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Spectroscopic and Physicochemical Characterization of P-Modified H-ZSM-5

G. LISCHKE,* R. ECKELT,* H.-G. JERSCHKEWITZ,* B. PARLITZ,*
E. SCHREIER,* W. STOREK,† B. ZIBROWIUS,† AND G. ÖHLMANN*

Zentralinstitut für physikalische Chemie, Bereich Katalyse† and Analytisches Zentrum,
Rudower Chaussee 5, O-1199 Berlin-Adlershof, Germany*

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Acidic properties of P-modified H-ZSM-5 have been characterized by means of ammonium exchange, temperature-programmed desorption of ammonia (NH_3 TPD), as well as IR, ^{27}Al MAS NMR, and ^{31}P MAS NMR spectroscopy. The introduction of phosphorus by impregnation of the zeolite with an aqueous solution of orthophosphoric acid decreases the number of Brønsted acid sites. Brønsted acidity can be restored completely by elution of the orthophosphoric acid with hot water. Only after calcination or steaming at elevated temperatures of the H_3PO_4-impregnated sample is an irreversible decrease of Brønsted acidity caused by dealumination observed. The formation of aluminum phosphates in nonframework positions proceeds simultaneously. Thermal treatment of H_3PO_4-impregnated H-ZSM-5 results in degrees of dealumination lower than those with nonimpregnated samples, indicating that phosphorus partially protects aluminum ions from being removed from their substitutional positions in the silica framework.

INTRODUCTION

ZSM-5 zeolites have been extensively investigated as the active components of catalysts for a variety of chemical reactions (*1–5*). The aptitude of this type of zeolite for catalysts is based on its acidity combined with the special features of the pore structure.

The acid catalytic behavior of ZSM-5, expressed in terms of activity, selectivity, and stability, is usually assumed to be connected with sites involving tetrahedral aluminum ions in substitutional positions in the framework of silica. Therefore the value of the acidity, being thus related to the number of aluminum ions within the zeolite framework, can be adjusted by a proper choice of conditions of zeolite synthesis to achieve the requirements of a reaction of interest. A reasonable way to decrease the content of framework aluminum of a zeolite with an originally low Si/Al ratio obtained, e.g., by synthesis in the absence of a template is offered by subsequent dealumination (*6*). Another method to reduce acidity is the introduction of a further chemical component into the zeolite system. Apart from metal cations and boron, phosphorus has been used successfully to improve the desired catalytic properties of ZSM-5 (*7–11*).

The subject of the present paper is the characterization of P-modified ZSM-5 by means of several spectroscopic and physicochemical methods. As temperatures of catalytic reactions often reach or even exceed 500°C, investigations include the study of the influence of thermal or hydrothermal strain on zeolite acidity. The methods of characterization used are NH_4^+ exchange, temperature-programmed desorption of ammonia (NH_3 TPD), IR, ^{27}Al MAS NMR, and ^{31}P MAS NMR spectroscopy, and temperature-programmed decomposition of previously NH_4^+-exchanged samples. The experiments have also included nonmodified zeolite. The investigation has been based on a ZSM-5 with a Si/Al_F (framework) ratio of

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about 19 corresponding to the total composition of

$$Na_{4.8}Al_{4.8}Si_{91.2}O_{192} \times H_2O.$$

EXPERIMENTAL

(*a*) *Preparation of Samples*

ZSM-5 type zeolite (HS-30, Chemie AG Bitterfeld-Wolfen) was converted into the H^+ form by a four-times repeated treatment with 0.2 *M* HNO_3 solution in a simple batch procedure. For dealumination, samples were held in a stream of air and steam (p_{water} = 90 kPa) at 500°C in a quartz tube for 4 h. Modification with phosphorus was carried out by impregnation with an aqueous solution of phosphoric acid and subsequent drying at 120°C for 1 h. After careful homogenization, the powdered material was steamed or calcined at elevated temperatures.

(*b*) *Ammonium Exchange*

The protons of H-ZSM-5 zeolites were exchanged by NH_4^+ ions by treatment with an aqueous solution of an ammonium salt. For this purpose the sample (approx. 4 g) was placed on a glass frit and exposed to a flow of 300 ml of an aqueous 0.2 *M* $NH_4(CH_3COO)$ solution at 70 to 80°C for at least 4 h. After careful washing, the content of ammonium was determined by the Kjeldahl method.

(*c*) *Determination of Phosphorus in Aqueous Solutions*

The same device as that used in the ammonium exchange was used to analyze phosphorus removed from H_3PO_4-impregnated samples by elution with hot water. Quantitative determination of the eluted phosphorus was based on the spectrophotometric molybdo-vanado-phosphoric acid method.

(*d*) *Temperature-Programmed Desorption of Ammonia* (*NH_3 TPD*)

After zeolite samples were cleaned by heating to 500°C in a He gas stream (v = 1 ml/s) for 1 h, ammonia was adsorbed at 120°C from a He gas stream containing 3 vol% of NH_3. After flushing by pure He at 120°C for 2 h, desorption of ammonia up to 500°C was started (flow rate of helium: 1 ml/s; heating rate 12 K/min). The concentration of NH_3 in the exit gas was determined using a thermoconductivity cell. The curve of the desorptogram, which normally exhibited two maxima, was recorded. In case of unsatisfactory separation, ammonia was adsorbed at 250°C, thus avoiding the low-temperature peak. Additionally ammonia was absorbed from the exit gas stream by a 0.05 *M* H_2SO_4 solution. Its total amount was determined by back titration of excess sulfuric acid.

(*e*) *IR Spectroscopy*

ZSM-5 zeolite samples were compressed to thin self-supporting wafers (approx 7 mg/cm^2) and placed in a quartz IR cell. The wafers were calcined at 400°C *in vacuo*. After cooling to 200°C, pyridine vapor was admitted into the system for 30 min. Afterward, the cell was degassed and evacuated to eliminate physisorbed pyridine. Transmission spectra were recorded in the range from 4000 to 1300 cm^{-1} both before and after pyridine adsorption, using a Specord M 85 spectrometer (Carl Zeiss, Jena) with a 4-cm^{-1} resolution.

(*f*) *^{27}Al and ^{31}P MAS NMR Measurements*

The NMR spectra were obtained on a Bruker MSL400 multinuclear spectrometer operating at a field of 9.4 T with a standard Bruker double-bearing MAS probe. The zirconium dioxide rotors were spun near 5 kHz with dry nitrogen as driving gas. About 200 mg of sample material was filled in the rotor with a volume of about 0.35 cm^3.

