Solid-state n.m.r. and catalytic studies of mildly hydrothermally dealuminated HZSM-5

E. Brunner, H. Ernst, D. Freude,* M. Hunger, C.B. Krause and D. Prager
Sektion Physik der Karl-Marx-Universität Leipzig, Linnéstrasse 5, DDR-7010 Leipzig, GDR

and W. Reschetilowski
Sektion Chemie der Karl-Marx-Universität Leipzig, Liebigstrasse 18, DDR-7010 Leipzig, GDR

and W. Schwieger and K.-H. Bergk
Sektion Chemie der Martin-Luther-Universität Halle-Wittenberg, Schlossberg 2, DDR-4020 Halle, GDR

Magic angle spinning (*MAS*) n.m.r. investigations and n-hexane cracking were carried out on HZSM-5, synthesized free of template, after mild hydrothermal dealumination. The maximum catalytic activity was obtained after 2.5-h treatment with water vapor at 50 Torr at 540°C. The n.m.r. data show that the enhanced activity is neither due to enhanced Brönsted acidity nor to a significant number of paired aluminium sites in the framework. The concentrations of the different OH groups and aluminium species suggest that the interaction of the molecule with both a bridging hydroxyl group and a nonframework aluminium species is the reason for the enhanced catalytic activity.

Keywords: Zeolite HZSM-5; catalytic activity; MAS n.m.r.

INTRODUCTION

Hydrothermal treatment of zeolites usually causes a dealumination of the framework (cf. Ref. 1–3). In certain circumstances, this dealumination gives rise to an enhancement of the catalytic activity (cf. Ref. 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 nonframework aluminium species. Lago *et al.*[6] observed an enhanced activity of HZSM-5 after mild steaming at 540°C and developed a kinetic model on the basis of paired framework Al atoms, which are partially hydrolysed, so that one aluminium atom in a nontetrahedral symmetry acts as a strong electron withdrawing center for the remaining tetrahedral Al, thus creating a stronger Brönsted site. Sendoda *et al.*[8] proved the enhanced activity of ZSM-5 after mild hydrothermal treatment for the conversion of propane.

All investigators agree that the enhanced-activity sites must be the result of an interaction of Brönsted and Lewis sites rather than the result of a decrease in the concentration of framework aluminium. The question arises, however, as to the nature of these sites. The existence of 3-coordinated Al in the framework after dehydroxylation[9] could be disproved by X-ray spectroscopy[10] and *MAS* n.m.r.[11] There is no evidence of nontetrahedral symmetry of the aluminium atoms in the framework. Scherzer[1] considered a variety of charged or neutral nonframework aluminium species. Jacobs and Beyer[12] propose the existence of AlO^+. *MAS* n.m.r. proved, however, the existence of tetrahedrally coordinated nonframework aluminium in the hydrated dealuminated zeolites.[13]

In the present study, we describe the mild hydrothermal dealumination of HZSM-5 synthesized free of template. The framework Si/Al ratio varies from 15 to 65, dependent on the temperature T, the water vapor pressure p, and the duration t of the steaming process. For the specific conditions T = 540°C, t = 2.5 h,.and varying water vapor pressure from 0 to 700 Torr, the samples have been investigated in detail by *MAS* n.m.r. and a catalytic test reaction to determine the nature of the enhanced-activity sites.

EXPERIMENTAL

Zeolite synthesis and hydrothermal treatment

The zeolite was synthesized without template

This paper is dedicated to Professor Harry Pfeifer on the occasion of his 60th birthday.

Address reprint requests to Dr. D. Freude at the Sektion Physik der Karl-Marx-Universität Leipzig, Linnéstrasse 5, DDR-7010, Leipzig, GDR.
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according to patent DD-WP 207 186 (GDR). The Na^+/H^+ ion exchange was carried out at room temperature with an aqueous solution of 0.5 molar HCl. The Si/Al ratio for this zeolite was determined by chemical analysis and found to be 15, in agreement with the ammonium-exchange capacity and ^{27}Al and ^{29}Si *MAS* n.m.r. The bulk Si/Al ratio is not changed during the dealumination procedure because the dealumination products are not removed. The concentration of Fe_2O_3 is less than 100 ppm.

