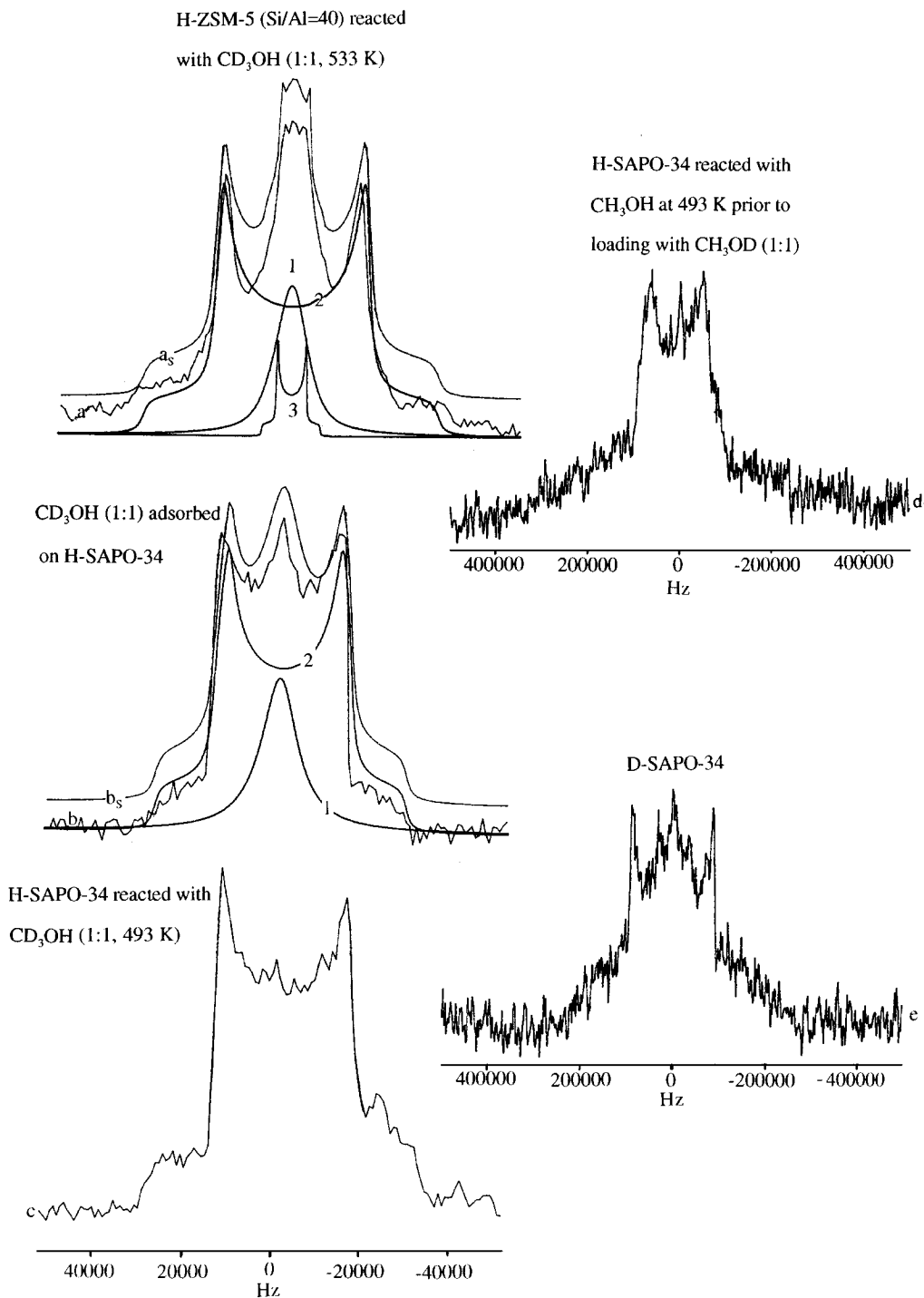


FIG. 7. ²H static NMR spectra of (a) methylated (d₃) H-ZSM-5 (Si/Al=40, 13400 transients), (b) CD₃OH adsorbed on H-SAPO-34 (12815 transients), (c) methylated H-SAPO-34 using CD₃OH (14030 transients), (d) pre-methylated H-SAPO-34 with the 1:1 loading of CH₃OD at room temperature (42497 transients), and (e) D-SAPO-34 (12032 transients) showing (a_s) and (b_s) the simulated spectra, comprising (1) a nearly isotropic component and (2) and (3) Pake doublet patterns.