Typically, 1500 to 2400 free induction decays were accumulated per sample for both nuclei. The pulse widths were 3.9 μs ($\pi/2$ pulse) with repetition times between 5 and 30 s and 0.6 μs ($\pi/12$ pulse) with a repetition time of 1 s for ^{31}P at 162 MHz and for ^{27}Al at 104 MHz, respectively. The line positions are given on the δ scale with a maximum uncertainty of ±0.5 ppm, referred to H_3PO_4 (85 wt%) or to an aqueous $Al(NO_3)_3$ solution, respectively. The chemical shifts given for aluminum were not corrected for second-order quadrupole effects. In order to obtain reliable quantitative results by the ^{27}Al MAS NMR measurements, the samples were hydrated in a desiccator in an atmosphere saturated with water for more than 20 h (*12*).

RESULTS AND DISCUSSION

(*a*) *Ammonium Exchange*

Protons of the acid sites of the zeolite can be exchanged totally by NH_4^+ ions (*6*). This is why determination of the number of these sites can be based on the quantitative analysis of the ammonium ions present in the zeolite after treatment with ammonium salt solutions. Provided that Brønsted sites are identifiable with the Al–O–Si groups of the zeolite framework, the Si/Al_F ratio can be calculated directly from analytical NH_4^+ data. Values of the conventional chemical analysis of ZSM-5 show that, within the margins of error, total aluminum is identical with that found by the ammonium exchange. Hence it follows that the original zeolite is free of nonframework aluminum.

Exchange data with the nonimpregnated zeolite (Table 1) show that the number of Brønsted acid sites is decreased after hydrothermal treatment of the sample at elevated temperatures. The degree of dealumination increases as temperature is raised (sample B and C).

Impregnation of the zeolite with orthophosphoric acid including subsequent drying at moderate temperatures does not influence NH_4^+ exchange capacity (sample I). As the exchange procedure itself includes the treatment with a hot aqueous solution, exchange data of H_3PO_4-impregnated samples must be compared with results of the otherwise eluted samples. After hydrothermal treatment at higher temperatures, the exchange value diminishes (sample J and K); i.e., the number of Brønsted acid sites is reduced.

TABLE 1

Nondealuminated P-Free H-ZSM-5

Sample	Treatment	NH_4^+ exchange			NH_3 TPD			IR pyridine adsorption 1546 cm^{-1}				^{27}Al MAS NMR	
		C_{H^+} (μmol/g)	Si/H^+	H^+/u.c.	C_{H^+} (μmol/g)	Si/H^+	H^+/u.c.	Absorbance	C_{H^+} (μmol/g)	Si/H^+	H^+/u.c.	Si/Al_F	Al/u.c.
A	H form dried at 120°C	840	18.9[a]	4.8	610	26	3.6	0.45	840	18.9[a]	4.8	18.9[a]	4.8
B	Sample A hydrothermally treated at 400°C for 3 h	469	34	2.8	310	53	1.8	0.16	300	53	1.8	42	2.2
C	Sample A hydrothermally treated at 750°C for 0.5 h	130	122	0.8	110	136	0.7	0.04	76	209	0.46	190	0.5
D	A impregnated with 0.1 *M* $Al(NO_3)_3$ solution, dried at room temp.	—	—	—	590	27	3.4	0.29	550	29	3.2	23	3.6
E	Sample D washed with hot water	—	—	—	620	26	3.6	0.34	640	25	3.7	18	4.8

[a] Experimental data of IR pyridine adsorption and ^{27}Al MAS NMR are related to the value of the NH_4^+ exchange.

TABLE 2

Nondealuminated, H_3PO_4-Impregnated H-ZSM-5 (P Content 2.5 wt%)

Sample	Treatment	NH_4^+ exchange			NH_3 TPD			IR pyridine adsorption 1546 cm^{-1}				^{27}Al MAS NMR	
		C_{H^+} (μmol/g)	Si/H^+	H^+/u.c.	C_{H^+} (μmol/g)	Si/H^+	H^+/u.c.	Absorbance	C_{H^+} (μmol/g)	Si/H^+	H^+/u.c.	Si/Al_F	Al/u.c.
F	Sample dried at 120°C	—	—	—	160	95	1.0	0.15	340	47	2.0	25	3.7
G	Sample F hydrothermally treated at 400°C for 4 h	—	—	—	120	136	0.7	0.14	260	61	1.5	75	1.3
H	Sample F hydrothermally treated at 700°C for 0.5 h	—	—	—	75	191	0.5	0.08	150	106	0.9	150	0.6
I	Sample F eluted removed fraction of total P: 99.6%	837	19	4.8	620	26	3.6	0.43	810	20	4.7	16	5.6
J	Sample G eluted removed fraction of total P: 89.7%	711	22	4.2	510	31	3.0	0.24	450	35	2.6	31	3.0
K	Sample H eluted removed fraction of total P: 60.0%	642	25	3.7	260	63	1.5	0.17	320	50	1.9	71	1.3

Comparison of data given in Tables 1 and 2 clearly indicates that a reduction of the number of the protonic sites by hydrothermal treatment is more effective with the nonmodified samples. Obviously, dealumination is rendered more difficult in the presence of phosphoric acid.

(*b*) *Temperature-Programmed Desorption of Ammonia* (*NH_3 TPD*)

With solid catalysts, NH_3 TPD is a valid method of identifying acid sites of various strength and to determine their number. With ZSM-5 samples, desorptograms show two well-resolved peaks with maximum intensities at 230 to 250°C and at 400 to 450°C (Fig. 1). The high-temperature peak (HTP) is assigned to Brønsted type acid sites of bridged hydroxyl groups of the zeolite framework. Therefore the determination of the number of Brønsted acid sites can be based on the amount of ammonia desorbed within the upper-temperature region. Low-temperature desorption is caused by weakly bonded ammonia.

Impregnation with orthophosphoric acid sharply decreases the analytical value of ammonia desorbed from Brønsted acid sites: The HTP area appears as a shoulder only (sample F). The reduction of the number of Brønsted acid sites by H_3PO_4, however, does not mean that the amount of aluminum ions within the framework is decreased equivalently. After treatment with hot water, which results in a practically complete elution of phosphorus, the original value of strong acid sites is recovered (sample I).