The hydrothermal treatment of 2 g samples was carried out in a tube of 50 mm inner diameter with a maximum bed-depth of zeolite of 8 mm. The temperature was increased at a rate of 10 K per min in a water-free nitrogen stream at a flow rate of 1 liter per min. The steaming was carried out at 540°C for 150 min under a water vapor pressure, which was adjusted by the temperature of the water bath, through which the nitrogen was flowing. The treatment temperature was maintained in the range of ±10 K. On completion of the steaming, the sample was slowly cooled in a water-free nitrogen stream.

N.m.r. measurements

^{29}Si and ^{27}Al *MAS* n.m.r. was generally carried out on as-prepared and rehydrated samples, which were kept in desiccator for 48 h over aqueous NH_4Cl. For the ^1H *MAS* n.m.r. samples, shallow-bed activation conditions were utilized in a glass tube of 5.5 mm inner diameter and with 10 mm bed-depth of zeolite. The temperature was increased at a rate of 10 K per h. The samples were kept at the final activation temperature of 400°C under a pressure below 10^{-2} Pa for 24 h and then cooled and sealed.

Measurements were made on a homemade spectrometer HFS 270 and on Bruker MSL 300 and 400 spectrometers. As a reference for the ^{27}Al intensity measurements, a well-characterized sample of ZSM-5 with a framework Si/Al ratio of 15 was used. The total concentration of OH groups in the activated samples was determined by comparison of the initial value of the free-induction decay of the samples with those of a capillary with an aqueous solution in a probe with a short ring-down time. To separate the relative intensities of different lines in an ^1H *MAS* n.m.r. spectrum quantitatively, the signals of the spinning side bands were added to the main signal. The homemade *MAS* equipment for the rotation of the fused glass ampoules was carefully cleaned to avoid spurious proton signals.

Catalytic test

Catalytic activity and activity/time stability were determined for the n-hexane cracking reaction in an integral flow reactor. The reactor contained 0.25 g zeolite in the form of binder-free pellets with diameters of 0.3–0.4 mm. The hydrogen flow rate was 3 liters per h, and the feed rate of n-hexane was 0.0035 mole per h. The catalyst was heated at a rate of 6 K per min to 450°C and then maintained at this temperature for 1 h in the hydrogen flow. After the

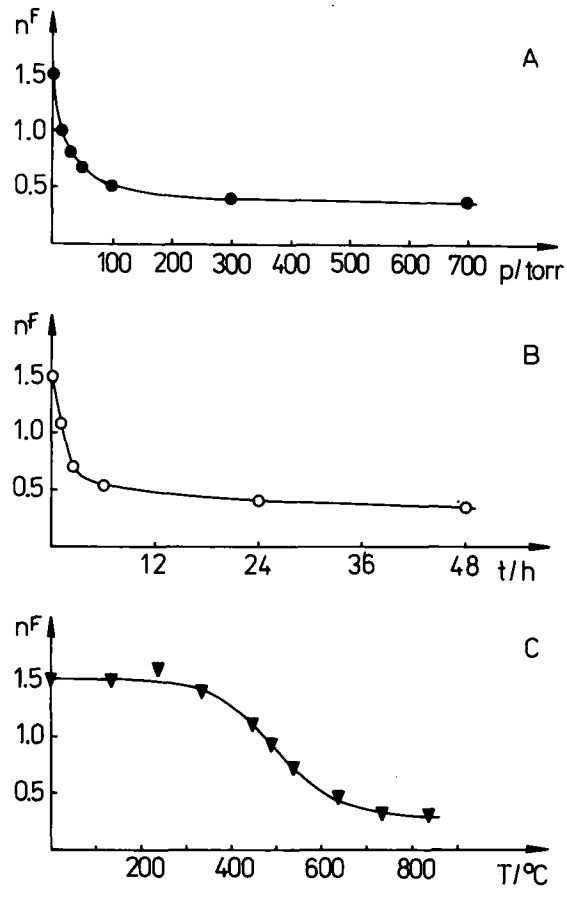


Figure 1 The concentration of framework aluminium atoms n^F per 24 framework tetrahedra (a unit cell contains 96 framework tetrahedra) of dealuminated HZSM-5. (A) Dependence of n^F on the water vapor pressure p for T = 540°C and t = 2.5 h. (B) Dependence of n^F on the time on stream t for T = 540°C and p = 75 Torr. (C) Dependence of n^F on the temperature of steaming T for p = 75 Torr and t = 2.5 h

