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New Developments in Zeolite Science and Technology

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Interaction of Tricoordinated Phosphorus Compounds with Zeolites

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Vapor phase chemisorption of dimethylphosphine (DMP), trimethylphosphine and trimethylphosphite (TMP) in acidic faujasite has been studied with in situ IR and MAS-NMR techniques. Effects of pore filling on the spectral properties of trimethylphosphine are discussed. Protonation of DMP in a reversible acid-base reaction with dry HY zeolite is indicated by a single ^{31}P resonance at -56 ppm due to $P(CH_3)_2H_2^+$ and by the appearence of different P-H stretching modes. An acid catalyzed Arbuzov rearrangement converts TMP into dimethylmethylphosphonate which splits off methoxy groups upon heat treatment in the zeolite.

INTRODUCTION

Phosphorus compounds have gained considerable interest in the surface chemistry of metal oxides. Research activity encompasses chemisorption studies [1-11], anchoring of phosphine ligands (see e.g., [12,13]), modification of acidic surface properties [14-16], selective poisoning of acid sites [17], titration of these properties [18,19], and fine tuning of zeolite pore geometries for shape selective catalytic reactions [20-22].

The chemisorption and protonation of trimethylphosphine in the acid form of faujasites has been studied by means of IR and ^{31}P-NMR techniques [8,18,19]. Different phosphonium species which depend on the degree of loading have been reported. ^{31}P MAS-NMR resonances between -32 and -58 ppm were assigned to Lewis acid-base complexes with acidic species like Al_2O_3 clusters generated upon dehydroxylation of the HY zeolite [19].

In contrast to the acid-base reactions discussed above, details of the more severe modifications of zeolites with other phosphorus compounds like $P(OR)_3$, PCl_3 or phosphates are much less understood. The purpose of the present work is to understand in the above context the interaction of HY zeolite with DMP, trimethylphosphine and with trimethylphosphite, respectively. The study also emphasizes the value of solid state NMR and in situ IR techniques as powerful diagnostic tools for phosphorus/zeolite systems.

EXPERIMENTAL

1. Materials

Vapor of dimethylphosphine (Alfa) was admitted into a storage flask with dried molecular sieve 4A. Trimethylphosphite and trimethylphosphine (Strem Chemicals) were stored over sieve 4A without further purification. NH_4Y zeolite with the composition $Na_8(NH_4)_{47}Al_{55}Si_{137}O_{384}\ nH_2O$ was obtained from Linde (LZ-Y62). Prior to use, the ammonium form of the zeolite was degassed by heating for 12 hours at 670 K under 10^{-5} torr to yield the dry proton form (HY). The linear heating rate was 2 K/min.

2. Methods

Samples for solid state NMR experiments were prepared as follows. Batches of dry HY were weighed into a small quartz holder, introduced into a tubular quartz reactor and evacuated at a greaseless vacuumline (10^{-5} torr) for 30 min. A degassed and frozen vial with the phosphine was allowed to warm up to 273 K and dosed manometrically onto the zeolite. After equilibrating for 120 min at 295 K, the zeolite was pumped off for 30 min, and weight changes were recorded in the drybox. Heat treatments were done in the same reactor under vacuum, with a heating rate of 1 K/min.

The ^{31}P and ^{13}C MAS-NMR spectra were obtained on a Bruker CXP-300 instrument. Andrews type rotors were filled with ca. 200 mg of sample in the drybox and introduced into the NMR probe in a glovebag under flowing nitrogen. Dry nitrogen was used as the drive gas for the rotor to obtain spinning rates between 2 and 4 kHz. For ^{31}P, a 30° to 90° pulse with 10 s recycle time was used, depending on the T_1, to obtain quantitative spectra. For ^{13}C, 5 ms cross-polarization with 1 to 10 s recycle time was used. ^1H-decoupling time was 20-60 ms in both cases. Chemical shifts were referred to 85% H_3PO_4 or $(CH_3)_4Si$. No significant oxidation of the phosphines was observed during the NMR experiments.

In situ infrared experiments were done with self-supporting zeolite wafers (5 mg/cm^2), compacted at 100 kg/cm^2, in a controlled-atmosphere cell with CaF_2 windows connected to a Nicolet 7000 FT-IR spectrometer. Sample treatment was similar to that of the NMR samples, with the exception of shorter temperature cycles.

