

Magic-Angle-Spinning NMR Studies of Acid Sites in Zeolite H-ZSM-5

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¹H, ¹³C, ²⁷Al, and ²⁹Si magic-angle-spinning (MAS) NMR was used to elucidate the nature of the catalytic activity of zeolite H-ZSM-5. ¹H MAS NMR of sealed samples after mild hydrothermal dealumination shows that the enhanced activity for *n*-hexane cracking is not due to an enhanced Brønsted acidity. The concentrations of the various OH groups and aluminous species suggest that the reason for the enhanced catalytic activity is the interaction of the *n*-hexane molecule with a bridging hydroxyl group and with extra-framework aluminium species. Loading the samples with HCOOH or HCl shows that those extra-framework aluminium species, which give rise to the enhanced activity, cannot be easily removed from their positions, and are therefore immobilized by the zeolitic framework. © 1991 Academic Press, Inc.

INTRODUCTION

Bridging hydroxyl groups capable of donating protons to molecules, which are adsorbed, are Brønsted-acid sites in heterogeneous catalysis. A hydrothermal treatment often leads to dealumination of the zeolitic framework (1–3), which is accompanied by a corresponding dehydroxylation of bridging OH groups (3). In certain circumstances this dealumination gives rise to an enhancement of the catalytic activity (4–8). Miradatos and Barthomeuf (4) found enhanced activity in mordenites after hydrothermal treatment and explained it by an interaction of bridging hydroxyl groups with extra-framework aluminium species. Lago *et al.* (6) observed an increased activity of H-ZSM-5 after mild steaming at 810 K and attributed it to paired and partially hydrolyzed framework Al atoms. Scherzer (1) considered a variety of charged or neutral extra-framework aluminium species. Jacobs and Beyer (9) proposed the existence of AlO⁺. MAS NMR proved the existence of tetrahedrally coordinated extra-framework

aluminium in the hydrated dealuminated zeolites (10). It is well-established that the so-called bridging hydroxyl groups are the source of the strong Brønsted acidity of the hydrogen form of the zeolite. The question arises as to the nature of the sites of enhanced activity in mildly dealuminated zeolites.

We describe hydroxyl groups and aluminium atoms on both framework and extra-framework positions in H-ZSM-5 after the zeolite has received a mild hydrothermal dealumination at 810 K for 150 min with water vapour pressures from 0 to 100 kPa. The framework Si/Al ratio varies from 15 to 60 depending on the water vapour pressure. Results of the *n*-hexane cracking catalytic test were taken from Ref. (11).

METHODS

Hydrothermal Treatment

ZSM-5 zeolite with Si/Al = 15 synthesized without template was provided by Dr. W. Schwieger. The mean crystallite diameter was 3 μm. Details of the synthesis are described in Ref. (12). The Na⁺/H⁺ ion exchange was carried out at room temperature with an 0.5 M aqueous solution of HCl. Hy-

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drothermal treatment of 2 g samples was carried out in a tube of 50 mm inner diameter with 8 mm maximum bed-depth of zeolite. Temperature was increased at a rate of 10 K/min in a water-free nitrogen stream at a flow rate of 1 litre per minute. Steaming was carried out at 810 K for 150 minutes under self-generated water vapour pressure, adjusted by the temperature of the water bath through which nitrogen was flowing. The bulk Si/Al ratio could not change during dealumination since the zeolite was not washed.

NMR Measurements

^{29}Si and ^{13}C MAS NMR measurements were generally carried out on as-prepared and rehydrated samples, which had been kept in a desiccator for 48 h over aqueous NH_4Cl . The same samples were used for the determination of the framework Si/Al ratio with ^{27}Al MAS NMR. The ^{27}Al pulse length was 1 μs , which corresponded to a $\pi/12$ pulse for nonselective excitation. For the ^1H MAS NMR measurements the samples were subjected to shallow-bed activation in a glass tube of 5.5 mm inner diameter and with a zeolite layer 10 mm thick. Temperature was increased at a rate of 10 K/h. The samples were kept at the final activation temperature of 670 K under a pressure below 10^{-2} Pa for 24 h, and then cooled and sealed. Similar activation procedure was used for samples, which were loaded after activation with HCOOH by diffusion from the gas phase and with HCl by immersion with a 0.5 M aqueous solution of HCl . Measurements were made on a homemade NMR spectrometer HFS 270 and on a Bruker MSL 300 with spinning frequencies of ca. 3 kHz and a homemade MAS equipment for the rotation of the fused glass ampoules. As a reference for ^{27}Al intensity measurements, a well-characterized sample of ZSM-5 with a framework ratio of $\text{Si}/\text{Al} = 15$ was used. The total concentration of OH groups in the activated samples was determined by comparison of the maximum amplitude of the free induction of the samples with those of