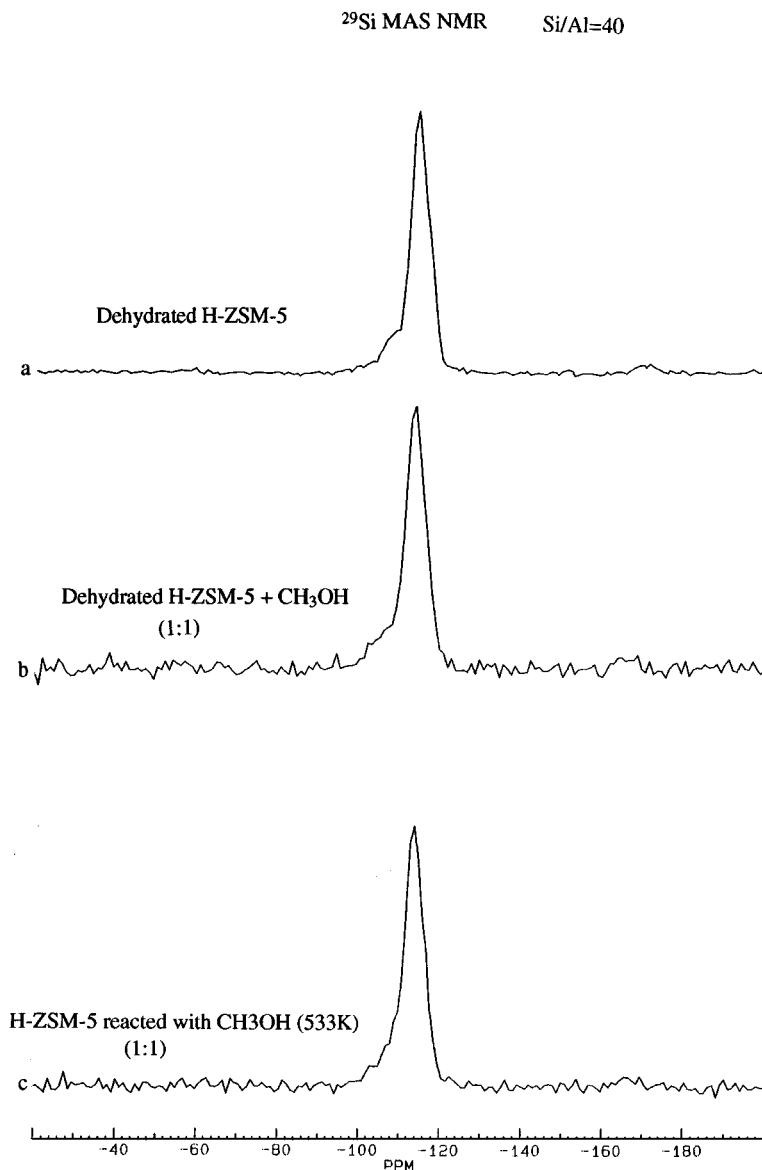


FIG. 8. ^{29}Si MAS NMR spectra of (a) dehydrated H-ZSM-5, (b) dehydrated H-ZSM-5, loaded with 1:1 methanol/acid site, and (c) H-ZSM-5 methylated with methanol. The Si/Al ratio for the samples was 40.

of the NMR spectra into a nearly isotropic signal approximately centred on a powder pattern-shaped component (Fig. 10, Table 2).

The ^2H wide-line NMR experiment of adsorbed CD_3OH over H-SAPO-34 reveals a narrow isotropic peak centred on a Pake doublet pattern with a width of 35.2 kHz. Quadrupole coupling constants (QCC) for the methyl groups of some organic compounds typically range between 45–55 kHz (47); the values are one-third those for the static state of the methyl groups due to a fast rotational motion about the pseudo-threefold spinning axis. On this assumption, the interaction of the deuteron nucleus with an axially symmetric field gradient at the nuclear site of a rigid

methyl group produces a Pake doublet with the QCC value of ca 165 kHz (47). Using this information the value of ca 70.4 kHz can be calculated for QCC (48) of the Pake doublet arising from the adsorbed CD_3OH over H-SAPO-34. This value, compared to that for a rigid system, shows motional restriction of the adsorbed molecule confined to methyl rotation about the C–O bond. Such rotation can average the field gradient tensor about the threefold axis to yield the above QCC value. As the spectrum (Fig. 7b) appears to be a superposition of two signals, it can be concluded that the complexation of methanol with active centres must be different. Again the nearly isotropic resonance arising from the high mobility of methanol over the catalyst

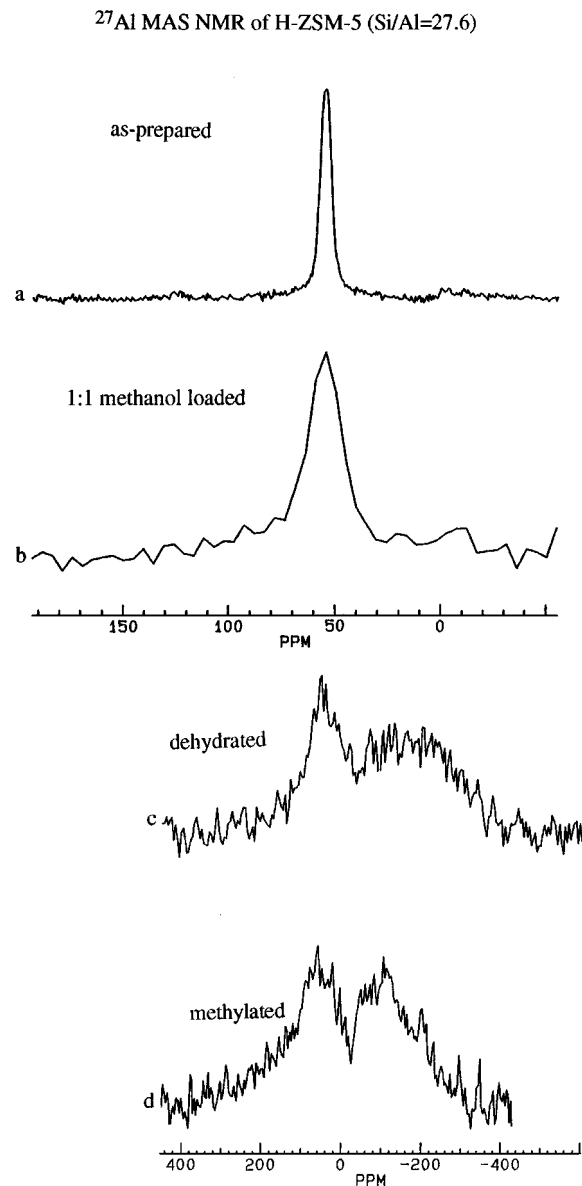


FIG. 9. ^{27}Al MAS NMR spectra of (a) as-prepared, (b) methanol loaded, (c) dehydrated, and (d) methylated H-ZSM-5 using, with the exception of (a), the quad echo pulse sequence. The Si/Al ratio for the samples was 27.6.

is consistent with complex I, whereas the Pake pattern line derives from complex II structure.