Hydrothermal treatment at elevated temperatures reduces Brønsted acidity in every case (Table 1 and 2; Fig. 2). The effect increases as the temperature is raised. With the P-free sample the portion of strong acid sites remaining after treatment at 700°C

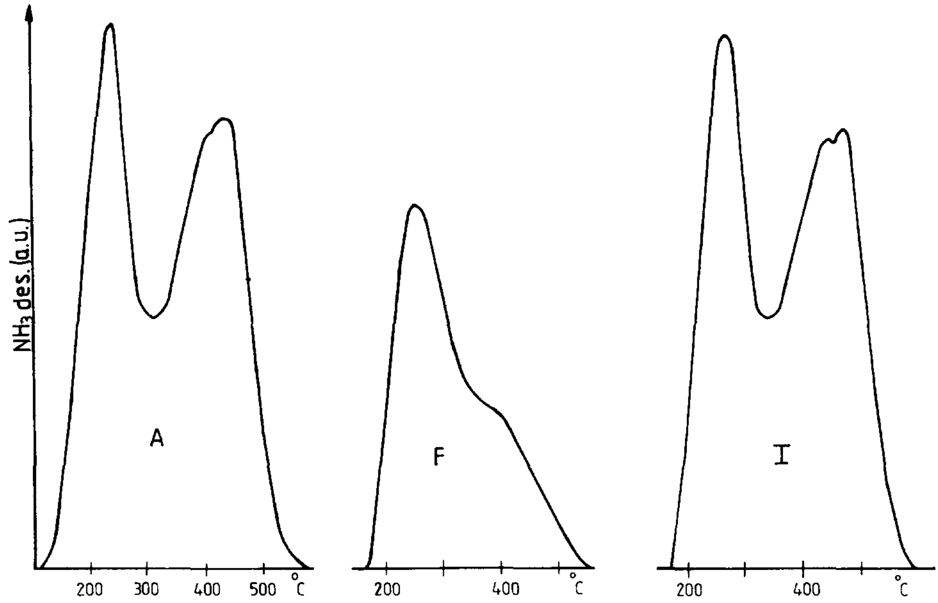

FIG. 1. Temperature-programmed desorption of NH_3 from thermally nontreated H-ZSM-5. Sample A: parent sample. Sample F: sample A after H_3PO_4 impregnation (content of phosphorus: 2.5 wt%). Sample I: sample F after elution (eluted fraction of phosphorus: 99.6%). Sample weight, heating rate, and helium flow rate were 0.6 g, 12 K/min, and 1 ml/s, respectively.

(sample C) amounts to only 18% of the value found with the parent sample.

Hydrothermal treatment causes a further decrease of Brønsted acidity (sample G and H). The number of strong acid sites can be raised again by subsequent elution with hot water. The recovered values (samples J and K) clearly exceed those of the corresponding nonmodified samples (samples B and C, respectively). They are, however, signifi-

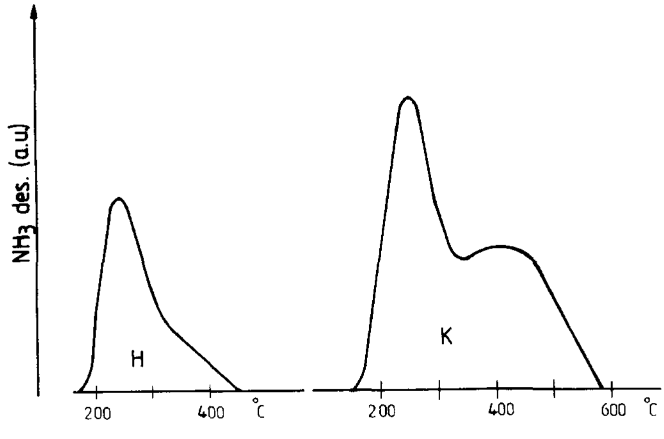

FIG. 2. Temperature-programmed desorption of NH_3 from hydrothermally treated, H_3PO_4-impregnated H-ZSM-5 (content of phosphorus: 2.5 wt%). Sample H: H_3PO_4-impregnated H-ZSM-5 after hydrothermal treatment at 700°C. Sample K: sample H after elution (eluted fraction of phosphorus: 60.0%). Sample weight, heating rate, and helium flow rate were 0.6 g, 12 K/min, and 1 ml/s, respectively.

cantly smaller than those with the original sample A (Table 1; Fig. 1).

Similarly to the NH_4^+ exchange, NH_3 TPD data reveal that impregnation with orthophosphoric acid protects the zeolite framework against dealumination by hydrothermal treatment. It is evident that with H_3PO_4-impregnated, hydrothermally treated samples, the concentration of Brønsted acid sites per unit cell (H^+/u.c.) derived from the data of ammonium exchange strongly exceeds the values found by other methods. An explanation of this remarkable effect is given later.

(*c*) *IR Spectroscopy*

IR spectra were recorded both in the wavenumber range between 3800 and 3400 cm^{-1} characterizing OH groups of the zeolite and between 1700 and 1400 cm^{-1}, representing the interaction of pyridine with different surface sites. The main results of spectroscopic investigation of the samples prior to pyridine loading are the following.

—The IR spectrum of the original zeolite (sample A) shows two OH bands, a weak one at 3740 cm^{-1} and a strong one at 3610 cm^{-1}, which are due to terminal Si–OH groups and to bridged hydroxyls (Brønsted sites), respectively (Fig. 3).

—Hydrothermal treatment (samples B and C), which is known to result in a removal of aluminum from its position within the zeolite framework (dealumination), gives rise to a band at 3665 cm^{-1}, which can be ascribed to nonframework aluminum OH groups formed due to dealumination. Simultaneously a sharp decrease of the band at 3610 cm^{-1} is observed.

—Impregnation with orthophosphoric acid (sample F) causes a distinct decrease of intensity for the band at 3610 cm^{-1} accompanied by broadening (Fig. 4).

—After hydrothermal treatment (samples G and H) only one extremely broad band remains in the region between 3450 and 3650 cm^{-1} (Fig. 4). Elution of phosphorus results in some restoration of the band at 3610 cm^{-1} (samples J and K) but with an intensity clearly diminished as compared with the parent zeolite (sample A). The shoulder at 3665 cm^{-1} indicates the presence of nonframework aluminum.

