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NMR and IR Studies of Zeolite H-ZSM-5 Modified with Orthophosphoric Acid

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By combined use of solid-state NMR, NMR self-diffusion techniques, and diffuse reflectance IR spectroscopy, important information on the nature of the interaction of orthophosphoric acid with zeolite H-ZSM-5 could be obtained. By ^{1}H NMR self-diffusion experiments it was found that the phosphoric acid enters the ZSM-5 channel system. However, with increasing amounts of H_3PO_4 deposited, there is an enrichment of phosphorus species near the external surface of the zeolite crystals, forming a transport barrier for diffusing molecules. ^{27}Al MAS NMR shows that the decreased concentration of Brønsted acid sites in H-ZSM-5 after impregnation with orthophosphoric acid and a subsequent thermal treatment at 500°C is a direct result of a framework dealumination. Combined ^{27}Al, ^{29}Si, ^{31}P, and ^{1}H MAS NMR studies reveal that this dealumination process is promoted by the presence of increasing amounts of H_3PO_4 and results in the formation of occluded aluminum phosphate species. Furthermore, ^{1}H MAS NMR shows that H_3PO_4 impregnation causes a drastic reduction in the concentration of nonacidic silanol groups. Both findings of ^{1}H MAS NMR have been verified by diffuse reflectance IR spectroscopy. Consequently, treatment of ZSM-5 with orthophosphoric acid modifies acidity and diffusivity in the sample series under study. These effects can combine to give a useful catalyst of enhanced paraselectivity.

INTRODUCTION

Modification of H-ZSM-5 zeolites (*1*) by impregnation with H_3PO_4 has become a common technique to alter their activity and/or selectivity (*2–13*). Despite the widespread application of phosphorus modification, little is known about the molecular interaction of orthophosphoric acid with H-ZSM-5. There are two topics that are worth studying in more detail:

(i) There is a disagreement as to where the phosphorus compounds are finally deposited: the question is whether they are homogeneously distributed over the zeolitic channel network (e.g., Refs. (*8, 12, 13*)) or concentrated at the pore mouths on the external surface of the crystals (e.g., Ref. (*6*)).

(ii) A decrease in the number of Brønsted acid sites (bridging hydroxyls) as a result of impregnation with H_3PO_4 is reported from TPD studies (*6, 8, 12, 13*). Notwithstanding the lack of detailed experimental evidence, this experimental finding is exclusively interpreted in terms of a reaction scheme shown in Fig. 1. On the other hand, acid attack as well as thermal treatment are known to cause a removal of Al ions from lattice positions, a process referred to as dealumination. Therefore, a lattice dealumination caused by phosphoric acid treatment in combination with a subsequent calcination could also be the origin of the decreased acidity.

The aim of this paper is to address the following problems using NMR and IR:

(i) The spatial distribution of the phosphorus deposits over the ZSM-5 crystal;

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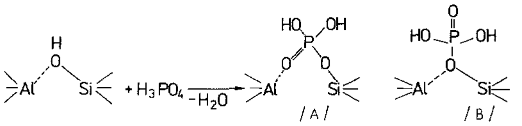

FIG. 1. Postulated reaction of H_3PO_4 with the Brønsted acid OH groups of H-ZSM-5 as proposed in the literature. (A) Refs. (*8, 13*). (B) Refs. (*6, 12*).

(ii) The real reason for the decreased number of Brønsted acid sites in H-ZSM-5 modifid by H_3PO_4;

(iii) The chemical nature of the phosphorus compounds after sample calcination.