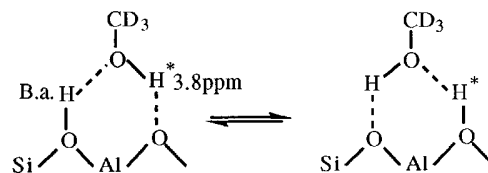
Nature of the Methanol/Zeolite Complexes at Variable Loadings

The investigation of the state of methanol/zeolite complexes is crucial in gaining a better understanding of the chemistry of the methanol conversion reaction. To address the state of methanol complexation with catalyst active centres we have performed the adsorption of different methanol isotopomers at different coverages over H-ZSM-5 and H-SAPO-34. Based upon the results obtained in this

study the possible nature of surface complexes formed at room temperature are discussed below.

H-ZSM-5

We have already shown that two structures of surface adsorbed methanol exist. Assuming that a hydrogen-bonded methanol/zeolite complex is prevalent at low coverage, an estimate can be made to calculate the bridging hydroxyl proton chemical shifts of these two strongly hydrogen-bonded complexes of methanol. The proton chemical shift of an isolated methanol hydroxyl group is expected to be analogous to an isolated water proton, i.e. 0.31 ppm (15). Considering methanol only to be hydrogen-bonded to H-ZSM-5 surface the hydroxyl protons of methanol should have a chemical shift of 3.8 ppm similar to that for CD_3OH over silicalite-1 (16). Taking into account both the observed experimental shift of 9.1 ppm for methanol hydroxyl protons and the following proton-exchange equilibrium, a value of 14.4 ppm is calculated for the bridging hydroxyl protons ($\delta_{\text{B.a.}}$, Brønsted acid = B.a.) as follows (the asterisk is referred to in subsequent text):



$$1/2(3.80) + 1/2\delta_{\text{B.a.}} = 9.1, \quad \delta_{\text{B.a.}} = 14.4 \text{ ppm.}$$

SCHEME 1.

This value is in good agreement with that recently reported by some workers (26) using *ab initio* quantum chemical methods. They report a value of 14.6 ppm for the bridging hydroxyl proton hydrogen bonded to methanol hydroxyl oxygen and a mean chemical shift value of 10.8 ppm for the hydrogen-bonded hydroxyl protons of complex II-b. Hunger and Horvath (43) also report the experimental shift values of 14.2 and 9.5 ppm (mean) for the Brønsted protons of H-ZSM-5/ CD_3OD and the protons of H-ZSM-5/ CD_3OH complexes, respectively. This is again in good agreement with the results of this study.

The chemical shift of ca 7 ppm obtained from the adsorption of one molecule of methanol per Brønsted acid site can be assigned to the protons of the methanol/zeolite complex of structure I. Such a value can be calculated by considering the fast site exchange between the bridging hydroxyl protons and the methanol hydroxyl protons in complex I:

$$\delta_{\text{av}} = 1/2(14.4) + 1/2(0.31), \quad \delta_{\text{av}} \approx 7.4 \text{ ppm.}$$

This shift value, which is calculated for hydroxyl protons of complex I, agrees very well with the corresponding experimental shift value. Therefore, loadings up to one

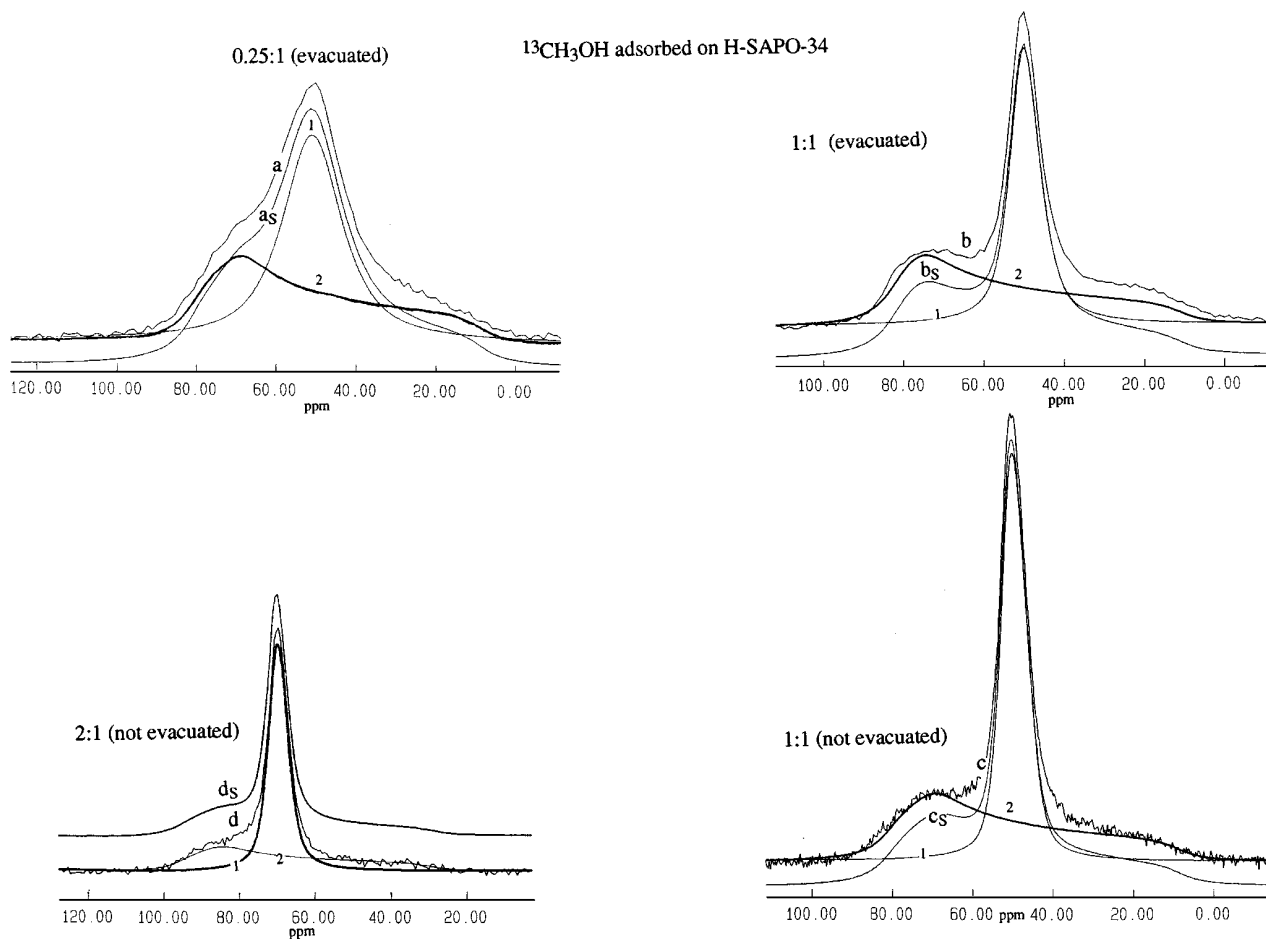
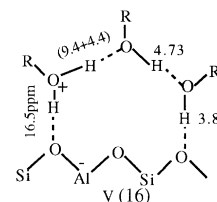
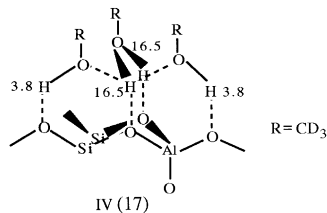