n-hexane feed was started, the gas chromatographic analysis of reaction products was carried out at half-hourly intervals for 4 h. If U denotes the relative molar conversion, the reaction rate constant k is determined by the equation $k = -\ln(1 - U)$. The parameter B characterizing the activity/time stability is obtained by fitting the experimental values by the equation[14] $1/k - 1/k_0 = B \cdot t$, where k_0 denotes the extrapolated reaction rate constant at $t = 0$.

RESULTS

The dependence of n^F, which denotes the number of framework aluminium atoms per 24 framework tetrahedra (a unit cell contains 96 framework tetrahedra), on the water vapor pressure, on the time on stream, and on the temperature of steaming are presented in *Figure 1A*, *B*, and *C*, respectively [the Si/Al ratio is given by $Si/Al = (24/n^F) - 1$].

Corbin *et al.*[15] proved that ^{27}Al *MAS* n.m.r. gives the true Si/Al ratio with a mean error of 10% if two conditions are met: (1) the amount of paramagnetic species is less than 0.05%, and (2) the sample does not contain "n.m.r.-invisible" aluminium. The maximum

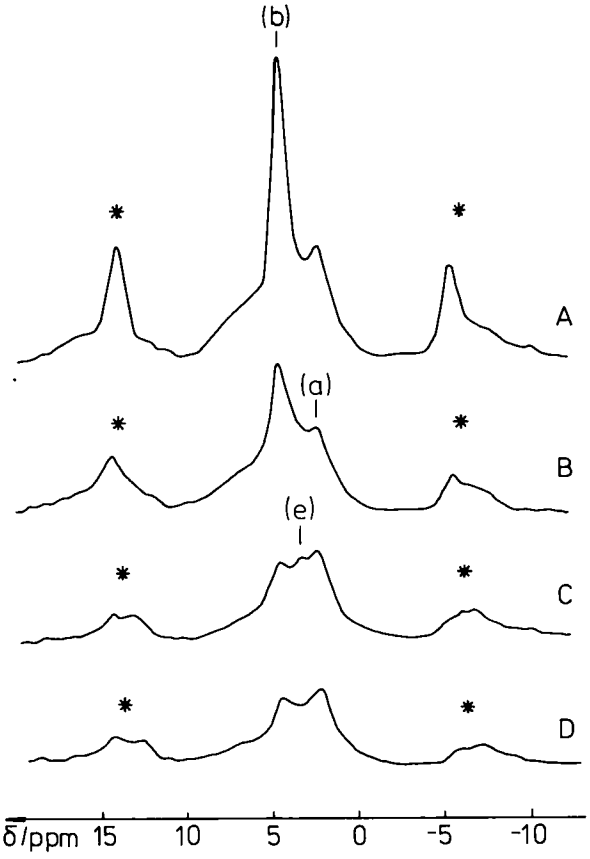


Figure 2 ^{1}H *MAS* n.m.r. spectra of HZSM-5 after hydrothermal treatment at $T = 540°C$ for $t = 150$ min and the following water vapor presssures: (A) $p = 0$ Torr; (B) $p = 50$ Torr; (C) $p = 300$ Torr; (D) $p = 700$ Torr. The samples were shallow-bed activated at 400°C and show line (a) at 2.0 ppm, line (b) at 4.3 ppm, and line (e) at ca. 3.0 ppm; * denotes spinning sidebands

concentration of 100 ppm Fe_2O_3 fulfills condition one. The second condition is tested by comparison of the ^{27}Al *MAS* n.m.r. free-induction decays. All samples that contain a constant total concentration of aluminium have the same initial value of the free-induction decay.