EXPERIMENTAL

(*a*) *Zeolite Synthesis and Impregnation with H_3PO_4*

The ZSM-5 type zeolites used as starting material were synthesized by established hydrothermal procedures by means of tetrapropylammonium (TPA) ions as template (*14, 15*). The mean crystal diameter was 14 μm, and all the crystals were twinned in the (010) plane. The zeolites were transformed into the H-form by direct ion exchange using 0.1 *M* HCl. The Si/Al ratio in the synthesis batch was 45; in the zeolites it was found from the ^{29}Si MAS NMR spectra to be 70 ± 10 (using the lineshape fitting program LINESIM) and from the ^{27}Al MAS NMR to be 65 ± 10. The high crystallinity of the material has been proved by X-ray diffraction and sorption equilibria measurements. Due to the use of TPA ions in the ZSM-5 synthesis, the zeolite under study contains $(1.30 \pm 0.15) \times 10^{20}\ g^{-1}$ internal silanol groups at positions of nonintact Si–O–Si bonds as shown by ^{1}H MAS NMR (cf. Fig. 7).

For impregnation with phosphoric acid, a suspension of water, ZSM-5, and H_3PO_4 was refluxed for 2 h, and then the water was evaporated under reduced pressure. The procedure is described in more detail in Refs. (*8, 13*). After H_3PO_4 impregnation, the samples were dried at 120°C for 5 h and afterwards calcined at 550°C for 6 h.

(*b*) *NMR Sample Preparation*

For the ^{1}H NMR self-diffusion measurements, the carefully outgassed zeolites were loaded with methane by vacuum distillation (sorbate concentration approx two molecules per $\frac{1}{4}$ u.c., i.e., per channel intersection). The methane loading was checked gravimetrically, and the glass ampoules were then sealed.

For the ^{1}H MAS NMR and IR studies, the zeolites were outgassed under shallow bed conditions. The zeolites were contained in glass tubes of 5.5-mm inner diameter and 10-mm height of the zeolite assemblage. The temperature was increased at a rate of 10 K/h. After maintaining the samples at the final activation temperature of 400°C under a pressure below 10^{-2} Pa for 24 h, they were sealed off. The same samples have been used in the ^{1}H MAS NMR and the diffuse IR reflectance spectroscopy.

The ^{27}Al, ^{29}Si, and ^{31}P MAS NMR measurements were performed on hydrated samples.

(*c*) *NMR and IR Measurements*

Two NMR methods have been applied to measure different features of molecular self-diffusion of sorbed methane molecules in phosphorus-modified H-ZSM-5 using the home-made NMR pulse spectrometer FEGRIS at the Sektion Physik der Karl-Marx-Universität Leipzig.

In contrast to sorption uptake/desorption experiments, the NMR pulsed field gradient technique (*16–18*) provides direct information about the intracrystalline molecular motion in a sorption equilibrium system. It measures the r.m.s. displacement, $\langle r^2(\Delta)\rangle^{1/2}$, of sorbate molecules marked by their nuclei (in our case by the protons of methane) as a function of the observation time Δ. Provided that $\langle r^2(\Delta)\rangle^{1/2}$ is less than the radius of the zeolite crystals under study, the intracrystalline self-diffusion coefficient D_i is obtained directly via the Einstein equation $D_i = \langle r^2(\Delta)\rangle/6\Delta$.

In the NMR tracer desorption technique

(*18*, *19*), the fraction of molecules which leaves a zeolite crystal during a fixed observation time Δ is determined. Varying this time of observation, desorption kinetics curves at sorption equilibrium are obtained. These desorption curves are completely equivalent to those of usual tracer desorption experiments. By fitting an appropriate solution of Fick's laws (*20*) for diffusion-controlled sorption processes to the desorption curves thus obtained, apparent self-diffusion coefficients D_d can be calculated. However, this quantity D_d indicates diffusion obstacles inside the zeolite crystals as well as on their outer surface.

The ^1H MAS NMR experiments were conducted at 300 MHz using a Bruker MSL 300 at the Sektion Physik der Karl-Marx-Universität Leipzig with a home-made probehead. The spinning rate of the sealed glass ampoules was 3 kHz, and 400 scans were taken, the recycle delay being 4 s. The total concentration of OH groups in the activated samples was determined by comparison of the maximum of the free induction decay of the samples with those of a capillary with an aqueous solution of paramagnetic ions. To separate quantitatively the relative intensities of different lines in a ^1H MAS NMR spectrum, the signals of the spinning side-bands were added to the main signal. For more details see Refs. (*21–25*).

