NMR CHARACTERIZATION OF ZEOLITE H-ZSM-5 AFTER POST-SYNTHESIS MODIFICATION WITH H_3PO_4

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SUMMARY

Important information on the nature of the interaction of orthophosphoric acid with zeolite H-ZSM-5 on a molecular scale was obtained using solid-state NMR and NMR self-diffusion measurements. ^1H NMR self-diffusion studies show that 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 resulting in the formation of a transport barrier to diffusing molecules. ^{27}Al MAS NMR shows that the decreased concentration of Brønsted acid sites in H-ZSM-5 after impregnation with phosphoric acid and subsequent thermal treatment at 500°C is a direct result of dealumination of the framework. ^{27}Al, ^{29}Si, ^{31}P and ^1H MAS NMR reveals that the dealumination process is promoted by the presence of increasing amounts of H_3PO_4 and results in the formation of occluded aluminium phosphate species. Furthermore, ^{31}P MAS NMR shows that sample calcination causes the occluded H_3PO_4 molecules to react forming polyphosphates. Treatment of ZSM-5 with orthophosphoric acid modifies acidity and diffusivity. These effects can combine to give a useful catalyst with enhanced para-selectivity for the selective disproportionation of toluene.

INTRODUCTION

Modification of zeolites H-ZSM-5 by impregnation with H_3PO_4 has become a standard technique for altering their activity and/or selectivity. Despite the widespread application of the process, little is known about the molecular interaction of orthophosphoric acid with H-ZSM-5. Two problems are particularly worthy of further study:

(i) The location of the phosphorus compounds in the crystal: homogeneously distributed over the zeolitic channel network (e.g. refs. 1-3) or concentrated at the openings of the pores at the external surface of the crystals (e.g. ref. 4).

(ii) A decrease of the number of Brønsted acid sites (bridging hydroxyls) as a result of impregnation with H_3PO_4 is reported from TPD studies (refs. 1-4).

Notwithstanding the lack of detailed evidence, this experimental result is normally interpreted only in terms of a postulated quasi-chemical reaction of H_3PO_4 with the Brønsted OH groups of H-ZSM-5 (refs. 1-5).

On the other hand, acid attack as well as thermal treatment are known to cause a removal of Al ions from the framework. Dealumination of the framework upon treatment with phosphoric acid and calcination could also give rise to decreased Brønsted acidity.

The aim of this work is to elucidate the spatial distribution of the phosphorus deposits over the ZSM-5 crystal and the chemical nature of the phosphorus compounds after sample calcination.

EXPERIMENTAL

The synthesis of ZSM-5 and its modification with H_3PO_4

The ZSM-5 zeolites used as starting material were synthesized by established hydrothermal procedures by means of tetrapropylammonium (TPA) ions as template (refs. 6,7). The mean crystal diameter was 14μm, and all crystals were twinned along the (010) plane. The zeolites were converted into the H-form by direct ion exchange with 0.1 M HCl. The Si/Al ratio of the synthesis mixture was 45; the Si/Al ratio of the as-prepared zeolite was 70±10 by ^{29}Si MAS NMR (using the lineshape fitting programme LINESIM) and 65±10 by ^{27}Al MAS NMR. X-ray diffraction and sorption measurements showed that the material was highly crystalline. For impregnation with phosphoric acid, a suspension consisting of ZSM-5, water and H_3PO_4 was refluxed for 2 h and then water was distilled off under reduced pressure. The procedure is described in more detail in refs. 1 and 3. After impregnation with H_3PO_4 the samples were dried at 120°C for 5 h and calcined at 550°C for 6 h.

NMR sample preparation

For the ^1H NMR self-diffusion measurements, the carefully outgassed zeolites were loaded with methane by vacuum distillation (sorbate concentration of approximately 2 molecules per 1/4 of the unit cell, i.e. per channel intersection). The methane loading was checked gravimetrically whereupon the glass ampoules were sealed. For the ^1H MAS NMR studies, the zeolites were outgassed under shallow bed conditions. The zeolites were contained in glass tubes of 5.5 mm diameter and 10 mm bed height. The temperature was increased at a rate of 10K/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. ^{27}Al, ^{29}Si and ^{31}P MAS NMR measurements were performed on hydrated samples.