Figure 1C shows that a significant dealumination takes place at temperatures above 450°C. *Figure 1A* and *B* show that a saturation of the dealumination process occurs at high water vapor pressures and long times on stream, respectively.

^{1}H *MAS* n.m.r. spectra are given in *Figure 2*, where three different signals are 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 (cf. Ref. 13). Line (e) at ca. 3.0 ppm represents nonacidic AlOH groups on nonframework aluminium species pointing toward framework oxygen atoms. This line is resolved in the spectrum of *Figure 2C* only, but the line-splitting procedure shows the existence of line (e) in the spectra of *Figure 2B* and *D*, too.

Figure 3 represents the ^{27}Al *MAS* n.m.r. spectra of the rehydrated samples. It was proved by the comparison of the initial value of the free-induction decay that the total concentration of aluminium atoms in all samples is the same. Thus, the hydrated samples do not contain "n.m.r. invisible" aluminium. In general, the spectra show two narrow lines at 60 and −2 ppm due to 4-coordinated framework and 6-coordinated nonframework aluminium, respectively. The spectra of hydrothermally treated samples additionally show a broad line, ca. 130 ppm wide, at ca. 30 ppm (see *Figure 3B, C, D,* and *E*). The existence of the latter line was reported[16] and interpreted[13] as due to nonframework AlOOH in which Al is in tetrahedral coordination through its proximity to two framework oxygens.

Figure 4 shows the ^{29}Si *MAS* n.m.r. spectra of the rehydrated samples. The concentration of framework aluminium atoms can be calculated from deconvoluted spectra using Gaussian lineshapes (cf. Ref. 2). The values agree well with the concentrations determined by ^{27}Al *MAS* n.m.r. A line at −94 ppm due to Si(2Al) coordination could not be found in the spectra. ZSM-5 spectra show the Si(2Al) line only for $Si/Al < 10$ (cf. Ref. 17). This means that the probability for one framework aluminium atom to be in an

AlOSiOAl

arrangement is less than 5% for the nonsteamed zeolite (*Figure 4A*) and the hydrothermally treated samples (*Figure 4B* and *C*).

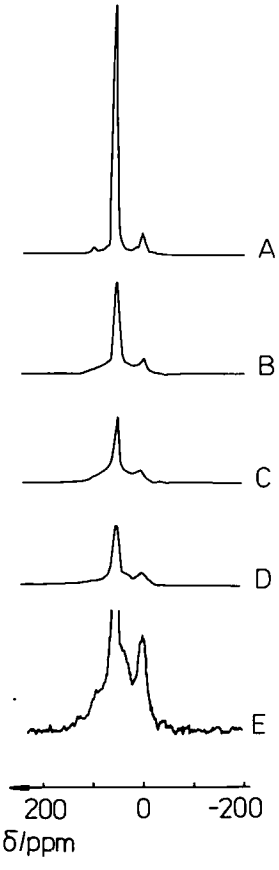


Figure 3 ^{27}Al *MAS* n.m.r. spectra of HZSM-5 after hydrothermal treatment at $T = 540°C$ for $t = 150$ min and the following water vapor pressures: (A) $p = 0$ Torr; (B) $p = 50$ Torr; (C) $p = 300$ Torr; (D) $p = 700$ Torr; (E) spectrum D with intensities × 8. The samples were rehydrated in desiccator for 48 h