The experimental conditions for the other MAS NMR measurements performed on a Bruker MSL 400 at the Zentralinstitut für physikalische Chemie, Berlin, are summarized in Table 1. In the case of ^{29}Si MAS NMR, Q_8M_8 (cubic octamer silicic acid trimethylsilyl ester) was used as secondary standard.

TABLE 1

Measuring Conditions for the ^{27}Al, ^{29}Si, and ^{31}P MAS NMR Spectra

Nucleus	Resonance frequency (MHz)	rf Pulse	Recycle delay(s)/ number of scans	Reference signal	Spinning rate (kHz)
^{27}Al	104.2	$\pi/12$	1/1800	$Al(H_2O)_6^{3+}$	5.3
^{29}Si	79.5	$\pi/4$	10/500	$(CH_3)_4Si$	3.5
^{31}P	161.9	$\pi/2$	3/1000	H_3PO_4 (85%)	4.8

Diffuse reflectance near-infrared spectra in the range 1750–2500 nm were measured at room temperature using a modified Beckman DK-2A spectrophotometer at the Sektion Physik der Karl-Marx-Universität Leipzig (*26*, *27*). A plate of pure MgO was measured as reference.

RESULTS AND DISCUSSION

(*a*) ^1H *NMR Self-Diffusion Studies*

Information on the distribution of the phosphorus deposits over the zeolite crystals could be derived from ^1H NMR self-diffusion measurements of methane in H-ZSM-5 modified by phosphoric acid.

The conclusions have been drawn from the following considerations:

(i) A reduction of the intracrystalline self-diffusivity of methane molecules as measured by the NMR pulsed field gradient technique has to be regarded as straightforward proof of the incorporation of phosphorus species into the ZSM-5 channel network, where they cause an additional transport resistance.

(ii) Limitations of the overall adsorption/desorption kinetics, as followed by the NMR tracer desorption technique, can be caused by both phosphorus deposits inside the crystals and on their outer surfaces. However, values of the tracer desorption coefficients being below the corresponding intracrystalline diffusion coefficients indicate the existence of additional mass transfer resistances in a layer near or even on the outer surface of the zeolite crystals.

The results of the corresponding self-diffusion measurements are displayed in Fig. 2.

Figure 2 shows that both the intracrystalline self-diffusivity (D_i) and the tracer desorption diffusivity (D_d) decrease with increasing phosphorus content. The continuous decrease of D_i is taken as proof that phosphoric acid is increasingly incorpo-

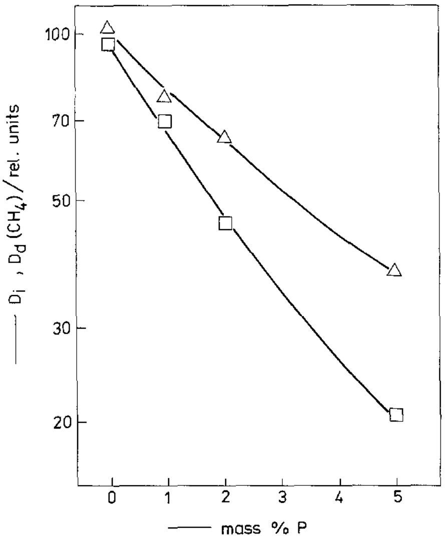

FIG. 2. Intracrystalline self-diffusion coefficient D_i (△) and tracer desorption coefficient D_d (□) of methane in H-ZSM-5 modified by impregnation with H_3PO_4. The starting self-diffusion coefficients amount to 1.0×10^{-8} $m^2\ s^{-1}$. Diffusion measurements at room temperature.

rated into the pore system of ZSM-5. However, since D_d decreases more steeply than D_i, it is concluded that with increasing amounts of phosphoric acid used, additional diffusion obstacles near the crystal surface arise. This is interpreted as an enrichment of phosphorus species near the outer surface of the zeolite crystals.

This result is expressed more clearly by Fig. 3 which shows the ratio D_i/D_d as a function of the phorphorus content.