NMR measurements

(a) ^{1}H NMR self-diffusion studies 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 FEGRIS pulse spectrometer at the Sektion Physik, Karl-Marx-Universität Leipzig.

(i) For the determination of the intracrystalline self-diffusivity the displacement $\langle r^2(\Delta)\rangle^{1/2}$ of the methane molecules inside the H-ZSM-5 crystals during an observation time Δ has been measured directly by the NMR pulsed field gradient technique (refs. 8-10).

(ii) In the NMR tracer desorption technique (refs. 10,11), the fraction of molecules which leave 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 (ref. 11) for diffusion-controlled sorption processes to the desorption curves thus obtained, apparent self-diffusion coefficients D_d can be calculated. However, the magnitude of D_d indicates the presence of diffusional barriers inside the zeolite crystals as well as on their outer surface.

(b) Solid-state NMR The ^{1}H MAS NMR experiments were carried out at Sektion Physik, Karl-Marx-Universität Leipzig at 300.13 MHz using a Bruker MSL-300 spectrometer equipped with a home-made probehead. The spinning rate of the sealed glass ampoules was 3 kHz and 400 scans were taken with a recycle delay of 4s. The total concentration of OH groups in the activated samples was determined by comparing the maximum of the free induction decay of the samples with those of a capillary with an aqueous solution of paramagnetic ions. To determine quantitatively the relative intensities of different lines in a ^{1}H MAS NMR spectrum, the intensities of the spinning sidebands were added to the main signal. For more details see refs. 12-16.

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. Q_8M_8 was used as secondary standard for ^{29}Si NMR.

TABLE 1.
Measuring conditions of the ^{27}Al, ^{29}Si and ^{31}P MAS NMR spectra.

Nucleus	Resonance frequency/MHz	rf pulse	recycle delay/s number of scans	reference	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

RESULTS AND DISCUSSION

^{1}H NMR self-diffusion studies

Information on the distribution of the phosphorus deposits over the zeolite crystals could be derived from ^{1}H NMR self-diffusion measurements of methane in H-ZSM-5 modified by phosphoric acid. The conclusions have been drawn from the following:

(i) A reduction of the intracrystalline self-diffusitivity of the methane molecules as measured by the NMR pulsed field gradient technique has to be regarded as straightforward proof for 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 self-diffusion measurements are given in Fig. 1.

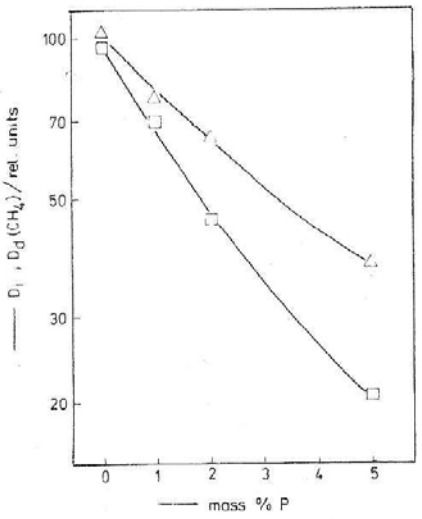

Fig. 1. Intracrystalline self-diffusion coefficient D_i(Δ) and tracer desorption coefficient D_d(□) of methane in H-ZSM-5 modified by impregnation with H_3PO_4. The starting self-diffusion coefficients amount to 1.1×10^{-8} m^2s^{-1}. Diffusion measurements were performed at room temperature.

Fig. 1 shows that both the intracrystalline self-diffusivity (D_i) and the tracer desorption diffusivity (D_d) decrease with the increasing phosphorus content. The continuous decrease of D_i proves that phosphoric acid is increasingly incorporated into the pore system of ZSM-5. However, since D_d decreases more steeply than D_i, we conclude that additional diffusion barriers near the crystal surface arise with

increasing amounts of phosphoric acid. This is interpreted as due to the enrichment of phosphorus species near the outer surface of the zeolite crystals.