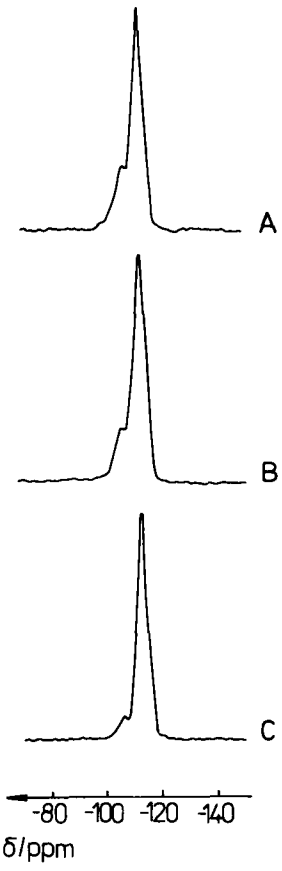


Figure 4 ^{29}Si *MAS* n.m.r. spectra of HZSM-5 after hydrothermal treatment at T = 540°C for t = 150 min and the following water vapor pressures: (A) p = 0 Torr; (B) p = 75 Torr; (C) p = 700 Torr. The samples were rehydrated in desiccator for 48 h

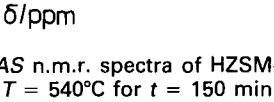
Table 1 lists the rate constants k_0 of n-hexane cracking obtained by the extrapolation of the dependence of the rate constant k on the time on stream to zero time. The activity/time stability is given by the value B obtained from the slope of the above curve. *Table 1* also contains the concentrations of aluminium atoms in the three different coordinations and the concentrations of different types of hydroxyl groups as a function of the water vapor pressure.

DISCUSSION

The values of the chemical shift of the isolated bridging hydroxyl groups are a measure of their acid strength and are found to increase with the Si/Al ratio for faujasites but remain constant above Si/Al = 10 (cf. Ref. 13). For zeolites of the HZSM-5 type, we measured[13] a constant chemical shift of (4.3 ± 0.1) ppm for the isolated bridging hydroxyl groups if the Si/Al ratio is greater than 10. The samples in this study, including samples with enhanced catalytic activity, also give spectra with the line of the bridging OH groups at 4.3 ppm (see *Figure 2*). This finding is in agreement with the i.r. spectra of Lago *et al.*,[6] which show no shift of the line at 3610 cm^{-1} due to acidic bridging OH upon steaming. The i.r. spectra of the samples (in fused glass ampoules prepared for ^{1}H *MAS* n.m.r.) in the region of combination vibrations and overtones were measured. A shift of the OH vibrations in these regions could not be observed. We conclude from both the ^{1}H *MAS* n.m.r. and the i.r. results 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" Brönsted site.

Lago *et al.*[6] propose that one member of a paired

Al site (AlOSiOAl) is modified during the steaming



(possibly partially hydrolysed) and acts as a strong electron withdrawing center for the remaining tetrahedral Al, thus creating a stronger Brönsted site. This model is in disagreement with ^{29}Si *MAS* n.m.r. The relevant spectra in *Figure 4* do not show a line at −94 ppm due to Si(2Al), which determines a value of 5% of the aluminium atoms (0.08 per 24 framework tetrahedra) as the upper limit of paired Al. This concentration is much less than the number of one paired Al per 24 framework tetrahedra required by the model of Lago *et al.*[6] for Si/Al = 15.

^{27}Al *MAS* n.m.r. detects all the ^{27}Al nuclei in the hydrated samples under study, that is, "n.m.r.-invisible" aluminium does not exist. The three lines at ca. 60, 30, and 0 ppm are due to 4-coordinated

Table 1 Concentration of aluminium species and hydroxyl groups and results of catalytic measurements with dependence on the water vapor pressure p

	Concentration/species per 24 framework tetrahedra								
p/Torr (1)	Al^F (2)	Al^{NF} oct. (3)	Al^{NF} tetr. (4)	^{1}H (5)	SiOH (6)	SiOHAl (7)	AlOH (8)	k_0 (9)	B (10)
0	1.3	0.1	–	1.6	0.3	1.3	–	6.0	0.6
14	1.0	0.1	0.4	1.4	0.3	1.1	–	12.8	0.9
50	0.7	0.1	0.7	1.3	0.3	0.7	0.3	16.0	1.0
100	0.5	0.2	0.8	1.2	0.4	0.6	0.2	12.7	1.1
300	0.4	0.2	0.9	1.0	0.3	0.4	0.3	4.1	3.3
700	0.4	0.2	0.9	0.9	0.3	0.4	0.2	3.1	15.5