FIG. 10. ^{13}C CP static NMR spectra of $^{13}\text{CH}_3\text{OH}$ adsorbed on H-SAPO-34 at room temperature, showing (a)–(d) the experimental spectra (19180 transients) and (as)–(ds) the simulated ones comprising (1) isotropic signals and (2) powder pattern components.

molecule of methanol per acid site can be explained quite well with the formation of neutral complexes of methanol, hydrogen bonded to the surface of acidic ZSM-5. This is further evidenced by the distance of 2.2 Å experimentally obtained for the separation of the two interacting proton dipoles (see complex II-b).

By increasing the coverage to 3 : 1 the shift values of 8.6–9 ppm for the Brønsted protons appear showing a small difference from those of the hydrogen-bonded complexes. This implies that the Brønsted proton chemical shift must be higher, averaging a value of ca 9 ppm in a cluster. Moreover, the proton affinity of three molecules of methanol must be higher than one molecule. Using an estimation method one can calculate the mean shift value of hydroxyl protons of a methanol cluster of three molecules. For such calculations the deshielding effect of a hydrogen bond on methanol hydroxyl proton is required. A chemical shift of 4.73 ppm has been reported (16) for the hydroxyl proton of methanol in liquid. Subtraction of the chemical shift of methanol hydroxyl proton in gas phase, i.e. ca 0.31 ppm, from the shift 4.73 ppm gives the deshielding effect of hydrogen bonds,

i.e. 4.4 ppm. Chemical shifts of 9.4 and 16.5 ppm, which are applied in this estimation have been reported for methoxonium ion OH_2 protons in a superacid (49) and in H-ZSM-5 (43), respectively. Using these values and considering the model cluster types IV and V involving the presence of the methoxonium ion, the mean chemical shifts of 10.2 and 9.7 ppm are determined for the hydroxyl protons:



$$\frac{1}{4}(16.5) + \frac{1}{4}(16.5) + \frac{1}{4}(3.8) + \frac{1}{4}(3.8) \approx 10.2 \text{ ppm}$$

using model IV

$$\frac{1}{4}(16.5) + \frac{1}{4}(9.4 + 4.4) + \frac{1}{4}(4.73) + \frac{1}{4}(3.8) \approx 9.7 \text{ ppm}$$