RESULTS AND DISCUSSION

1. Acid/base Reactions between Zeolites and $P(CH_3)_3$, $PH(CH_3)_2$

1.1. Reactions with trimethylphosphine

Vapor of trimethylphosphine was dosed into the cage system of dry HY. The qualitative details of our results are consistant with both IR and NMR data reported in the literature [8,19].

In Fig. 1, a series of ^{31}P MAS-NMR spectra of trimethylphosphine dosed on dry HY to different degrees of loading is presented. At a temperature of 295 K, the zeolite is saturated with 5.0 molecules of phosphine per supercage (5.0/s.c.). A sharp resonance at -69 ppm (Fig. 1a) is assigned to physisorbed phosphine (2.0/s.c.) and the broader band at -3.4 ppm, proton decoupled, represents 3.0 trimethylphosphonium ions per s.c. In a proton coupled spectrum, a doublet with the typical P-H scalar coupling constant of ca. 500 Hz and strong sideband intensity due to P-H dipolar coupling is observed (Fig. 1b).

IR data demonstrate that upon saturation less than 3.0 protons per s.c. represent the accessible "supercage protons" observed at 3650 cm^{-1} since also the 3550 cm^{-1} band is reduced in intensity.

If 2.8 molecules of trimethylphosphine per s.c. are dosed into the zeolite, protonation is complete as shown in Fig. 1c: only the phosphonium resonance appears, shifted to -6 ppm with significantly reduced sideband intensity. Degassing the sample at 570 K under vacuum for 60 min further narrows the phosphonium resonance at -5 ppm with a well resolved doublet due to P-H scalar coupling (Fig. 1d).

The results of the quantitative dosing and desorption experiments can be understood in terms of the following model: At lower loadings of the phosphine, there are only phosphonium ions present in the supercage. Weak repulsion between these species as well as the space available in the cage account for a relatively high mobility of the ions which results in a narrow ^{31}P resonance. If the loading exceeds the number of protons available, a crowded situation is expected with trimethylphosphine filling up the remaining space and hindering the mobility of the phosphonium ion, thus changing the chemical shift of the ion to -3 ppm. The ^{31}P chemical shift of the ion remains -6 ppm up to a loading of 2.8 per s.c. which closely corresponds to the maximum number of protons available. No evidence can be found for different species due to different origins of the protons as invoked in a former study [19]. The data obtained in

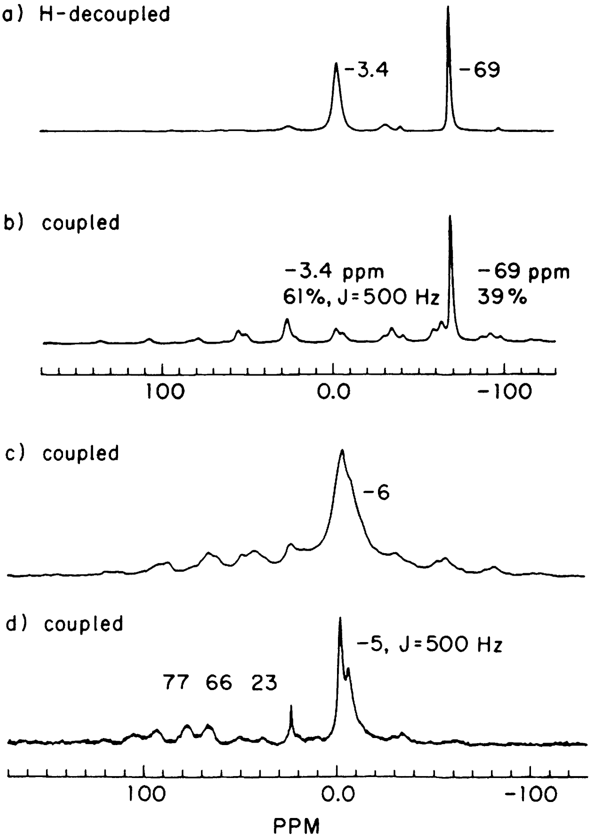


Fig. 1. Effect of pore filling on the ^{31}P MAS-NMR spectrum of $P(CH_3)_3$ adsorbed in dry HY zeolite. A, 5.0 per s.c. at 295 K, ^{1}H-decoupled. B, spectrum A, ^{1}H-coupled. C, 2.8 per s.c. at 295 K, ^{1}H-coupled. D, sample C, degassed at 570 K for 60 min, ^{1}H-coupled.

this study suggest that the chemisorption of trimethylphosphine in HY is essentially an acid/ base reaction which is only reversible under severe degassing conditions.