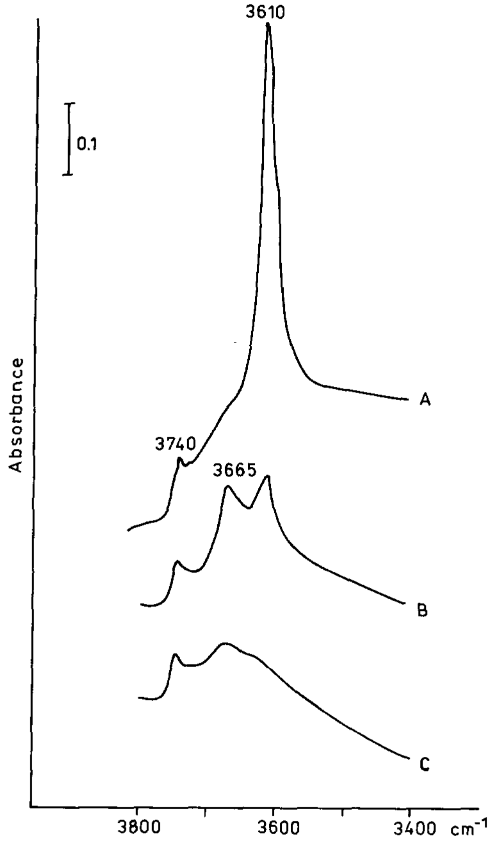

FIG. 3. IR spectra of P-free H-ZSM-5 (cf. Table 1).

After adsorption of pyridine, the band of the Si–OH groups remains unchanged, whereas that of the bridged hydroxyl groups completely vanishes. New bands in the region of lower wavenumbers are detected at 1446, 1456, 1490, 1546, 1600, and 1636 cm^{-1}. Quantitative estimation of the absorbance as given in Table 3 is based on the bands at 1546 cm^{-1} and at approximately 1450 cm^{-1}, which characterize adsorption of pyridine at acid OH groups or coordinatively bonded pyridine, respectively. Both bands are present in all of the spectra; i.e., each of the samples shows acidity of both Brønsted and

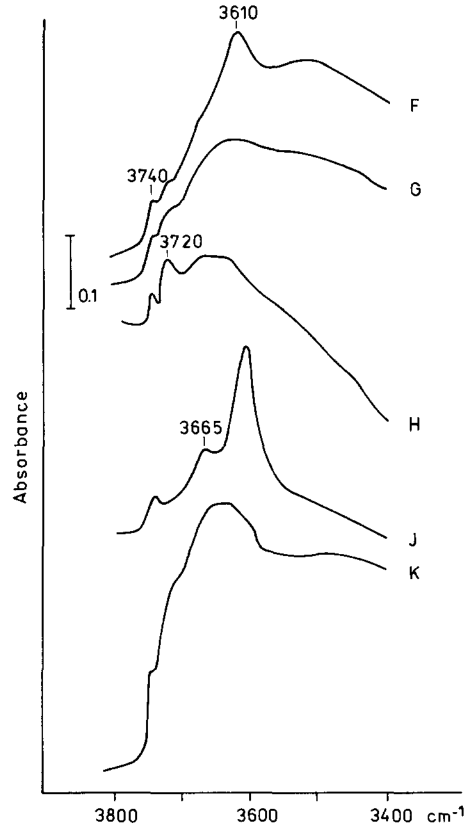

FIG. 4. IR spectra of H_3PO_4-impregnated H-ZSM-5 (cf. Table 2).

TABLE 3

Absorbance (Standardized) of Pyridine Absorption Bands

Sample	A_{1546}	%	A_{1450}
A	0.45	100	0.17
B	0.16	36	0.33
C	0.04	9	0.08
F	0.18	40	0.11
G	0.14	31	0.10
H	0.08	18	0.14
I	0.43	96	0.42
J	0.24	53	0.23
K	0.17	38	0.22

Lewis type. Data reveal that impregnation with orthophosphoric acid results in a decrease of the intensity of both bands. The intensity of the band at 1450 cm^{-1} is raised sharply for eluted samples, exceeding even the original value. This increase indicates that sites of coordinative adsorption are generated as a result of the interaction between the orthophosphoric acid and the zeolite as well as by hydrothermal treatment. Concentration of Brønsted acid sites (μmol/g), the Si/Brønsted site ratio, and the average number of Brønsted sites per elementary unit of the zeolite, derived from the value of absorbance of the band at 1546 cm^{-1}, are represented by Tables 1 and 2. As can be seen clearly, hydrothermal treatment results in a drastic decrease of the concentration of strong acid sites. Their number is also diminished by modification with phosphorus and can be increased again by subsequent elution with hot water. As observed by TPD, Brønsted acidity of thermally treated samples after elution with hot water, however, does not reachieve the original value of the parent sample. Obviously partial dealumination during hydrothermal treatment proceeds in every case, as is indicated by the appearance of the bands at 3665 cm^{-1} and by the increase of the band at 1450 cm^{-1} with the eluted modified samples. A comparison of hydrothermally treated samples reveals a much sharper decrease of Brønsted acidity in the case of the unmodified zeolite.

(*d*) ^{27}*Al MAS NMR Spectroscopy*

NMR spectroscopic evaluation of the Si/Al_F ratios of samples A to K is based upon the signal of the tetrahedrally coordinated framework aluminum atoms at 54 ppm (Fig. 5). For quantitative estimation its intensity is related to that of the parent sample A, the molar Si/Al_F value of which is 18.9 as is known from NH_4^+ exchange.

At first the influence of impregnation with H_3PO_4 without subsequent thermal treatment (sample F) was investigated. Additionally the parent sample was impregnated with a dilute aqueous solution of $Al(NO_3)_3$ (sample D) in order to investigate whether the