using model V

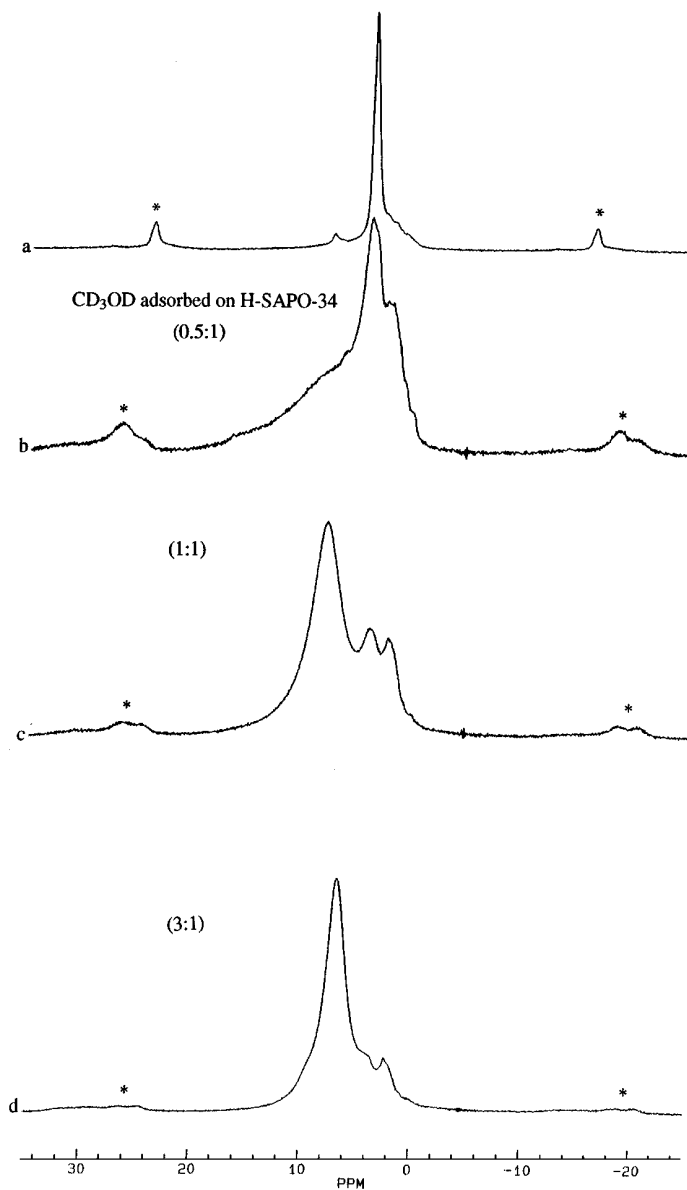


FIG. 11. ^1H MAS NMR spectra of (a) bare H-SAPO-34 and (b)–(d) CD_3OD adsorbed on H-SAPO-34 at room temperature with different loadings. Asterisks denote spinning sidebands.

The estimated values reasonably agree with the value obtained experimentally from this study. Therefore, the existence of the methoxonium ion is likely over zeolite H-ZSM-5 at a methanol coverage greater than one molecule per acid site. Such behaviour in production of a hydroxonium ion upon the adsorption of more than one water molecule per acid site has been reported (25) over the same zeolite. Taking the percentage area of the two signals resulting from ^1H static NMR and those from ^{13}C CP static NMR spectra (Table 2, loading 3:1), as rough measures, it appears that a methanol cluster of type IV is slightly favoured. Such a cluster may be preferred to form in the intersection of the two

channels, whereas cluster type V can occur readily along the channels.

H-SAPO-34

Our results, obtained from a bare H-SAPO-34, clearly show the presence of two signals at the chemical shifts 3.7 and 7.3 ppm. The upfield shift of 3.7 ppm results from the Brønsted protons located in eight-ring channels, as previously reported (50). The downfield shift of 7.3 ppm is indicative of a different chemical environment and is possibly assigned to second Brønsted acid sites, which are probably sited in the 6-rings. In connection with this, infrared spectroscopy has revealed (23) that there are two types of bridging Brønsted hydroxyls with stretching frequencies at 3626 and 3599 cm^{-1} .

The adsorption of CD_3OD over H-SAPO-34 at room temperature reveals that the Brønsted protons are deshielded. The downfield chemical shift of 8 ppm results from adsorbing 0.5 and 1 methanol molecules per acid site. Such a value, in comparison with that obtained from the adsorption of methanol on H-ZSM-5, the acidity of which is slightly stronger, could be attributed to the neutral hydrogen-bonded methanol/H-SAPO-34 complexes. An increase in the methanol coverage (see loading 3:1) in the pores of the catalyst leads to a lower chemical shift value of Brønsted protons (6.8 ppm). Comparing this shift with the corresponding one of H-ZSM-5 it appears that the difference of ca 2 ppm must be associated with methanol molecules clustering with the first strongly bonded molecule to the Brønsted acid sites of SAPO-34. Methanol up to approximately three molecules can remain strongly bonded to the Brønsted protons of ZSM-5 catalyst (17). In conjunction with this we performed adsorption/desorption of methanol over H-SAPO-34 using the same conditions. The results (not shown) indicate that about one methanol molecule can remain strongly bonded to the catalyst surface. In conclusion, the decrease in the shift of acid site protons by increasing the coverage could arise from a fast chemical exchange between the hydroxyl protons of the first methanol molecule, as either methoxonium or neutral hydrogen-bonded, and those of the other weakly hydrogen-bonded methanol in a resulting cluster. Proton transfer at a higher coverage of methanol (2:1 or 3:1) may be possible in H-SAPO-34. Methanol clusters of such nuclearity are generally expected to promote more charge transfer, because the corresponding ionic clusters can be stabilised by the negatively charged framework. The question of whether the intrinsic Brønsted acidity of H-SAPO-34 is high enough to be readily transferred to the methanol cluster, however, remains open since our results do not allow us to analyse this concept further. Finally, considering the percentage areas of the two signals resulting from the deconvolution of the ^{13}C CP static NMR spectrum (see Table 2, loading 2:1) it follows that a methanol cluster of type IV is probably favoured.