a capillary with an aqueous solution in a probe with a short ring-down time.

RESULTS

The dependence of Al^{F} , the number of framework aluminium atoms per unit cell, on the water vapour pressure of steaming is given in Table 1. The framework Si/Al ratio is $(96/\text{Al}^{\text{F}}) - 1$. Al^{F} was determined from the intensity of the narrow line at 60 ppm in the ^{27}Al MAS NMR spectra. In general, the spectra show two narrow lines at 60 and -2 ppm due to 4-coordinated framework and 6-coordinated extra-framework aluminium, respectively. For hydrothermally treated samples an additional broad line appears at about 30 ppm due to extra-framework AlOOH in which Al is in tetrahedral coordination through its proximity to two framework oxygens (cf. Fig. 3A and Refs. (10, 11)).

^1H MAS NMR spectra are shown in Fig. 1. Three different signals can be seen: line (a) at 2.0 ppm is due to nonacidic hydroxyl groups at the outer surface of zeolite crystallites, at framework defects, and in the amorphous part of the sample; line (b) at 4.3 ppm is caused by bridging (acidic) OH groups; line (e) at ca. 3.0 ppm represents nonacidic AlOH groups on extra-framework aluminium species pointing towards framework oxygen atoms (cf. Ref. (10)). This line is resolved in the spectrum of Figs. 1C and 1D only, but the line fitting procedure shows the existence of line (e) also in the spectrum of Fig. 1B. The corresponding concentrations are given in Table 1.

Figures 2A and 2B show the ^{29}Si MAS NMR spectrum of the parent H-ZSM-5 measured with 24,000 scans. A fitting procedure using the program "Linesim" yields four lines (Fig. 2C). It is well known that the unresolved signal of $\text{Si}(\text{OAl})$ groupings in zeolites ZSM-5 consists of a peak at ca. -111 ppm with a shoulder at ca. -115 ppm (2). Therefore, we assigned the signal consisting of the two fitted lines at -111.5 ppm and -113.5 ppm to $\text{Si}(\text{OAl})$ groupings. The line at -106.4 ppm arises from $\text{Si}(\text{1Al})$ group-

TABLE 1

The Dependence of the Concentrations of the Species on the Water Vapour Pressure of Steaming

Pressure in kPa	Concentration in "species per unit cell"										k_0
	Al ^F	Al ^{NF} oct.	Al ^{NF} tetr.	Al ^{NF} form.	Al ^{NF} sol.	Al ^{NF} insol.	¹ H	SiOH	b OH	AlOH	
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
0	6.0	0.6	—	—	—	—	6.4	1.2	5.2	—	6.0
2	4.0	0.6	1.8	—	—	1.6	5.6	1.2	4.4	—	12.8
7	2.8	0.6	3.0	—	—	2.8	5.2	1.2	2.8	1.2	16.0
13	2.0	0.6	3.4	0.2	0.2	3.0	4.8	1.6	2.4	0.8	12.7
40	1.6	0.6	3.8	2.8	2.8	0.8	4.0	1.2	1.6	1.2	4.1
93	1.5	0.6	3.8	4.0	4.0	—	3.6	1.2	1.6	0.8	3.1