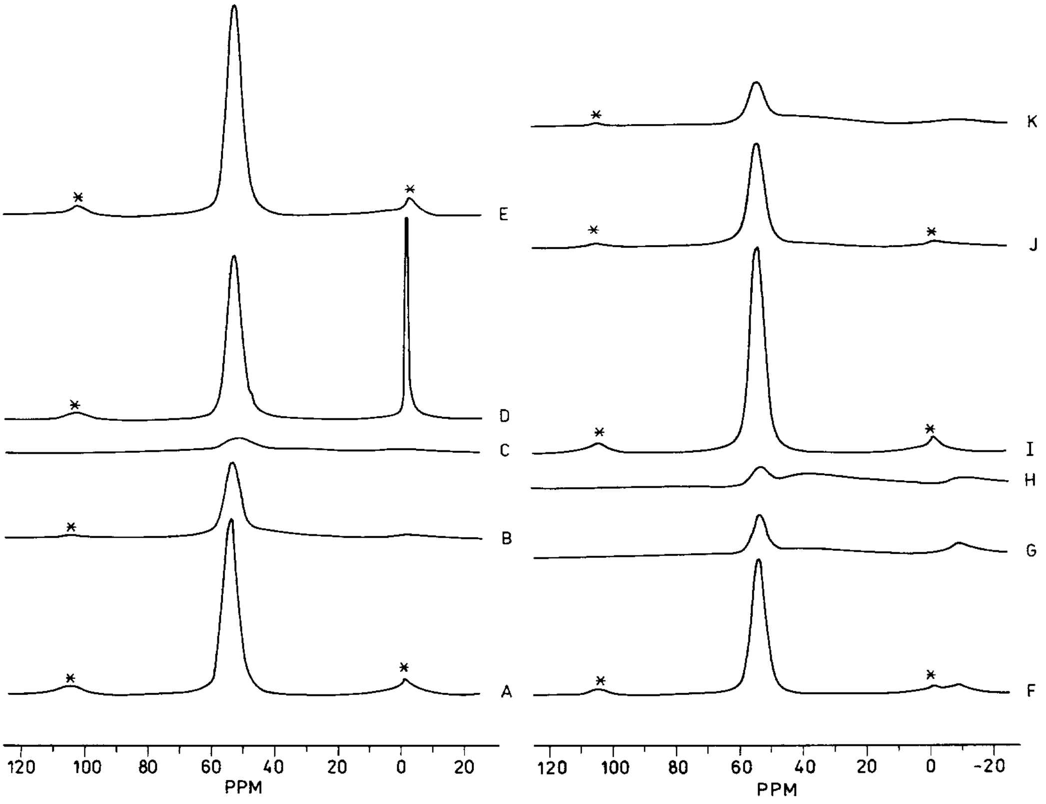

FIG. 5. ^{27}Al MAS NMR spectra of the samples A to K (cf. Tables 1 and 2). Asterisks denote spinning sidebands. The sharp signal at 0 ppm in spectrum D arises from $Al(NO_3)_3$.

^{27}Al NMR spectrum is influenced by the presence of aluminum cations. Spectroscopic data (Tables 1 and 2; Fig. 5) of both impregnated samples differ from that of the parent sample. The observed changes, however, are completely reversible. After removal of the impregnating agent by elution with hot water and subsequent drying (samples E and I), nearly the original intensity of the signal of the tetrahedrally coordinated framework aluminum reappears.

Spectroscopic results are clearly different, if impregnation with orthophosphoric acid is followed by hydrothermal treatment at 400°C (sample G) or at 700°C (sample H), respectively. Considerable changes are found:

—The intensity of the signal of tetrahedrally coordinated framework aluminum decreases sharply at 54 ppm. Simultaneously signals at about − 11 ppm and 39.5 ppm appear. The positions of both signals are known from the literature (*13*); they are characteristic of octahedrally or tetrahedrally coordinated Al nuclei, respectively, in aluminum phosphates, which are probably present here in an amorphous state.

—The spinning sideband patterns differ from those of the noncalcined samples, indicating local structural changes within the zeolite framework.

According to previous results (*14*), tetrahedrally coordinated nonframework aluminum in the absence of phosphate ions also gives rise to an NMR signal at about 40 ppm. Therefore, in the case of calcined H_3PO_4-impregnated HS-30 samples, a superposition of broad signals (at 39–41 ppm) of tetra-

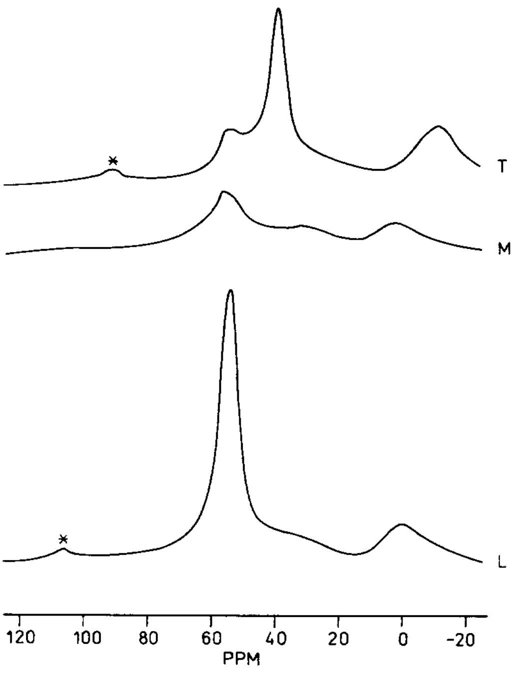

FIG. 6. ^{27}Al MAS NMR spectra of the thermally treated samples L, M, and T. Asterisks again denote spinning sidebands.

hedrally coordinated aluminum stemming from *different* sources (i.e., from aluminum–oxygen and from aluminum phosphate species) cannot be excluded (see also the ^{31}P NMR data). The results mentioned before are confirmed by the ^{27}Al MAS NMR spectra (Fig. 6) of a dealuminated HS-30 (sample L, $Si/Al_F = 95$). In addition to the signal at 0 ppm of the octahedrally coordinated nonframework aluminum, the spectrum exhibits a broad signal at about 40 ppm (adjacent to the main signal at 54 ppm) for the tetrahedrally coordinated nonframework aluminum species. After calcination of sample L at 700°C for 3 h (sample M) the spectrum shows reduced intensities for all signals, especially for the tetrahedrally coordinated framework aluminum. This finding can be explained by aluminum species invisible in the NMR spectrum due to larger quadrupole couplings (*15*). Calcination of the H_3PO_4-impregnated sample T (with a P content of 1.5 wt%) similarly results in a sharp decrease of the signal at 54 ppm. Simultaneously, signals of the two differently coordinated Al species in the aluminum phosphates (39.2 and −11.5 ppm) appear, whereas a signal of remaining octahedrally coordinated Al in aluminum–oxygen species at 0 ppm could not be identified, since the signal at −11.5 ppm is broad and intense.

Elution of the calcined H_3PO_4-impregnated samples with hot water results in an increase of the signal of the framework aluminum (samples J and K). As distinct from the thermally nontreated sample I, the original value of the parent sample A, however, is not reachieved. Elution exerts no significant effect on the signals of the nonframework aluminum in the aluminum phosphates (Fig. 5). It is worth mentioning that the H_3PO_4-impregnated sample F, although nondealuminated, already exhibits a weak signal in the position of the octahedrally coordinated nonframework aluminum in aluminum phosphates (at about −11 ppm). Contrary to the spectrum of calcined samples J and K, this signal vanishes here completely after elution (sample I).