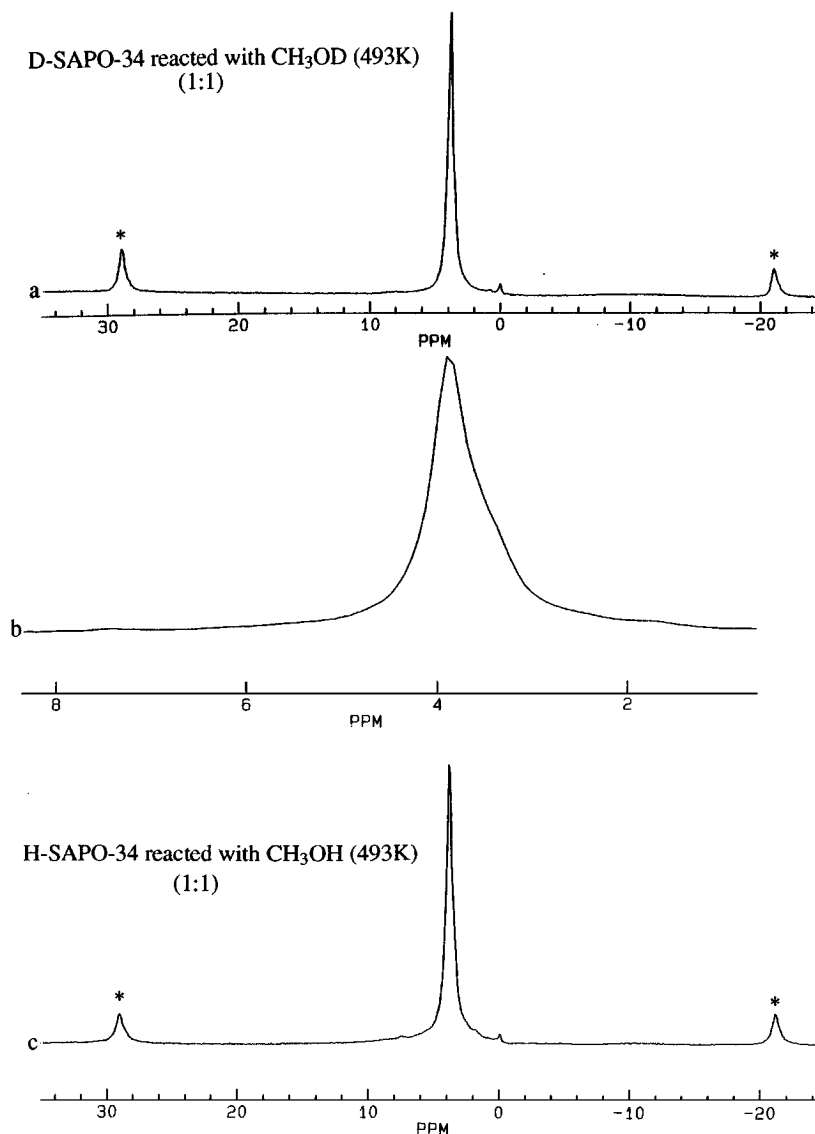


FIG. 12. ^1H MAS NMR spectra of methylated samples using (a) D-SAPO-34 reacted with CH_3OD and (c) H-SAPO-34 reacted with CH_3OH . (b) is an expansion of spectrum (c). Asterisks denote spinning sidebands.

Note that the values must be taken as rough measures since cross polarisation has been employed and this is not strictly quantitative.

Surface Methoxy Groups on H-SAPO-34

The treatment of $^{13}\text{CH}_3\text{OH}$ over H-SAPO-34 at 493 K using ^{13}C CP MAS NMR reveals that strongly surface-bonded species are produced (Fig. 13a), evidenced by spinning sidebands. The ^1H MAS NMR spectrum of a similarly methylated sample indicates a strong signal at 3.9 ppm with a small shoulder on the right at a chemical shift of 3.7 ppm assigned to the Brønsted acid site. Further experimentation with a sample methylated under the same conditions using D-SAPO-34 and CH_3OD illustrates a single resonance at the same chemical shift of 3.9 ppm. Based on these experimen-

tal results, it is concluded that the signal at 3.9 ppm results from surface methoxy protons. No indication of methoxonium ions, the OH_2 protons of which are shifted to ca 10–16.5 ppm is present under these conditions. As the ^{13}C CP MAS NMR of the methylated sample shows, three shoulders are apparent, two on the left and one on the right of the main signal, at 56.9 ppm. The total contributions of these shoulders amounts to less than 24% of the total area. These shoulders most probably arise also from surface methoxy groups but with slightly different chemical environment. The ^{13}C CP MAS NMR of the sample at a slow-spinning rate reveals that the main signal gives rise to four or more orders of spinning sidebands, consistent with restricted motion. Sideband analysis of the spectrum using Herzfeld and Berger's method yields the principal shift tensor elements