Column: (1) Water vapor pressure p; (2) concentration of framework aluminium atoms determined by ^{27}Al *MAS* n.m.r. (60 ppm line); (3) and (4) concentration of nonframework aluminium species in an octahedral (0 ppm line) and a tetrahedral (30 ppm line) coordination, respectively; (5) total concentration of ^{1}H obtained from the initial value of the free-induction decay; (6), (7), and (8) concentration of SiOH, bridging OH, and AlOH groups, respectively, determined by ^{1}H *MAS* n.m.r.; (9) reaction rate constant k_0 in the unit mole·MPa^{-1}·g^{-1}·h^{-1}; (10) parameter B, characterizing the activity/time stability in the unit 10^{-3}·MPa·g·mole^{-1}. The experimental error is ±0.1 in columns (2)–(8), ±10% in column (9), and ±20% in column (10). "0 Torr" indicates a thermal treatment in a water-free nitrogen stream. All samples were steamed for 150 min at 540°C.

framework aluminium, 4-coordinated nonframework aluminium, and 6-coordinated nonframework aluminium, respectively. There is no evidence for the partially hydrolysed framework aluminium proposed by Lago *et al.*[6] in the ^{27}Al *MAS* n.m.r. spectra of the hydrated samples. In conclusion, *MAS* n.m.r. cannot confirm the nature of the enhanced-activity sites as proposed by Lago *et al.*[6]

Table 1 shows that the concentration of 4-coordinated and 6-coordinated nonframework aluminium in the rehydrated samples increases with increasing water vapor pressure during the steaming procedure. Note that ^{27}Al *MAS* n.m.r. gives no spectrum of the dehydrated samples. All aluminium in the dehydrated samples is "n.m.r.-invisible," because the "ideal" tetrahedral or octahedral symmetry of aluminium atoms in H-zeolites exists only in hydrated samples.[18] The ^{27}Al *MAS* n.m.r. shows a 4-coordinated nonframework aluminium that has been formed in the rehydration process from a precursor, that is, from the actual catalytically important part of the enhanced-activity site. Thus, the nature of the new site is still not resolved; what has been added to knowledge about the enhanced-activity sites is what kind of nonframework Al species can be formed upon transforming it in the rehydration process. The concentration of charged nonframework aluminium species in the dehydrated samples under study must be very small: The concentration of framework aluminium does not exceed the concentration of bridging hydroxyl groups significantly (see *Table 1*). Therefore, the concentration of negatively charged AlO_4-tetrahedra in the framework, which can compensate positively charged nonframework aluminium species, must be very small. *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 nonframework aluminium. The intensity of line (e) due to AlOH groups on nonframework Al species pointing toward framework oxygen atoms is very weak. Therefore, the hydroxylation of nonframework aluminium species must be very small. The degree of polymerization of the species should be low, because the rehydration transforms them into AlOOH or $Al(H_2O)_6^{3+}$ complexes. Our conclusion concerning the "n.m.r.-invisible" nonframework aluminium in the mildly dealuminated dehydrated samples is that it mostly exists in noncharged, nonhydroxylated, and nonstable small complexes. Such complexes are known to be electron pair acceptors, the so-called Lewis sites.

The existence of nonframework aluminium species obviously enhances the catalytic reaction, but the presence of bridging OH groups is also necessary for the activity enhancement. A convenient spatial arrangement of an n-hexane molecule on a bridging OH group and a nonframework aluminium species may be considered as an 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 nonframework 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* n.m.r. The activity/time stability is not degraded by a mild hydrothermal treatment, but it deteriorates at water vapor pressures greater than 300 Torr (see *Table 1*). It should be noted that the dealumination of the zeolitic framework reaches a saturation value for $p > 300$ Torr. However, the concentration of bridging OH groups after such a strong dealumination is now small and it is difficult to detect an activity enhancement in this range confidently.

In general, the conclusion with regard to the effect of the steaming process on the catalytic activity—first increase, then decrease—agrees very well with the data published by Lago *et al.*[6]

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