For $D_i/D_d = 1$, a homogeneous distribution of the phosphorus deposits over the crystals is indicated. $D_i/D_d > 1$ is taken as proof of an enrichment of phorphorus species near the outer crystal surface. Figure 3 clearly shows that such an enrichment occurs with increasing amounts of phorphorus deposits.

This result is not surprising. In a series of ZSM-5 samples modified by H_3PO_4, applying the identical mode of impregnation, for P contents larger than 2 mass %, phosphorus species in the form of plates covering the zeolite surface could be detected by electron microscopy (*8*). However, no information on the chemical nature of these transport resistances can be obtained from ^1H NMR self-diffusion experiments. For this purpose, several kinds of MAS NMR and IR methods have been applied.

(*b*) *MAS NMR Spectroscopy*

Figure 4 shows the ^{27}Al MAS NMR spectra of the samples under study. It can be seen that the intensity of the line at 54 ppm (which is attributed to tetrahedrally coordinated framework aluminum) strongly decreases with increasing amounts of H_3PO_4 deposited. The small and narrow signal at 0 ppm in the spectrum of the parent zeolite is due to aluminum chloride resulting from ion exchange using NH_4Cl. It is extracted by the H_3PO_4 treatment in an aqueous solution, and consequently this signal disappears in the impregnated samples. In the samples modified with H_3PO_4, an increasing signal at −8 ppm appears which is attributed to aluminum phosphate. This value of the chemical shift is characteristic of aluminum phosphates where the sixfold oxygen coordination of the aluminum nucleus is partially accomplished by crystal water (*28*).

Also the ^{29}Si MAS NMR spectra shown

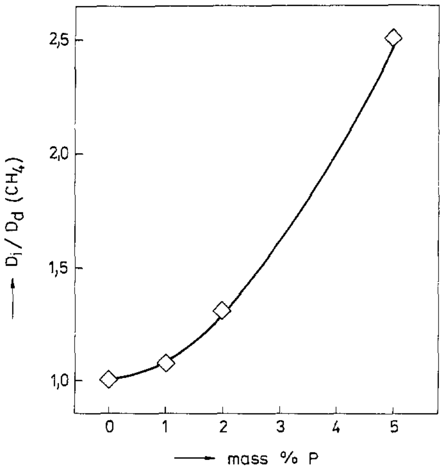

FIG. 3. Ratio D_i/D_d for methane self-diffusion in H-ZSM-5 impregnated with H_3PO_4 (experimental data of Fig. 2).

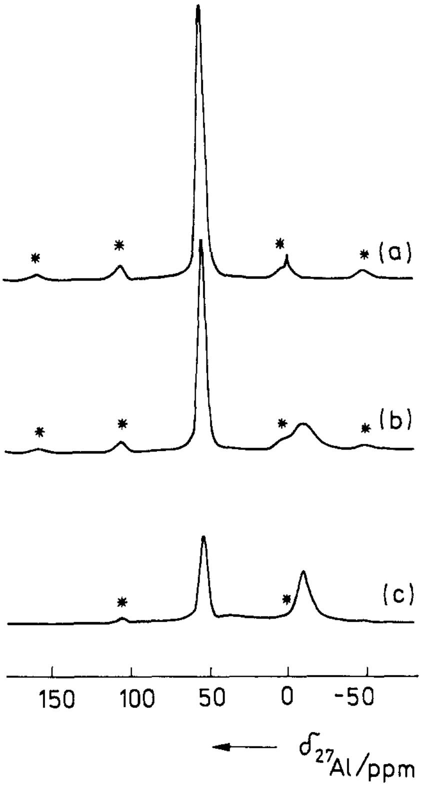

FIG. 4. ^{27}Al MAS NMR spectra of the starting H-ZSM-5 (a) as well as of the samples containing 1 (b) and 2 (c) mass % P. The asterisks denote spinning side bands.