Note. (1) Water vapour pressure; (2) concentration of framework aluminium atoms as determined by ²⁷Al MAS NMR (60 ppm line); (3) and (4) concentration of extra-framework aluminium species in an octahedral (~2 ppm line) and a tetrahedral (30 ppm line) coordination, respectively; (5) concentration of aluminium formate; (6) concentration of acid-soluble aluminium; (7) concentration of tetrahedral Al^{NF}, which is acid-insoluble; (8) total concentration of OH groups obtained from the maximum amplitude of the free induction decay; (9), (10), and (11) concentrations of SiOH, bridging OH and AlOH groups, respectively, determined by ¹H MAS NMR; (12) *n*-hexane cracking rate constant in mol MPa⁻¹ g⁻¹ h⁻¹ (taken from Ref. (11)). The experimental error does not exceed 0.4 species per unit cell.

ings. The fitted line at -100.8 ppm must be assigned to signals of Si(2Al) and SiOH groupings superimposed (2). This assignment could be confirmed by ²⁹Si CP MAS NMR spectra, which show a strong and a weak signal at -100.8 and -111.5 ppm, respectively. The fitted lines at -111.5 and -113.5 ppm correspond to 79.5% of the total intensity, the line at -106.4 ppm to 19%, and the line at -100.8 ppm to 1.5 ± 0.5%. ¹H MAS NMR (see Table 1) shows that there are 1.2 SiOH groups per 90 Si atoms in the unit cell; in other words, 1.3% of the total ²⁹Si signal must be assigned to the SiOH grouping and the portion of the signal due to the Si(2Al) grouping is 0.2 ± 0.5%. After steaming the percentage of silicon with Si(1Al) environment decreases (11).

The ²⁷Al nuclei in activated zeolites H-ZSM-5 are "NMR invisible" (13). This is because of heavy distortion of the tetrahedral or octahedral symmetry around the Al atom which causes a strong electrical field gradient at the place of the nucleus and, therefore, broadens the ²⁷Al NMR signal so

strongly that it becomes NMR invisible. ²⁷Al NMR measurements on H-ZSM-5 versus the water coverage yield the signal from all framework aluminium nuclei if at least one water molecule is adsorbed per one framework aluminium atom (14). Furthermore six molecules are necessary to build one aluminium hexaquo complex. A line narrowing of the ²⁷Al NMR signals can be achieved by complete rehydration in a desiccator (14).

Figure 3 shows ²⁷Al MAS NMR spectra of H-ZSM-5 after hydrothermal treatment at *T* = 810 K for *t* = 150 min and a water vapour pressure of 93 kPa. Figure 3A gives the spectrum of the sample rehydrated in a desiccator for 48 h. A line fitting procedure shows two narrow lines at 60 and -2 ppm due to 4-coordinated framework and 6-coordinated extra-framework aluminium and a broad line at about 30 ppm due to extra-framework AlOOH, respectively. Gilson *et al.* (15) assigned a broad line at ca. 30 ppm to 5-coordinated extra-framework aluminium in the dealuminated zeolite H-Y. How-

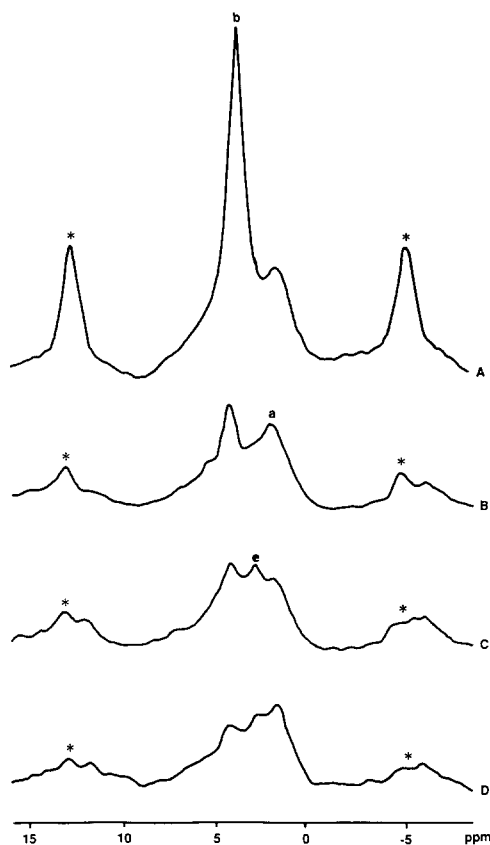


FIG. 1. ^1H MAS NMR spectra of H-ZSM-5 after hydrothermal treatment at $T = 810\text{ K}$ for $t = 150\text{ min}$ and the following water vapour pressures: 0 kPa (A); 7 kPa (B); (C) 40 kPa (C); 93 kPa (D). The samples were shallow-bed activated at 670 K and show line (a) at 2.0 ppm, line (b) at 4.3 ppm, and line (e) at ca. 3.0 ppm. Asterisks denote spinning sidebands.