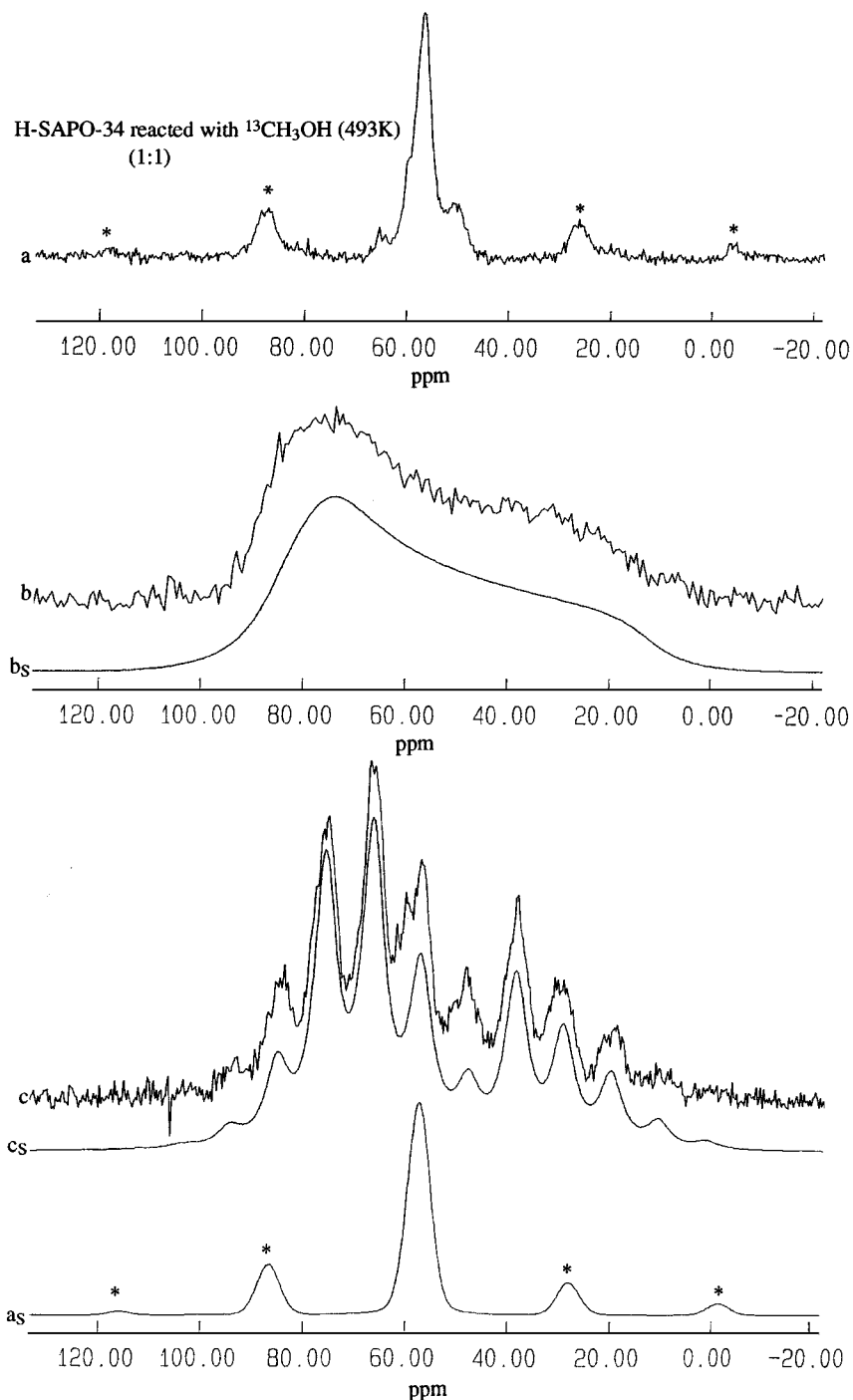


FIG. 13. ^{13}C CP NMR spectra of methylated H-SAPO-34 using (a) a spinning rate of ca 3 kHz (5818 transients), (b) no spinning (16218 transients), and (c) a low spinning rate (ca 940 Hz, 12318 transients). The simulated profiles a_s , b_s , and c_s were obtained with no, low, and high spinning rates (as mentioned above), respectively.

shown in Table 2. Such values are also obtained by line simulation of Fig. 13b. The discrepancies between these two measurements are in the range of errors associated to the different methods employed in this analysis. These elements imply that surface methoxy groups formed on H-SAPO-

34 are not axially symmetric. Further support in assigning the ^1H signal at 3.9 ppm to surface methoxy groups can also be deduced from the ^{13}C shift tensor elements when comparing to those reported (51) for dimethylether, i.e., $\delta_{11} = \delta_{22} = 88$ and $\delta_{33} = 6$ ppm. The 3.9 ppm ^1H shift is also

unlikely to be associated to protonated dimethylether. This species would be expected, first, to have different shift tensor elements from surface methoxy groups and, second, to be converted to stable species such as either methanol and a surface methoxy group or dimethylether. The ^2H wide-line NMR spectrum of methylated (d_3) SAPO-34 consists of only a powder pattern Pake doublet with a splitting of 35.5 kHz. This is characteristic of a methyl rotor with only rotation about the C–O bond and lends strong support to the verification of its attachment to the lattice oxygen ($-\text{AlOSi}-$).

In order to gain a better understanding from the role of surface methoxy groups in the formation of the first C–C bond in methanol conversion, a premethylated H-SAPO-34 sample was loaded with 1 : 1 CH_3OD per acid site and its ^2H wide-line NMR was recorded. The spectrum shows a Pake pattern with a width of ca 114 kHz. To assign this, the ^2H wide-line NMR of a D-SAPO-34 sample was recorded. The spectrum clearly exhibits an axially symmetric Pake pattern with a width of ca 179 kHz resulting from the bridging OD groups ($-\text{SiODA1}-$). In comparison to this, the splitting value of ca 114 kHz shown in Fig. 7d is quite high, indicating that a complexation of methanol OD with methylated SAPO-34 may be involved in restricting the deuterium motional freedom. Further investigation revealed that the methylated sample, which was loaded with CH_3OD , contained some unreacted Brønsted acid sites. This will result in interaction of CH_3OD with the Brønsted protons and consequently deuterium exchange between methanol OD and the remaining Brønsted protons (see Scheme 1 by changing $-\text{CD}_3$ to $-\text{CH}_3$ and H^* to D). Consider the one example, where the external magnetic field (H_0) lies parallel to the O–C bond; then the angle between the field gradient at the deuterium site (V_{ZZ} , approximately along the O–D bond) and H_0 can be 0 or 60° . For a powder sample due to distribution of all directions for complexes with respect to H_0 the quadrupolar splitting resulting from a deuterium involved in a site exchange with the Brønsted hydroxyl proton may average ca 114 kHz. A theoretical calculation of such a process is required to prove if this averaging mechanism is operative. The resulting splitting (114 kHz), leading to $\text{QCC} = 152$ kHz, implies that the molecular reorientation, occurring via the site exchange is relatively slow. The isotropic signal centred at 0 ppm on the Pake pattern (Fig. 7d) arises from an isotropic motion of gas phase CH_3OD .

Surface Methoxy Groups on H-ZSM-5

Recently, Bosacek, in his studies of methanol (in the case of H-ZSM-5) and methyl iodide over different basic zeolites, has shown that surface methoxy groups can appear at chemical shifts ranging from 53–59 ppm. It has also been discussed that methyl iodide on Na-ZSM-5 gives rise to a broad signal, the deconvolution of which indicates four

peaks in the chemical shift range 55.7–60.5 ppm, attributed to methoxy species. The assignment of a signal at the chemical shift of 61 ppm, resulting from methanol treatment over H-ZSM-5 using ^{13}C CP MAS NMR, to methoxonium or dimethylether is also pointed out.