This result is not surprising. For P contents larger than 2 mass % in a series of ZSM-5 samples modified by H_3PO_4 using the same procedure, phosphorus species in the form of plates covering the zeolite surface were detected by electron microscopy (ref. 1). However, no information on the chemical nature of these transport barriers can be obtained from ^1H NMR self-diffusion experiments. We have therefore resorted to several other MAS NMR techniques.

MAS NMR spectroscopy

Fig. 2 shows the ^{27}Al MAS NMR spectra of the samples. The intensity of the line at 54 ppm (attributed to four-coordinated framework aluminium) strongly decreases with increasing amounts of H_3PO_4 deposited. The narrow low intensity signal at 0 ppm in the spectrum of the parent zeolite is due to aluminium chloride produced during ion exchange with NH_4Cl. The chloride is extracted by aqueous H_3PO_4, as a result of which the signal disappears. In samples modified with H_3PO_4 an increasing signal at -8 ppm appears which has to be attributed to aluminium phosphate. This

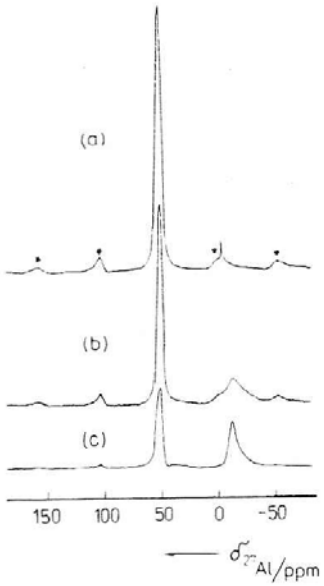

Fig. 2. ^{27}Al MAS NMR spectra of (a) the parent H-ZSM-5 and samples containing (b) 1 and (c) 2 mass % P.

value of the chemical shift is characteristic of aluminium phosphates in which the sixfold oxygen coordination of the ^{27}Al nucleus is partially achieved by coordination to intracrystalline water molecules (ref. 17). The ^{29}Si MAS NMR spectra also confirm that impregnation of zeolite H-ZSM-5 with H_3PO_4 followed by thermal treatment at 550°C results in the dealumination of the framework. The Si/Al ratios of the samples were estimated by deconvoluting the ^{29}Si MAS NMR spectra. With

increasing amounts of H_3PO_4 the Si/Al ratios increase from 70±10 in the parent ZSM-5 to 160±20 and to >200 in the samples containing 1 and 2 mass % P, respectively. This is to be compared with the ^{27}Al MAS NMR spectra (Fig. 2), showing that the intensity of the line at 54 ppm decreases by about 23% and 68% in samples containing 1 and 2% P, respectively, in comparison with the starting material.

However, the accuracy of both results has to be considered with care. The application of ^{27}Al MAS NMR for the quantitative determination of aluminium necessitates a complete hydration. This hydration enhances the symmetry of the electric field gradient at the aluminium nuclei, reduces the quadrupole coupling constant and renders all framework aluminium nuclei "visible" to NMR (ref. 18). Intracrystalline deposits of polyphosphates and/or aluminium phosphates, the presence of which is confirmed by ^{31}P NMR (see Fig. 3), might limit this restoration of symmetry either by preventing the complete hydration of the aluminium nuclei in the framework or by their steric constraints preventing the equilibration of the framework bond angles. Electrostatic interaction of a dislodged Al cationic species with a Brønsted acid site also seems possible, thus causing aluminium atoms to become "invisible" to 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 unreliable.

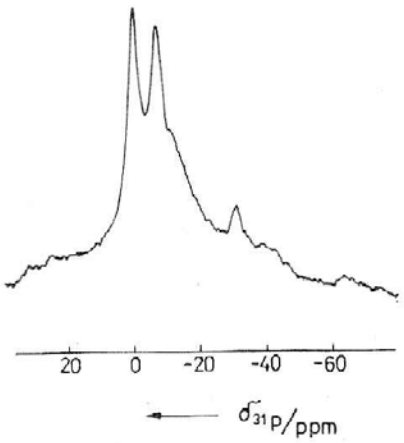

Fig. 3. ^{31}P MAS NMR spectrum of H-ZSM-5 with 2 % P prepared by treatment with H_3PO_4 followed by thermal treatment at 550°C.