ever, using 2D NMR technique Samoson *et al.* (16) established the fourfold coordination of the extra-framework aluminium species in hydrothermally treated zeolites. This finding was confirmed by recent studies of Man and Klinowski (17). Figure 3B demonstrates the formation of the aluminium formate complex after loading the zeolite with HCOOH. A strong narrow line appears in the ^{27}Al MAS NMR spectrum at 3 ppm, which can be assigned to octahedrally coordinated extra-framework aluminium in the aluminium formate complex.

In Table 1 (column 5) the concentration

of aluminium atoms which are involved in the formation of the complex giving rise to the line at 3 ppm is given versus steaming pressure. Upon mild dealumination the complex cannot be observed. Figure 3C gives the spectrum of the sample loaded with 0.5 M aqueous solution of HCl. In this spectrum the line at -2 ppm is increased due to the conversion of 4-coordinated extra-framework aluminium into the 6-coordinated aluminium hexaquo complexes. Table 1 (columns 6 and 7) gives the concentration of tetrahedral extra-framework aluminium, which can be and which cannot be converted, respectively (acid-soluble and acid-insoluble, respectively) to 6-coordinated extra-framework aluminium by treatment with 0.5 M aqueous solution of HCl.

Figure 4 shows ^{27}Al and ^{13}C NMR spectra of the sample steamed at a vapour pressure of 93 kPa. All samples were activated at 670 K, loaded with 16 (A, C, D, F) or 24 (B, E) molecules HCOOH per unit cell, calcined at 370 K (A, B, D, E) or 470 K (C, F) and measured in fused glass ampoules without MAS. The ^{13}C NMR spectra of all samples loaded with HCOOH and calcined at 470 K consist of only one line at 184 ppm. At low coverages (if the number of loaded HCOOH molecules is comparable with the number of bridging OH groups) only the line at 184 ppm can be observed. Figures 4D and 4E show the ^{13}C NMR spectra of samples loaded with

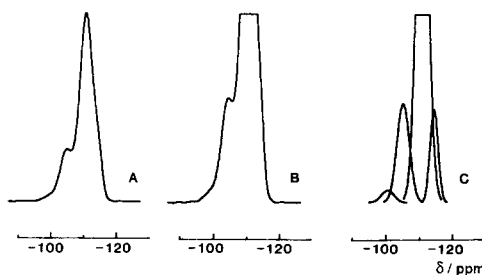


FIG. 2. ^{29}Si MAS NMR spectrum of H-ZSM-5 without hydrothermal treatment. The sample was hydrated in a desiccator for 48 h. Experimentally measured spectrum (A); enlarged experimental spectrum (B); and fitting of the enlarged spectrum (C).

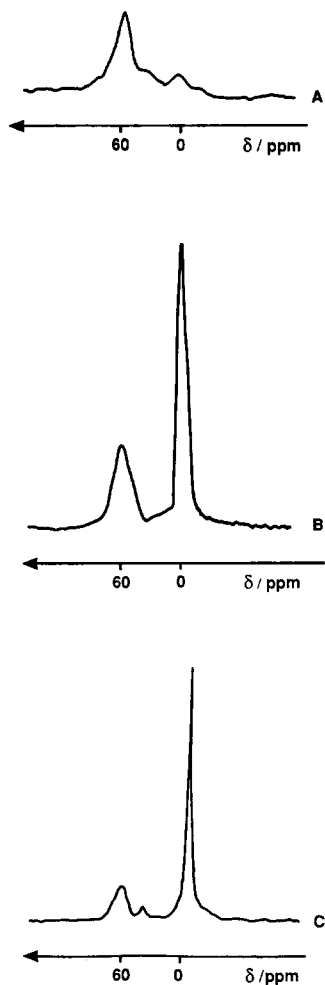


FIG. 3. ^{27}Al MAS NMR spectra of H-ZSM-5 after hydrothermal treatment at 810 K for 150 min and 93 kPa water vapour pressure: Sample rehydrated in a desiccator (A); sample activated at 670 K and loaded with 16 molecules HCOOH per unit cell (B). After loading the sample was calcined at 370 K; sample activated at 670 K and loaded with 0.1 M aqueous solution of HCl (C).