Results of ^{27}Al MAS NMR measurements reveal that calcination of HS-30 at elevated temperatures causes dealumination of the framework, i.e., a partial conversion of the tetrahedrally coordinated framework aluminum into tetrahedrally and octahedrally coordinated nonframework aluminum species. Calcination of H_3PO_4-impregnated samples gives rise to the formation of nonframework aluminum phosphates containing aluminum nuclei in tetrahedral and octahedral oxygen coordination. The aluminum for this process is supplied by nonframework aluminum produced during dealumination prior to impregnation and/or by nonframework aluminum generated during calcination itself. This finding is in accordance with the results of an earlier NMR study of nature and location of phosphorus species formed by postsynthesis modification of ZSM-5 by orthophosphoric acid (*16*). The fact that the degree of dealumination for the impregnated samples

J and K is lower than that of the nonmodified H-ZSM-5 (samples B and C) indicates a protective effect of the phosphorus against "aging" processes simulated by hydrothermal treatment at elevated temperatures.

(*e*) ^{31}P *MAS NMR Spectroscopy*

The influence of thermal treatment of H_3PO_4-impregnated H-ZSM-5 on the final state of phosphorus was studied in detail for the dealuminated zeolite. Samples P to W were treated between 400 and 700°C both with and without steam. The ^{31}P MAS NMR spectrum (Fig. 7) of the impregnated *parent* material (at least) exhibits three different resonance lines (sample P). Two of them (at -5 and -13 ppm) show chemical shifts usually obtained for end and middle groups in pyrophosphates or in other short chain polyphosphates, respectively (*17, 18*). These phosphate species likely to be present after impregnation with orthophosphoric acid and subsequent desiccation at 120°C are removed by elution with water (sample Q): both lines vanish (cf. Fig. 7). The remaining broadline at about -28 ppm exhibits a chemical shift in the range characteristic of aluminum phosphates (*13*). They result from the reaction between nonframework aluminum present due to dealumination with the orthophosphoric acid used for impregnation. Aluminum phosphates, although of orthophosphate type, show an exceptionally high field shift (*19*). Further evidence for this interpretation is given below. It should be mentioned that in a recently published NMR study of the state of phosphorus in $(NH_4)_2HPO_4$-impregnated and subsequently calcined H-ZSM-5 (*20*), lines at -6 and -12 ppm were without further explanation "attributed to the phosphorus compound reacted with different aluminum sites." In our opinion, this assignment is at least questionable. Furthermore, the results of ^{27}Al MAS NMR in the same paper should be considered with caution. First, the measurements were performed with dry samples. It is well known (*12*) that under these

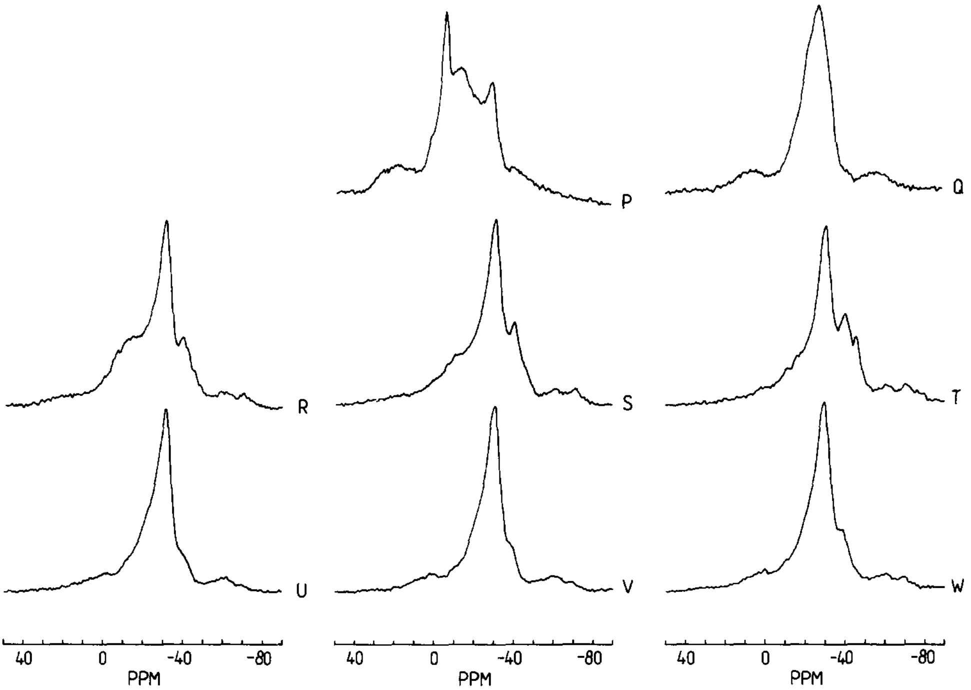

FIG. 7. ^{31}P MAS NMR spectra of the dealuminated and subsequently P-modified samples P to W (cf. Table 4). Samples Q, U, V, and W were obtained by elution of samples P, R, S, and T, respectively.

circumstances ^{27}Al NMR spectroscopy is by no means a quantitative method. Second, it is surprising that the authors did not consider any framework dealumination during thermal treatment performed at elevated temperatures.

All ^{31}P MAS NMR spectra of the *hydrothermally treated* samples R, S, and T are dominated by an intense line at about −30 ppm, which we also assign to aluminum phosphate. In comparison to sample Q, the linewidth is reduced, reflecting structural changes of the aluminum phosphates during thermal treatment. With increasing temperature the relative intensity of the broad low field signal with a maximum at about −12 ppm decreases, whereas that of the high field signal at −40 ppm increases. (Note that due to the spinning frequency used, an overlap of the center bands and the first side bands of these two signals occurs.) An additional fourth line on the high field side appears after treatment at 700°C only (sample T). According to the values of chemical shift, both high field lines can be assigned to highly condensed polyphosphate species (*18*). A chemical shift at −46 ppm is known for the branching groups in P_4O_{10} (*17, 18*). In the above mentioned paper (*20*), a broadline at about −40 ppm was tentatively ascribed to phosphorus reacted with impurities or vacancies in the zeolite structure. We see no evidence for this interpretation.

The differences among the spectra taken after different hydrothermal treatment can be interpreted in terms of a transformation of less condensed polyphosphates into higher condensed ones. As shown in Fig. 7, the species represented by the signals at −12, −40, and −46 ppm are almost completely removable by simple elution with water (samples U, V, W). For highly condensed polyphosphates, this process can take place via hydrolysis.