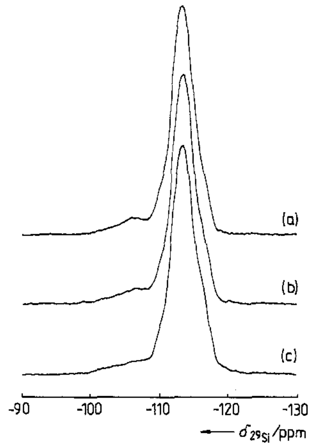

FIG. 5. ^{29}Si MAS NMR spectra of the starting H-ZSM-5 (a) as well as of the samples containing 1 (b) and 2 (c) mass % P. The small line at about − 106 ppm is caused by $Si(OSi)_3OAl$ units.

in Fig. 5 prove that H_3PO_4 impregnation of H-ZSM-5 followed by a subsequent thermal treatment at 550°C results in a framework dealumination. By lineshape fitting of the ^{29}Si MAS NMR spectra given in Fig. 5, the Si/Al ratios in the sample series under study could be estimated. With increasing amounts of H_3PO_4, the Si/Al ratios increase from 70 ± 10 in the parent ZSM-5 to values of 160 ± 20 and >200 in the samples containing 1 and 2% P, respectively. This finding must be compared with the quantitative analysis of the ^{27}Al MAS NMR spectra (cf. Fig. 4), showing that the intensity of the line at 54 ppm is decreased by about 23 and 68% in the H-ZSM-5 samples containing 1 and 2 mass % P, respectively, in comparison with the starting material.

However, with respect to their accuracy, both findings must be considered with care. Applying the ^{27}Al MAS NMR for a quantitative aluminum determination necessitates a complete hydration. This hydration enhances the symmetry of the electric field at the aluminum nuclei, reduces the quadrupole coupling constant and renders all framework aluminum nuclei "visible" by NMR (*29*). Intracrystalline deposits of polyphosphates and/or aluminum phosphates, the presence of which follows from the finding of ^{31}P MAS NMR (cf. Fig. 6), might affect this reduction of symmetry distortions in the present case either by pre-

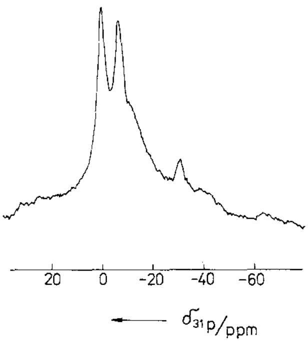

FIG. 6. ^{31}P MAS NMR spectrum of H-ZSM-5 with 2% P brought about by H_3PO_4 soaking and subsequent thermal treatment at 550°C.

venting the complete hydration of the aluminum nuclei in the framework or by their steric constraints preventing the equilibration of the zeolitic bonding angles. Also an electrostatic interaction of a dislodged Al^+ species with a Brønsted acid site seems possible, thus causing aluminum atoms to become "invisible" by NMR. On the other hand, above a Si/Al ratio of about 20, the determination of Si/Al ratios based on ^{29}Si MAS NMR spectra is generally unsharp. This holds especially if the zeolite contains a high concentration of internal silanol groups as in the present case.

Figure 6 shows the ^{31}P MAS NMR spectrum of the sample containing 2 mass % P. Three signals can be distinguished. The line at 1 ppm stems from monomeric $[PO_4]^{3-}$ groups like those in orthophosphoric acid; the line at -6 ppm is due to the P atoms in pyrophosphoric acid or due to the terminal $[PO_4]^{3-}$ groups in polyphosphoric species (*30, 31*). Since the ^{31}P MAS NMR spectra were recorded after hydrating the samples, the two lines dominating the phosphorus spectra are due to hydrolysis products of highly condensed polyphosphoric compounds. When the samples calcined at 550°C without any hydration are measured, the ^{31}P MAS NMR spectra show only a small shoulder in this lowfield region, but intense lines in a region of -40 . . . -46 ppm characteristic of branching groups $(OP[PO_4]_3)$ (*32*). The third signal of -30.7 ppm is attributed to aluminum phosphate (*33, 34*). The intensity of this signal grows with increasing amounts of H_3PO_4 added.