16 and 24 HCOOH molecules per unit cell, respectively, and then calcined at 370 K. The spectra consist of three lines: (i) the line at 184 ppm due to adsorbed carbon monoxide which is formed during the catalytic disintegration of HCOOH (see below); (ii) the line at ca. 166 ppm caused by the adsorbed HCOOH molecules; and (iii) the broad line, found in the spectra of the samples steamed

at 40 or 93 kPa, due to the aluminium formate complexes. The ^{27}Al NMR spectra consist of two lines: the line at ca. 60 ppm due to framework aluminium and the line at 3 ppm caused by the aluminium formate complexes. After the calcination at 470 K the intensity of the line at +3 ppm decreases.

n -Hexane adsorbed on H-ZSM-5 gives a triplet in the ^{13}C NMR spectrum. The chemical shifts of 14.7, 24.8, and 32.6 ppm which can be compared with the values of 13.7 ppm (terminal carbons), 22.8 ppm, and 31.9 ppm (midchain carbons) of liquid n -hexane (18), are independent of the hydrothermal pretreatment. The triplet can also be observed on samples after n -hexane cracking. The triplet due to residual n -hexane or cracking products is removed by heating the

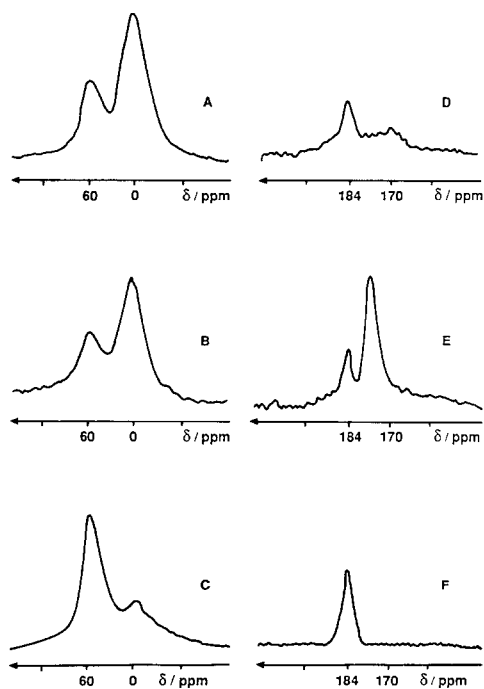


FIG. 4. ^{27}Al NMR spectra (A, B, C) and ^{13}C NMR spectra (D, E, F) of the sample steamed at a vapour pressure of 93 kPa, activated at 670 K, loaded with 16 (A, C, D, F) or 24 (B, E) molecules HCOOH per unit cell, calcined at 370 K (A, B, D, E) or 470 K (C, F) and measured in fused glass ampoules to avoid water adsorption.

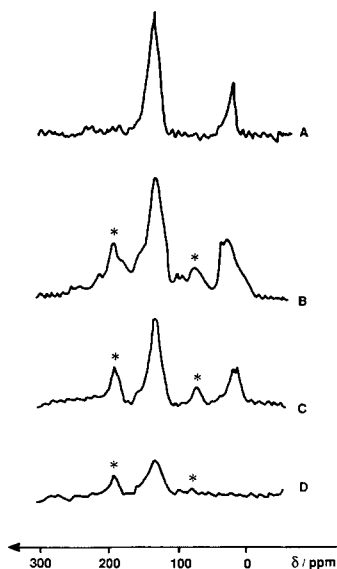


FIG. 5. ^{13}C CP MAS NMR spectra of H-ZSM-5 (steamed at different water vapour pressures of 0 kPa (A, B); 13 kPa (C); 40 kPa (D)) after *n*-hexane cracking measured with TOSS (A), and without TOSS (B, C, and D).