This interpretation of the experimental results from ^{31}P NMR is supported by the findings of the elution experiments with ammonium acetate solution summarized in Table 4. The elution was performed with hot 0.2 *M* aqueous solution of ammonium acetate using a three-step procedure with 250 ml of solution per 3.5 g of zeolite. Even in the case of the merely dried sample P, the fraction of removable phosphorus is definitely smaller than that with the corresponding nondealuminated sample I which is free of nonframework aluminum. The amount of eluted phosphorus is decreased after thermal treatment. The effect increases as temperature of treatment is raised (samples R, S, T). The presence of steam during thermal treatment has nearly no influence on the total amount of phosphorus being removed, but distinctly exerts a retarding effect on the elution. The reduction of the amount of phosphorus removable by elution is suppos-

TABLE 4

Influence of the Thermal Treatment of H_3PO_4-Impregnated, Previously Dealuminated H-ZSM-5 at Different Temperatures (3 h Each) on the Fraction of Phosphorus Removed in a 3-Step Elution by Ammonium Acetate Solution

Previous dealumination by steaming at 500°C for 4 h
$Si/Al_F = 95 = 0.167$ mmol $Al_F/g_{zeolite}$
Content of nonframework aluminum: 0.704 mmol $Al/g_{zeolite}$
Content of phosphorus: 1.5 wt% = 0.484 mmol $P/g_{zeolite}$

Sample	Treatment	Fraction of eluted phosphorus (%) after the		
		First step	Second step	Third step
P	Parent sample	51.7	55.1	59.1
R	Sample P steamed at 400°C	19.7	25.5	25.5
R′	Sample P calcined at 400°C	24.8	26.9	26.9
S	Sample P steamed at 550°C	9.8	19.6	21.9
S′	Sample P calcined at 550°C	17.9	20.1	22.1
T	Sample P steamed at 700°C	4.3	8.0	14.4
T′	Sample P calcined at 700°C	10.4	12.8	16.0

edly due to the formation of aluminum phosphates in nonframework positions in the case of dealuminated zeolite. The ^{31}P NMR spectra for the eluted samples are more or less identical. Hence it follows that the chemical nature of the phosphorus deposits that are *not* removable by water is not influenced if the temperature of treatment is varied in the range between 400 and 700°C. Thermal treatment without steam results in the same spectra (not represented in Fig. 7).

Ample evidence for the formation of aluminum phosphate species is also found by ^{31}P NMR when part of the nonframework aluminum was removed prior to H_3PO_4 impregnation by acid leaching. An example is given in Fig. 8. The line at −30 ppm dominant with the nonleached sample *X* is clearly reduced in the case of the leached sample *Y*. The small residual signal at about −30 ppm in the spectrum can be attributed to the fraction of the nonframework aluminum not removable by acid leaching (*21*).

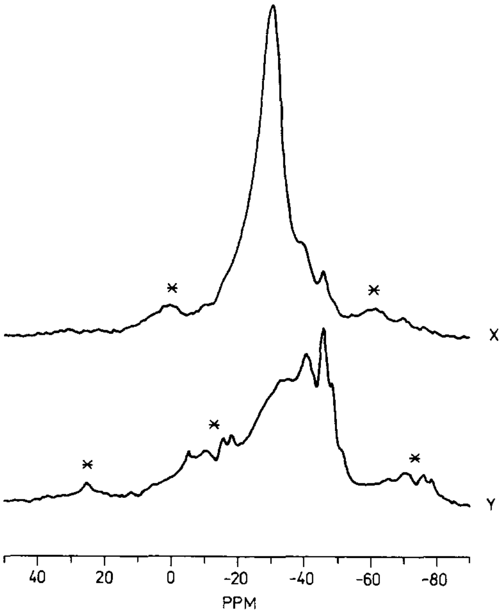

FIG. 8. ^{31}P MAS NMR spectra of two dealuminated, H_3PO_4-impregnated, and subsequently thermally treated (700°C, 3h) samples. In the case of sample Y the nonframework aluminum was removed by acid leaching prior to the impregnation with H_3PO_4.

Aluminum phosphates were also found in a previous study of postsynthesis modification of H-ZSM-5 by orthophosphoric acid based on a nondealuminated parent zeolite synthesized by means of a templating agent (*16*).

According to our results no spectroscopic evidence can be given in favor of a *direct* modification of the acid centers as proposed by several authors (*7, 11*). The Si–O–P bond postulated there is fairly unlikely to occur. In an NMR study of phosphorus-modified silica (*22*), a line at about −32 ppm was attributed to phosphorus bonded via oxygen to silicon. In our opinion, however, this assignment seems to be inconclusive. Furthermore, with dealuminated samples a line at this position within the ^{31}P NMR spectrum is not detectable due to the presence of the aluminum phosphate species. It should be noted that ^{31}P NMR lines between −46 and −54 ppm have been observed previously for a silicon pyrophosphate (*23*). These results cannot easily be used to assign the lines at −40 and −46 ppm, observed after high-temperature treatment of our samples, to phosphorus atoms bonded to silicon, since silicon in the case of the silicon pyrophosphate is completely in an octahedrally coordinated state. Our ^{29}Si NMR spectra, however, gave no hint of the presence of any octahedral coordination for silicon. Consequently, we can neither prove nor disprove the suggested models for the *direct* modification of the strong acid sites.

(*f*) *Temperature-Programmed Decomposition of NH_4^+-Exchanged Samples*

Comparison of the values in Table 2 shows that with H_3PO_4-impregnated hydrothermally treated samples the number of Brønsted sites derived from NH_4^+ exchange data is definitely higher than those found by the three other methods. As deviation by random experimental errors can be excluded, this discrepancy deserves further investigation to find a plausible explanation.