1.2. Dimethylphosphine as a probe for acid suface sites

Dimethylphosphine (DMP) is a weaker base compared to trimethylphosphine and different behavior in acid zeolites can therefore be anticipated. If HY zeolite is saturated with DMP and subsequently degassed under vacuum at 295 K, only one species is detected in the ^{31}P NMR at -56 ppm. The ^{31}P resonance of neat DMP is at -99 ppm. We assign the observed species to the dimethylphosphonium ion (DMPH$^+$) adsorbed in the zeolite (Fig. 2). In the IR experiment, DMP shows a strong band at 2289 cm^{-1} due to the P-H stretching vibration. The intensity of this band allows the determination of adsorbed quantities of the phosphine. Upon adsorption of the molecule in HY zeolite, the band is broadened. (Fig. 3a). The concomitant disappearence of the 3650 cm^{-1} band indicates complete proton transfer in the supercage. Two new bands at 2495 and 2450 cm^{-1} appear. These bands are interpreted as due to the symmetric and antisymmetric P-H stretching vibrations of DMPH$^+$ generated in the zeolite. Degassing experiments indicate that adsorption and proton transfer are reversible with DMP (Fig. 3b). The hydroxyl groups are restored to the original intensity, whereas both the P-H and C-H bands dissappear.

These features demonstrate some advantages of DMP as a probe molecule for acid sites on oxide surfaces compared to trimethylphosphine: In the IR, independent determination of DMP and DMPH$^+$ is possible. In the NMR experiment, DMP is a reversible probe for acid sites showing no interference with remaining unprotonated species.

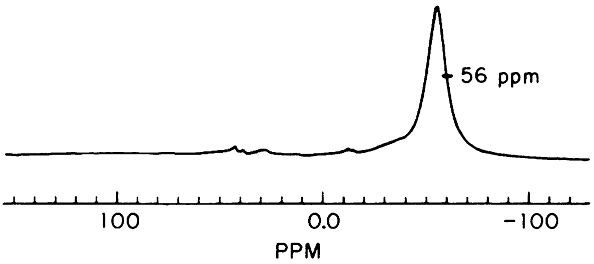


Fig. 2. (Top) ^{31}P MAS-NMR of $P(CH_3)_2H$ in HY, degassed at 295 K, ^{1}H-decoupled.

2. Reactions of Trimethylphosphite with Zeolites

2.1. Adsorption at 295 K

If HY is saturated with 3.6 molecules trimethylphosphite (TMP) per supercage, one dominant species is observed in the ^{31}P NMR at +36 ppm with a moderate sideband intensity (Fig.4a) This resonance indicates a substantial change in the isotropic shift as compared to the value of the starting phosphine at +140 ppm. A small amount of a second species which shows cross-polarization (CP) is represented by a resonance at +21 ppm.

The ^{13}C NMR spectrum of the same system is dominated by resonances in the methoxy-region at +55 and 53 ppm, in addition to a smaller peak at +8 ppm which is assigned to $P-CH_3$ (Fig.4b). The key for understanding these results is a rearrangement reaction of the TMP to yield tetracoordinated dimethylmethylphosphonate (DMMP) adsorbed in the zeolite.

A reaction sequence is proposed which resembles the well-known Arbusov rearrangement of trialkylphosphites:

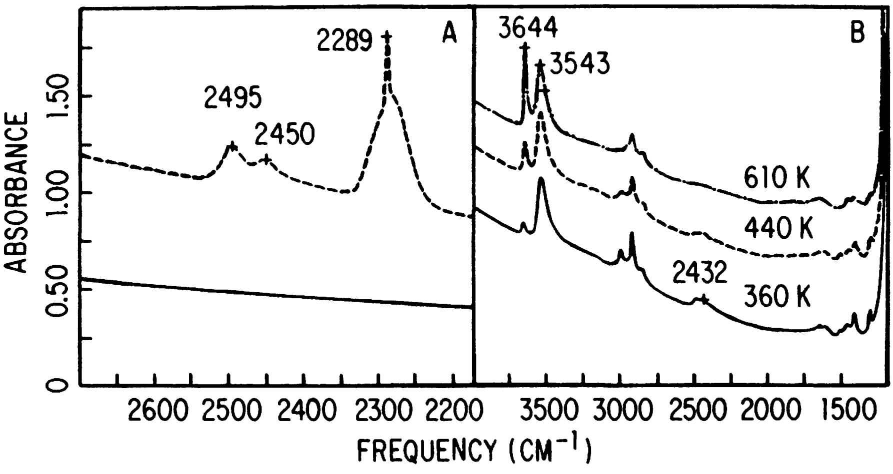


Fig. 3. IR spectra of a wafer of HY, degassed at 670 K, loaded with $P(CH_3)_2H$. A, 30 torr of the phosphine added at 295 K. B, degassed at 360, 440 and 610 K for 60 min.

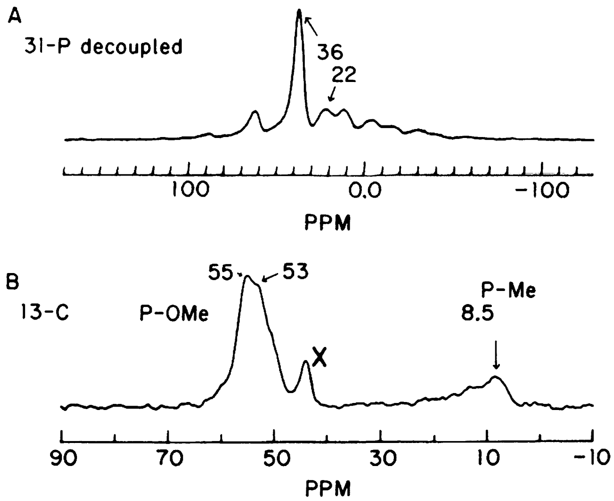
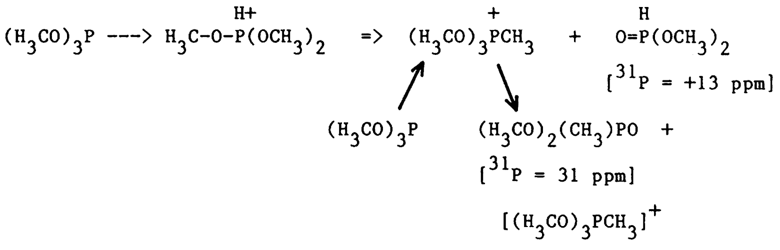


Fig. 4. NMR spectra of trimethylphosphite adsorbed on HY zeolite. A, ^{31}P MAS-NMR of HY, saturated with TMP at 295 K (^{1}H-decoupled). B, ^{13}C spectrum of sample A, cross-polarized and ^{1}H-decoupled. (X = rotor signal)



$$(H_3CO)_3P \xrightarrow{H+} H_3C\text{-}O\text{-}P(OCH_3)_2 \Rightarrow \overset{+}{(H_3CO)_3PCH_3} + \overset{H}{O{=}P(OCH_3)_2}$$

$[^{31}P = +13\ ppm]$

$(H_3CO)_3P$ $\quad (H_3CO)_2(CH_3)PO +$

$[^{31}P = 31\ ppm]$

$[(H_3CO)_3PCH_3]^+$

Nucleophilic attack of TMP at a methoxy carbon of protonated TMP generates a trimethoxymethylphosphonium ion which acts as chain propagating species. Reaction of this ion with TMP results in DMMP. Dimethylhydrogenphosphite is expected to be a byproduct of this reaction, and the ^{31}P resonance of this molecule adsorbed into HY indeed resembles the second species observed upon adsorbing TMP in HY.

If DMMP is adsorbed into HY, both the ^{31}P and ^{13}C NMR features are similar to those obtained with TMP. This presents strong evidence for the reaction proposed above.

2.2. Infrared results

A thin wafer of HY saturated with TMP has been studied in the infrared cell. Proton transfer from both supercage and weaker acid sites towards the adsorbed phosphorus compounds is observed in the hydroxyl region (consumption of the 3650 and 3550 cm^{-1} bands). A new, broad band at ca. 2440 cm^{-1} is indicative for a P-H interaction (Fig. 5a).