samples to 670 K and no ^{13}C MAS NMR signal can be observed. However, through cross polarization it is possible to monitor the coke deposits on these samples. Figures 5B–5D show the ^{13}C CP MAS NMR spectra of a sample without hydrothermal pretreatment and samples steamed at 13 and 40 kPa, respectively. A spectrum with total sideband suppression (TOSS) is given in Fig. 5A. This is proof that the lines denoted by asterisks in Fig. 5B–5D are spinning sidebands.

DISCUSSION

The magnitude of the chemical shift of an isolated bridging hydroxyl group is a measure of its strength of acidity, and has been found to increase as the Si/Al ratio of zeolites increases to ca. 10 (10). For higher values of the Si/Al ratio the chemical shift of the isolated bridging hydroxyl groups of zeolites of type H-ZSM-5 is constant at 4.3 ± 0.1 ppm (10). The samples in this study, including samples with enhanced catalytic

activity, also give spectra with a shift of 4.3 ppm for the bridging OH groups (see Fig. 1). This is in agreement with the infrared spectra of Lago *et al.* (6), which show that the line at 3610 cm^{-1} due to acidic bridging OH groups does not shift upon steaming. The infrared spectra of the samples (in fused glass ampoules prepared for ^1H MAS NMR) in the region of combination vibrations and overtones were measured. No shift of the OH vibrations in these regions could be observed. We conclude therefore that the enhanced catalytic activity cannot be explained by a decrease of the electron density on the hydrogen atom and the enhanced-activity site cannot be called a “stronger” Brønsted site.

Lago *et al.* (6) suggest that during the steaming one member of a paired Al site (Al–O–Si–O–Al) is modified (and possibly partially hydrolyzed) and acts as a strong electron acceptor for the remaining tetrahedral Al, thus creating a stronger Brønsted site. This model disagrees with our ^{29}Si MAS NMR measurements. The line fitting of the spectrum in Fig. 2 yields less than 1% of the silicon atoms in Si(2Al) grouping. The assumption of Lago *et al.* (6) that aluminium atoms preferentially occupy positions in 4-rings yields for Si/Al = 15 a concentration of two paired Al sites per unit cell and 4.2% of the silicon atoms in Si(2Al) grouping. A statistical distribution of aluminium on T-positions (Al–O–Al is forbidden) gives for Si/Al = 15 1.7 paired Al sites per unit cell and 2.3% of silicon as Si(2Al). However, the portion of less than 1% silicon atoms in Si(2Al) groupings as determined from the spectrum in Fig. 2 is smaller than the above calculated values.

Our results agree with the finding of Derouane and Fripiat (19) that aluminium does not preferentially occupy 4-membered rings. The nonempirical quantum chemical study gives the maximum probability of the substitution of Si by Al for the T_{12} position. However, we cannot confirm the formation of Al pairs (Al₁₂–O–Si–O–Al₂) as proposed in that study (19). It seems that the alumin-

ium atoms tend to occupy such positions where their mutual distance is maximum since the concentration of paired Al is smaller than predicted by the statistical distribution. Hence an increased concentration of paired Al sites, which is required by the model of Lago *et al.* (6) can be excluded by ^{29}Si MAS NMR.

^{27}Al MAS NMR detects all the ^{27}Al nuclei in the hydrated samples under study with an accuracy of $\pm 10\%$. This means that the samples do not contain NMR-invisible aluminium (11). The three lines at about 60, 30, and -2 ppm are due to 4-coordinated framework aluminium, 4-coordinated extra-framework aluminium, and 6-coordinated extra-framework aluminium, respectively. ^{27}Al MAS NMR spectra of hydrated samples do not support the existence of partially hydrolyzed framework aluminium proposed by Lago *et al.* (6). In conclusion, our study agrees well with Ref. (6) with regard to the catalytic effect of the steaming process (see Table 1), but MAS NMR does not confirm the proposed structure of the enhanced-activity sites.