Ammonium ions can substitute any pro-

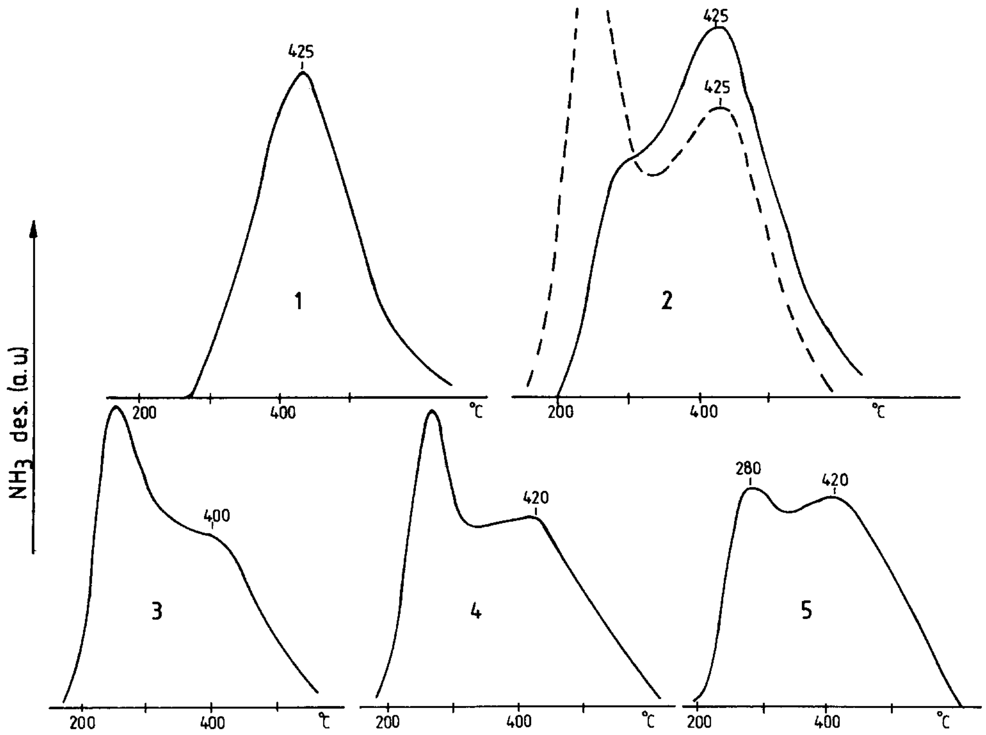

FIG. 9. Temperature-programmed decomposition of NH_4^+-exchanged H-ZSM-5. Sample 1: P-free parent zeolite. Sample 2: sample 1 after H_3PO_4 impregnation (dotted line, TPD curve after adsorption of ammonia at 120°C). Sample 3: sample 2 after hydrothermal treatment at 700°C. Sample 4: sample 3 after elution with hot water. Sample 5: sample 3 after elution with dilute nitric acid.

ton of the zeolite including those of the phosphoric acid surface species of P-modified samples, which are not removed by aqueous elution. Temperature-programmed decomposition of NH_4^+-exchanged P-modified zeolite is considered to be a suitable means of detecting this type of proton.

The desorptogram of the H_3PO_4-impregnated, thermally nonpretreated sample (2, Fig. 9) shows a distinct shoulder on the ascending front of the high-temperature peak of ammonia desorbed from the strong acid Brønsted sites. The additional area absent in the desorptogram of the P-free parent sample (1, Fig. 9) is obviously caused by the decomposition of less thermally stable complexes. Hydrothermal treatment of the H_3PO_4-impregnated sample at 700°C drastically reduces the amount of strong Brønsted acid sites, whereas the number of sites with lower Brønsted acidity is slightly increased (3, Fig. 9). Elution of the zeolite with hot water prior to NH_4^+ exchange has no significant influence (4, Fig. 9). Elution with dilute HNO_3, however, sharply decreases the amount of lower Brønsted acid sites (5, Fig. 9).

These results reveal that the impregnation of ZSM-5 with phosphoric acid is accompanied by the creation of Brønsted sites with an acid strength lower than that of the bridging hydroxyls. This type of site can be ascribed to surface-bonded species of phosphoric acid, which are nearly insoluble in hot water. They are not identified by the usual NH_4^+ exchange characterization, as this method gives information of the *sum* of both types of Brønsted sites only.

After thermal decomposition of the NH_4^+ complexes, samples can be subjected to the normal NH_3 adsorption procedure. Subsequent TPD (2, Fig. 9) shows the broadband of ammonia desorbed from Lewis acid sites overlapping the signal of the low Brønsted acidity. The high-temperature maxima of the curves of desorption of NH_3 and of decomposition of NH_4^+-exchanged samples coincide, indicating that the interaction of both gaseous NH_3 and NH_4^+ ions with the strong Brønsted sites gives rise to the formation of identical surface products.

CONCLUSIONS

With ZSM-5 zeolites, impregnation by orthophosphoric acid exerts an effect which is similar to that obtained by thermal and hydrothermal treatment: The number of Brønsted acid sites is decreased, as is shown by temperature-programmed desorption of ammonia and IR spectroscopy. Simultaneously the intensity of the ^{27}Al NMR signal of the tetrahedral framework aluminum atoms is decreased.

The effect turns out to be reversible. By elution with hot water, which results in a nearly complete removal of the impregnated phosphorus, the number of Brønsted sites (NH_3 TPD, IR spectroscopy) of the original sample is almost completely recovered. In a like manner the intensity of the NMR signal of the framework aluminum is increased again.

The results of the spectroscopic and physicochemical investigations reveal that impregnation with orthophosphoric acid indeed gives rise to a decrease of the number of Brønsted sites of the zeolite framework, but that dealumination does not proceed. The recorded diminution of Brønsted acidity is due to a reversible interaction between orthophosphoric acid and part of the acid-bridged hydroxyl groups of the zeolite framework. As a consequence of this, the identity between the number of strong Brønsted acid sites and the number of aluminum atoms of the zeolite framework, existing for H-ZSM-5 of different degrees of dealumination (*6*), no longer holds for H_3PO_4-impregnated samples.

With H_3PO_4-impregnated zeolites, hydrothermal treatment results in dealumination, too. Its degree, however, is clearly weaker than in the absence of orthophosphoric acid. Phosphorus obviously exerts a certain influence that protects aluminum in the framework from being removed from its positions. Part of the phosphoric acid can be extracted again by elution with hot water. The fraction of removable phosphorus is decreased by calcination or steaming at elevated temperatures.

Phosphate ions react also with nonframework aluminum as is shown by signals of ^{27}Al NMR spectra, which can be unambiguously assigned to tetrahedrally and octahedrally coordinated aluminum in aluminum phosphates. Evaluation of ^{31}P NMR spectra confirms that dealumination is accompanied by the formation of aluminum phosphates, which are extremely insoluble in water.

Apart from NH_4^+ exchange, methods commonly used to determine Brønsted acidity of H-ZSM-5 zeolites can be applied to P-modified samples, too. Experimental data are nearly identical. NH_4^+ exchange produces deviating results: The number of Brønsted sites is distinctly higher than that obtained by the three other kinds of characterization. As could be shown, the difference is caused by the ability of the ammonium ions to react with *any* protons, including those of the surface species of phosphoric acid. Temperature-programmed decomposition of NH_4^+-exchanged samples is a satisfactory means of discriminating between these sites and the bridged hydroxyl groups attached to framework aluminum atoms. This method allows a separate determination of both types of Brønsted acid sites due to the different thermal stability of their NH_4^+ complexes.

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