Fig. 3 shows the ^{31}P MAS NMR spectrum of the sample containing 2 mass % P. Three signals can be distinguished: the line at +1 ppm is due to monomeric $[PO_4]^{3-}$ groups like those in orthophosphoric acid, the line at -6 ppm is to P in pyrophosphoric acid or to the terminal $[PO_4]^{3-}$ atoms in polyphosphoric species (refs. 19,20). Since ^{31}P NMR spectra were recorded after hydrating the samples, the two

dominant lines are due to the products of hydrolysis of highly condensed polyphosphoric compounds. The spectra of samples calcined at 550°C and not rehydrated show only a small shoulder in the low-field region, but intense lines at -40 to -46 ppm characteristic of branching groups ($OP[PO_4]_3$) (ref. 21). The signal at -30.7 ppm is due to aluminium phosphate (refs. 22,23); the intensity of this signal increases with the increasing amount of H_3PO_4 added.

Dealumination is also seen from the ^1H MAS NMR spectra shown in Fig. 4.

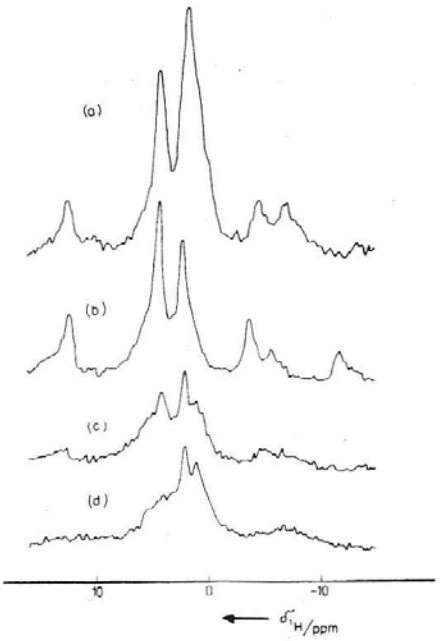

Fig. 4. ^1H MAS NMR spectra of H-ZSM-5 containing different amounts of phosphoric acid. (a) Parent H-ZSM-5; (b) 1 (c), 2 and (d) 5 mass % P.

The ^1H MAS NMR spectra of H-ZSM-5 consist of two lines (refs. 14-16). The line (b) at 4.3 is due to Brønsted acid sites (bridging OH groups) and hence its intensity yields directly the concentration of framework aluminium atoms involved in the formation of intact bridging OH groups. Line (a) at between 1.8 and 2.2 ppm is caused by non-acidic (silanol) OH groups, either at the outer surface of the crystals (terminal OH groups), at lattice defects or associated with amorphous material. Since the number of silanol groups as measured by the ^1H MAS NMR is ca. 10^3 times larger than the maximum number of terminal silanol groups on the external surface of the crystal, these high concentrations measured have to be considered as unambiguous proof of their intracrystalline nature (refs. 14-16,22).

As a result of H_3PO_4 impregnation followed by thermal treatment at 550°C, the intensity of line (b) steadily decreases. A semi-quantitative comparison of the concentration of the bridging OH groups as obtained by ^1H MAS NMR with the results of ^{27}Al and ^{29}Si MAS NMR as a function of the phosphorus content reveals that the decrease of peak (b) in proton NMR (see Fig. 4) can only be explained as due

to dealumination of the zeolitic framework. On the other hand, from the substantial decrease of the intensity of line (a) in Fig. 4 it follows that the H_3PO_4 molecules cause a strong decrease of the concentration of the non-acidic silanol groups.

There are two possible explanations for these results:

(i) In some recent work (refs. 25-28) internal silanol groups were attributed to unoccupied framework positions (crystal defects), each of which may represent a nest of four non-acidic hydroxyl groups. In terms of this lattice-defect model, the reduction of peak (b) could be interpreted in terms of an incorporation of phosphorus into the framework, thus substituting the missing T-atoms. However, NMR does not provide experimental evidence for such a reaction. Even the NMR results given in ref. 29 do not provide convincing proof for the existence of Si-O-P linkages.