Dealumination is also reflected by the ^{1}H MAS NMR spectra which are shown in Fig. 7. The ^{1}H MAS NMR spectra of H-ZSM-5 consist of two lines (*22–24*). Line (b) at 4.3 ppm is due to Brønsted acid sites (bridging OH groups) and hence its intensity yields directly the concentration of framework aluminum atoms involved in the formation of intact bridging OH groups. Line (a) between 1.8 and 2.2 ppm is caused by nonacidic OH groups at the outer surface of the pentasil crystals (terminal OH groups), inside the crystals as lattice defects, or associated with some amorphous material.

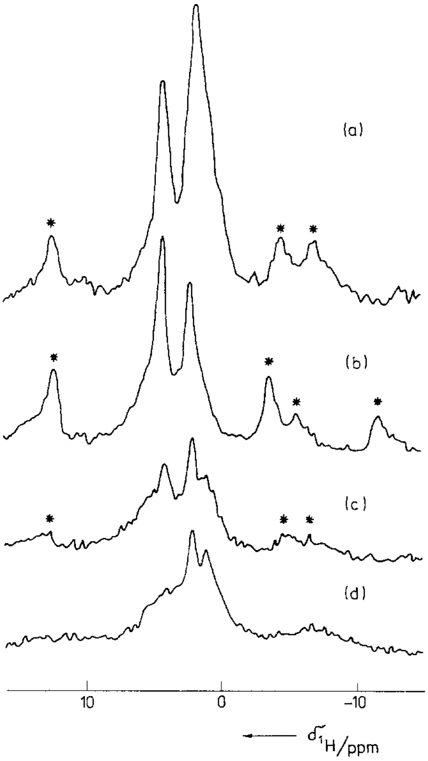

FIG. 7. ^{1}H MAS NMR spectra of H-ZSM-5 containing different amounts of phosphoric acid: starting H-ZSM-5 (a), with 1 (b), 2 (c), and 5 (d) mass % P; 1000 scans. The asterisks denote spinning side bands.

As a result of H_3PO_4 impregnation followed by thermal treatment at 550°C, the intensity of line (b) decreases continuously. A semiquantitative comparison of the concentration of the bridging OH groups as obtained by ^{1}H MAS NMR with the results of ^{27}Al and ^{29}Si MAS NMR as a function of the phosphorus content reveals that the decrease in peak (b) in proton NMR (cf. Fig. 7) can be explained exclusively by a framework dealumination. In other words, there is no reason for considering a reaction as shown in Fig. 1.

On the other hand, from the substantial decrease in the intensity of line (a) in the proton NMR spectra with increasing P contents it follows that the H_3PO_4 molecules cause a strong decrease in the concentration of the nonacidic silanol groups. It should be noted that in the present case also POH groups can contribute to the remaining intensity of the signal of line (a). Nevertheless, since the number of these silanol groups as measured by the ^1H MAS NMR is approx 10^3 larger than the maximum number of terminal silanol groups on the external crystal surface, these high concentrations measured must be considered unambiguous proof of their intracrystalline nature (*23–25*).

There are two different possibilities for explaining this experimental finding.

(i) In some recent papers (*35–38*) these internal silanol groups were attributed to unoccupied lattice positions in the zeolite framework, each of which may represent a nest of four nonacidic hydroxyl groups. In terms of this lattice-defect model, the reduction of peak (a) could be interpreted in terms of an incorporation of phosphorus into the zeolite lattice, thus substituting the missing T-atoms. However, NMR does not provide experimental evidence for such a reaction. Despite their interpretation, the NMR results given in Ref. (*39*) do not provide a convincing proof for the existence of Si–O–P bonds.

(ii) The polyphosphate deposits might act as an intracrystalline means of desiccation, thus causing dehydroxylation accompanied by annealing of two vicinal silanol groups into an intact Si–O–Si bond.

(*c*) *Diffuse Reflectance Near-Infrared Spectroscopy*

The findings of ^1H MAS NMR have been confirmed by IR spectroscopy using the same sealed samples as those in the NMR experiments. Figure 8 shows the diffuse reflectance NIR spectra in the region of the OH combination vibration (*26, 27*).