To investigate the nature of the stable surface species being produced in the reaction of methanol on H-ZSM-5, the methylation process was carried out on a premethanol-loaded sample in excess of 533 K, followed by prolonged evacuation under the same conditions. Both $^{13}\text{C}\{\text{H}\}$ and ^{13}C CP MAS NMR spectra of the sample reveal that at least four resonances are present at the chemical shifts of ca 53.7, 58.8, 61.5, and 65.6 ppm. Assignment of these signals to methoxonium ion or to dimethylether is unlikely, based on the following reasons: (1) The temperature of 533 K, at which the sample has been highly evacuated, seems sufficient to bring about the release of water by methoxonium since the ion, as reported (16), is stable only up to 333 K. The possibility of retention of physisorbed dimethylether at these conditions also seems unlikely. (2) The ^1H MAS NMR spectrum of the sample shows two signals at 1.9 and 3.9 ppm with a broad shoulder on the downfield side (ca 7 ppm) of the latter signal (Fig. 6a). There is no signal at the chemical shift of ca 10–16.5 ppm corresponding to methoxonium hydroxyl protons. Consequently, the 3.9 ppm chemical shift is assigned to surface methoxy groups.

The shoulder centred at ca 7 ppm (Figs. 6a and 6b) could be assigned to:

(a) the second Brønsted acid site unreacted with methanol. This assignment implies that the Brønsted protons at 4.2 ppm are preferred for the methylation process. However, there is no experimental approach to prove this. Note that the other Brønsted site appears as a broad shoulder centred at ca 6 ppm (Fig. 4). The shift difference of ca 1 ppm has been reported (40) to be related to a site exchange with the 4.2 ppm Brønsted protons.

(b) $-\text{OH}_2$ protons of methoxonium which are in fast exchange with hydroxyl protons of hydrogen-bonded methanol (physisorbed). This assignment is unlikely since the reaction conditions, particularly both the temperature and the heating time, do not favour the presence of physisorbed methanol.

(c) hydroxonium $-\text{OH}_2$ protons, which are in fast proton exchange with a small amount of strongly hydrogen-bonded water retained by the catalyst from the methylation reaction.

Both (a) and (c) are likely owing to the fact that there may not be sufficient methanol for the conversion of the all Brønsted acid sites and to the possibility of a small amount of water remaining in the catalyst, respectively. The main signal at 3.9 ppm, as previously discussed, must be due to surface methoxy species and is shown by the difference

spectrum (Fig. 6c). The resonance at ca 2 ppm results mainly from unreacted silanol groups and the remaining resonance at the same shift after subtraction (Fig. 6c) could be associated either to a kind of methoxy group or to an experimental error resulting from the sample preparation. To this end, similar experiments were performed with silicalite-1 under the same conditions and the same problem; i.e., a signal at 2 ppm was present in the difference spectrum corresponding to the bare and methylated samples. However, the ^{13}C CP MAS NMR spectrum of the methylated silicalite-1 exhibited only one resonance at 48.1 ppm, implying that the ca 2-ppm chemical shift is more likely to be related to unreacted silanol protons.

To further verify the assignments made for surface methoxy groups, a few more experiments were carried out with H-ZSM-5 catalyst. A methylated (d_3) ZSM-5 sample was characterised using ^2H wide-line NMR. The corresponding spectrum reveals a nearly isotropic component centred on two Pake patterns with widths of ca 4.9 and 37.9 kHz. The isotropic signal derives from a mobile species such as $-\text{SiOCD}_3$. The Pake pattern-containing components are characteristic of methyl rotors bonded to extraframework aluminium and the zeolite framework. Of great interest is the comparison of both the ^{29}Si and the ^{27}Al MAS NMR spectra of dehydrated, the 1:1 methanol per acid site loaded and methylated ZSM-5 with those of the bare H-ZSM-5. By methylating the catalyst the broad shoulder corresponding to silicon in Si(1Al) groupings at ca -106 ppm (Fig. 8) is slightly shielded to a more negative shift value overlapping with the line centered at ca -113 ppm (Si(0Al) groups). More interesting is the aluminium spectrum of the methylated sample (Fig. 9), which is quite different from that of the 1:1 methanol loaded H-ZSM-5. Substitution of methyl groups for Brønsted protons in the dehydrated zeolite, the ^{27}Al NMR of which is quite broad due to strong quadrupolar interactions, does not significantly improve the distorted tetrahedral sites, making its ^{27}Al MAS NMR spectrum still broad.

CONCLUSION

Chemical shift anisotropy interactions for strongly hydrogen-bonded adsorbed molecules on acidic zeolite and zeotype materials give significant information regarding structures of guest molecules/microporous material complexes. Both the powder pattern and the nearly isotropic signals obtained from the adsorption of $^{13}\text{CH}_3\text{OH}$ on H-ZSM-5 and H-SAPO-34 using ^{13}C CP static NMR clearly support the presence of two types of surface complex, one singly hydrogen bonded and one bridged (I and II). Fast exchange at high methanol loadings of hydroxyl protons between hydrogen-bonded methanol and adsorbed methoxonium ion is a plausible answer to the downfield shift value of ca 9 ppm caused by adsorption of CD_3OD

(3 : 1) on zeolite H-ZSM-5. At the low coverage of 0.5 and 1 methanol molecule per acid site of H-ZSM-5, our results are in good agreement with hydrogen bonded methanol, i.e. complexes I and II. Adsorption of methanol (up to 1 : 1) over H-SAPO-34 appears to deshield the Brønsted protons ($\delta_{\text{av}} = 8$). Such a chemical shift compared to that of the methanol/H-ZSM-5 (1 : 1) complex agrees with neutral hydrogen-bonded complexes. High coverage of methanol (3 : 1) on H-SAPO-34 decreases the chemical shift of 8 to 6.8 ppm. A cluster of methanol molecules with fast exchange between weakly hydrogen-bonded molecules and the first hydrogen-bonded methanol or methoxonium ion could account for the low chemical shift value of 6.8 ppm for H-SAPO-34 Brønsted protons. Finally, methanol treatment over both microporous materials leads to a variety of surface methoxy species in the mild temperature range of 493–533 K. Solid-state NMR proves to be particularly useful in differentiating these species.

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