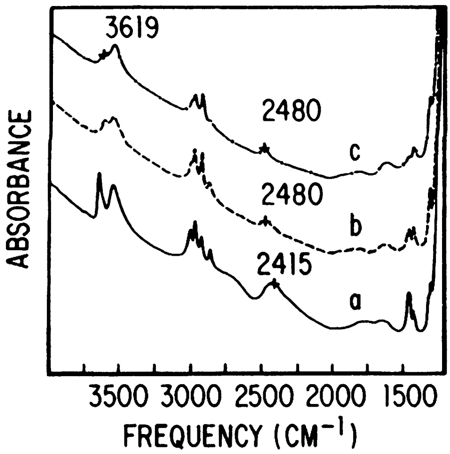


Fig. 5. IR spectra of a wafer of HY, degassed at 670 K, loaded with TMP. A, loaded at 295 K(5.5 torr), degassed at 295 K for 30 min.
B, degassed at 440 K for 60 min.
C, degassed at 610 K for 60 min.

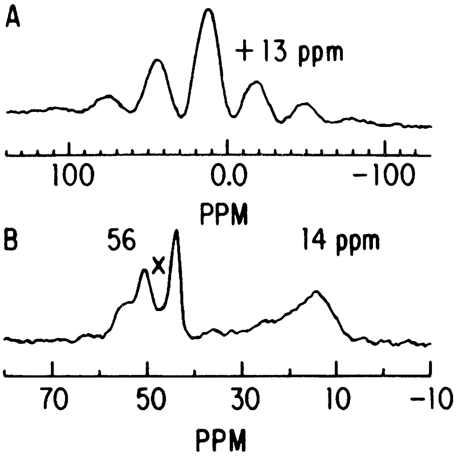


Fig. 6. NMR spectra of TMP/HY adduct, degassed at 670 K for 12 hours. A, ^{31}P MAS-NMR of TMP/HY, ^{1}H-coupled. B, ^{13}C MAS-NMR of TMP/HY, cross-polarized and ^{1}H-decoupled. (X = rotor)

Evidence for the generation of DMMP is found in the C-H bending region: The new methyl group is represented by a band at 1304, whereas a pair at 1460/30 cm^{-1} accounts for the methoxy group. In addition, a shoulder at 1250 cm^{-1} can be understood as being due to the newly generated P=O double bond.

2.3. Thermal decomposition of the TMP/zeolite adducts

Heating the phosphine-loaded wafer in the infrared cell under vacuum (60 min at 440 K and at 610 K) reduces the overall C-H intensity (Fig. 5b,c). However, the hydroxyl bands are not restored as would be expected upon simple dissociation of a phosphonium species. In contrast, the OH-intensity decreases with heating time, indicating an irreversible reaction with the phosphorus compound.

NMR data provide further evidence for the species obtained upon thermal desorption treatments. If TMP adsorbed in partially exchanged HY is degassed at 670 K for 12 hrs, the rearrangement product DMMP transforms to another species with a ^{31}P resonance at +13 ppm and strong anisotropy as indicated by the sideband intensity (Fig. 6a).

The ^{13}C spectrum of TMP heated in HY at 570 K for 12 hrs substantiates the findings of the IR experiments: The methoxy-bands are considerably smaller compared to the system at 295 K, whereas a large fraction of methyl groups is indicated by a resonance at 14 ppm (Fig. 6b).

Both IR and NMR results suggest that the rearrangement product DMMP reacts irreversibly with the zeolite hydroxyl groups upon heating under vacuum. This reaction is accompanied by a loss of methoxy groups which probably desorb from the zeolite as methanol.

We propose the generation of stable condensation products between a $(-O)_2P(O)CH_3$ unit and the zeolite framework. Similar behavior of DMMP upon reaction with the hydroxyl groups of Al_2O_3 has been reported in the literature [3,4]. Thermal desorption data together with chemical probing of the modified zeolite will be required to confirm the nature of this reaction, including possible oligomerization of organic fragments in the pore system.

A more detailed discussion of our studies on organophosphorus and organosilicon chemistry in zeolites will be published in the near future [23].

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