Two bands will be discussed:

(i) the band due to the bridging OH groups (Brønsted acid sites) at (2148 ± 15) nm corresponding to line (b) at 3.8 . . . 4.4 ppm in the ^1H MAS NMR spectra (*26*), and

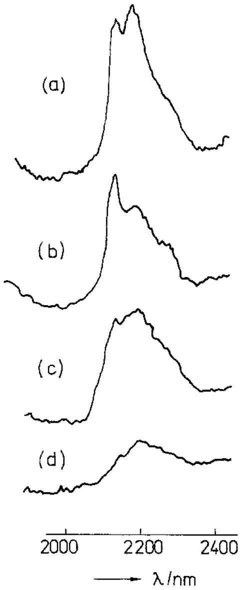

FIG. 8. Diffuse reflectance NIR spectra of the starting H-ZSM-5 (a), and the zeolites containing 1 (b), 2 (c), and 5 (d) mass % P. Measurements at room temperature.

(ii) the band due to silanol groups at (2200 ± 15) nm which corresponds to line (a) at 1.8 . . . 2.3 ppm in the ^1H MAS NMR spectra (*26*). Figure 8 shows that the intensity of both bands decreases with increasing amounts of H_3PO_4 added. However, in accordance with the results of the ^1H MAS NMR measurements (cf. Fig. 7), Fig. 8 demonstrates that the first H_3PO_4 molecules added cause a reduction of the concentration of the internal silanol groups rather than that of the bridging OH groups.

In a catalytic test reaction, the influence of the H-ZSM-5 impregnation with H_3PO_4 on selective toluene disproportionation (STD) has been investigated. By comparison of the starting H-ZSM-5 with the zeolite containing 5% P, it was found that the activity falls by a factor of 10 while the paraselectivity increases from an amount of initially 57% *para*xylene to more than 95% (*40*). However, the understanding of this effect on a molecular level is still incomplete. Effects such as dealumination and formation of nonframework aluminum phosphate and polyphosphate species can alter the diffusion behavior as well as the strength, amount, and accessibility of catalytically active sites.

Our results might become a basis for a critical reconsideration of the interpretation of the decreased acidity of H-ZSM-5 impregnated by H_3PO_4.

CONCLUSIONS

(i) Applying the ^{1}H NMR pulsed field gradient and ^{1}H NMR tracer desorption techniques to the study of the molecular self-diffusion of methane in H-ZSM-5 modified by H_3PO_4 has allowed the distribution of phosphorus deposits over the ZSM-5 crystal to be determined. It was found that phosphoric acid penetrates into the channel network. On increasing the concentration of H_3PO_4, an enrichment of phosphorus deposits in the outer regions of the zeolite crystals is observed.

(ii) ^{27}Al and ^{29}Si MAS NMR show that during sample calcination at 550°C, framework dealumination takes place. From ^{27}Al and ^{31}P MAS NMR it follows that the dislodged aluminum species react with H_3PO_4, forming aluminum phosphate. Furthermore, ^{31}P MAS NMR proves the formation of polyphosphoric acids by sample calcination.

(iii) The decrease in the number of Brønsted acid sites with increasing phosphorus content of the samples, as measured by ^{1}H MAS NMR, can be explained exclusively by the effect of lattice dealumination. The MAS NMR method does not lend support to a quasi-chemical reaction of phosphoric acid with the Brønsted acid OH groups of H-ZSM-5, as shown in Fig. 1. On the other hand, the impregnation with orthophosphoric acid followed by a thermal treatment at 550°C leads to a dominant decrease in the amount of internal silanol groups.

(iv) Diffuse reflectance IR spectroscopy verifies both findings of ^{1}H MAS NMR, namely, the preferred reduction of the concentration of internal silanol groups and the simultaneous decrease in the bridging OH groups as a result of the lattice dealumination.

(v) After treatment with orthophosphoric acid, the sample series under study displayed an increased paraselectivity and lowered activity in the selective disproportion of toluene.

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