No ^{27}Al MAS NMR signals can be observed for the dehydrated samples. All aluminium in such samples is NMR invisible, since a tetrahedral or octahedral symmetry of aluminium atoms in H-zeolites exists only in hydrated samples (13). The ^{27}Al MAS NMR spectra of hydrated samples show a 4-coordinated extra-framework aluminium species formed in the rehydration process from a precursor, which must be assumed to be the catalytically important part of the enhanced-activity site. The concentration of 4-coordinated extra-framework aluminium increases with increasing water vapour pressure during steaming. The concentration of octahedral aluminium atoms is constant in the samples under study (cf. Table 1).

It is well known that acid leaching removes only a part of the extra-framework aluminium from the crystallite (20). We have used formic acid to investigate which portion of extra-framework Al can be re-

moved. The conclusions from our ^{27}Al MAS NMR and ^{13}C NMR measurements are that the H^+ of the acidic bridging OH groups reacts with HCOOH forming H_3O^+ and CO . At temperatures up to 370 K one acidic OH group splits one HCOOH molecule. However, at 470 K a catalytic reaction splits all molecules. If the number of loaded molecules is much larger than the number of acidic OH groups and the temperature is below 370 K, HCOOH can react with extra-framework aluminium to give aluminium formate. This reaction did not occur in mildly dealuminated zeolites, which show the effect of the enhanced activity (see Table 1). Also the loading of an aqueous solution of 0.5 M HCl shows that the extra-framework aluminium species produced by mild dealumination are acid-insoluble. It follows that the aluminium species, which is the important part of enhanced-activity sites, is not easily removable, although it could be easily removed from the framework position and must be accessible for the hexane cracking reaction.

The nature of the new site is still not entirely clear. However, information has been added to our knowledge of the enhanced-activity sites. The concentration of charged extra-framework aluminium species in the dehydrated samples under study must be very small, because the concentration of framework aluminium does not significantly exceed the concentration of bridging hydroxyl groups (see Table 1). Therefore, the concentration of negatively charged AlO_4 tetrahedra in the framework, which can compensate positively charged extra-framework aluminium species, must be very low. Table 1 also shows that the concentration of nonacidic hydroxyl groups (sum of intensities of lines (a) and (e)) does not increase with increasing concentration of extra-framework aluminium. The intensity of line (e) due to AlOH groups on extra-framework Al species pointing towards framework oxygen atoms is weak, which means that the degree of hydroxylation of extra-framework aluminium species must be small (cf. Table 1). The de-

gree of polymerization of the species should be low, because the rehydration transforms them into AlOOH or $\text{Al}(\text{H}_2\text{O})_6^{3+}$ complexes.

Our conclusion concerning the NMR-invisible extra-framework aluminium in the mildly dealuminated dehydrated samples is that it exists in small uncharged and unstable complexes, which are mostly nonhydroxylated. Since they cannot be easily removed from their position by acid treatment they must be immobilized by the zeolitic framework.

Using the crystal structure determined by Olson *et al.* (21) for a computer representation of ZSM-5, narrow channels can be shown parallel to the straight channels. In such a narrow channel small cavities exist, for instance a cavity with a diameter of 0.26 nm and a window of 0.19 nm to the straight channel (22). If an oxygen atom of an extra-framework aluminium species were to be included in this small cavity it could not be easily removed.

The existence of extra-framework aluminium obviously enhances the catalytic reaction but the presence of bridging OH groups is also necessary for the activity enhancement. A suitable spatial arrangement of a bridging OH group and extra-framework aluminium species may be considered as the enhanced-activity site for the *n*-hexane cracking. The maximum number of such sites should be given by the smaller of the following two values: the number of extra-framework aluminium complexes or the number of bridging OH groups. This model is in agreement with the results of the catalytic measurements and the concentrations determined by MAS NMR.

It should be noted that enhanced activity after mild dealumination is not combined with an enhanced coke formation. The cross polarization spectra in Fig. 5 show a more or less intense peak at the position of the aromatic (100–170 ppm) and the aliphatic (ca. 30 ppm) region, respectively. The maximum deposition of coke is found for the nondealuminated sample.

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