(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.

Selective disproportionation of toluene

The influence of the impregnation of H-ZSM-5 with H_3PO_4 on the selective disproportionation of toluene (STD) is shown in Fig. 5.

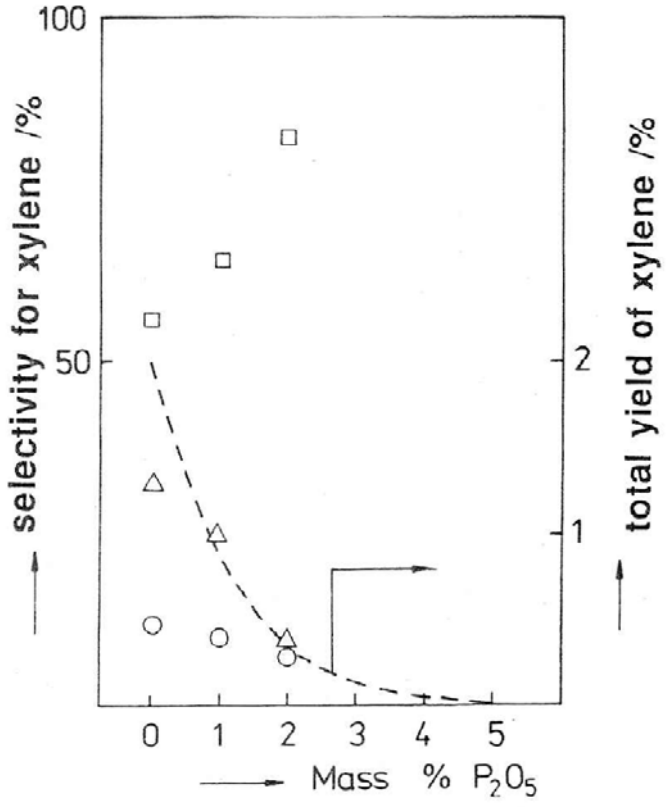

Fig. 5. Xylene selectivites and toluene yield in the selective disproportionation of toluene (STD) on ZSM-5 at 350°C; (O) ortho-xylene, (Δ) meta-xylene, (□) para-xylene).

Comparing 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 para-selectivity increases from 57% para-xylene initially to more than 95%.

Our understanding of this effect on a molecular level is still incomplete. Dealumination, formation of non-framework aluminium phosphate and polyphosphate species can all alter the diffusion behaviour as well as the strength, amount and accessibility of the active sites. We have shown (refs. 30,31) that for samples modified by hydrothermal dealumination, the enhanced para-selectivity found upon increasing degrees of dealumination was due to true shape selectivity rather than to kinetic effects caused by the decreased catalytic yield. Our results might become a basis for a critical re-consideration of the interpretation of the decreased acidity of H-ZSM-5 impregnated by H_3PO_4.

CONCLUSIONS

(i) Applying the ^1H NMR pulsed field gradient and ^1H NMR tracer desorption techniques to the study of the molecular self-diffusion of methane in H-ZSM-5 modified by H_3PO_4 allowed the distribution of phosphorus deposits in the ZSM-5 crystal to be determined. It was found that phosphoric acid penetrates 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 aluminium species react with H_3PO_4 forming aluminium phosphate. Furthermore, ^{31}P MAS NMR indicates that polyphosphoric acids are formed upon sample calcination.

(iii) The decrease in the number of Brønsted acid sites with increasing phosphorus content can be explained exclusively by dealumination of the zeolitic framework. Treatment with orthophosphoric acid followed by a thermal treatment at 550°C leads to a decrease in the amount of internal silanol groups.

(iv) After treatment with orthophosphoric acid, the samples show an increased p-selectivity and a decreased activity for the selective disproportionation of toluene.

ACKNOWLEDGEMENTS

We thank Professors R.M. Barrer (London), G. Öhlmann (Berlin) and D. Freude (Leipzig) for discussions; Dr. R. Mostowicz (Warsaw) for the synthesis of the zeolite and Dr. W. Heink (Leipzig) for the development of the FEGRIS pulse spectrometer.

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