MAGIC-ANGLE-SPINNING NMR STUDIES OF ZEOLITE SAPO-5

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SAPO-5 was synthesized using triethylamine as template. Magic-angle-spinning (MAS) NMR of ^{1}H, ^{27}Al, ^{29}Si and ^{31}P was used to study the silicon incorporation into the framework and the nature of the Brønsted sites. ^{1}H MAS NMR shows two types of bridging hydroxyl groups. ^{29}Si MAS NMR indicates that silicon substitutes mostly for phosphorus and that there is a small amount of crystalline SiO_2 in the zeolite powder.

1. Introduction

SAPO-5 belongs to the family of zeolites created by silicon substitution into an aluminium–phosphate framework of structure type 5 (AlPO-5) [1]. Two possibilities of substitution are discussed: The substitution of two silicons for an aluminium plus phosphorus and the substitution of silicon for phosphorus only [1]. The latter results in a net negative charge with potential for Brønsted acid sites. We present magic-angle-spinning NMR experiments for the characterization of the silicon incorporation and of the Brønsted acid sites in a zeolite SAPO-5 synthesized with triethylamine as template.

2. Synthesis and sample preparation

The sample was synthesized using a procedure based on those given by Union Carbide with some modifications [2]. The batch composition expressed in mole ratios was as follows:

$$5\,Et_3N * 1\,Al_2O_3 * 1.33\,P_2O_5 * 1\,SiO_2 * 300\,H_2O * 3\,HNO_3 .$$

The product was calcined at 600°C in air. X-ray analysis shows the stability of the material up to a treatment temperature of 900°C. Chemical analysis gave the composition of the crystalline products as

$$0.082\,SiO_2 * 1\,Al_2O_3 * 0.95\,P_2O_5 * 0.12\,H_2O .$$

The samples for ^{1}H MAS NMR were heated in a glass tube 6 mm in diameter with the zeolite layer 10 mm thick under vacuum with a rate of 10 K/h. After keeping the samples for 2 h at 400°C they were evacuated to a pressure below 0.01 Pa for 20 h and sealed off. Before sealing one portion was loaded at room temperature under vacuum with 6×10^{20} molecules of perdeuterated pyridine per gram or with a pressure of 5 kPa methane. For measurements of other nuclei the non-activated calcined zeolite powder was used.

3. NMR studies

NMR spectra were measured at room temperature using a Bruker MSL 300 instrument and a home-made magic-angle-spinning equipment. The latter

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was carefully cleaned to avoid spurious proton signals. The total concentration of OH groups in the activated sample was determined by comparison of the maximum amplitude of the free induction of the non-spinning sample with those of a capillary with an aqueous solution in a home-made probe with a short ring-down time. For cross-polarization (CP) measurements the contact times were 1 and 3 ms for ^{29}Si and ^{27}Al, respectively. The spinning rate was 3–5 kHz.

4. Results and discussion

Fig. 1a shows that the ^1H spectrum of the activated sample consists of three well resolved lines. To prove the accuracy of the chemical shift measurements the sample was loaded with a small amount of methane as an internal standard ($\delta_H = 0.175$ ppm [3]). In fig. 1b the signal of methane appears at 0.18 ppm. The experimental error is less than 0.05 ppm in ^1H MAS NMR measurements.

Loading with NC_5D_5 quenches the lines at 3.9 and 4.9 ppm and gives a new line at 16.5 ppm due to the pyridinium ion (see fig. 1c). The signal at 16.5 ppm is not narrowed by MAS, since the motion of the pyridinium ions is faster than the speed of rotation of the sample. Because the OH groups giving rise to these lines are involved in the protonation of pyridine to pyridinium, they must be acidic and accessible to pyridine.

The signal at ≈ 1.5 ppm is decreased in intensity to about one half by loading with pyridine. Two new signals appear at 8.7 and 7.0 ppm. These can be assigned to POH interacting via a hydrogen bond with the pyridine nitrogen. This gives a positive chemical shift of 7 ppm (cf. ref. [4]). However, spurious hydrogen atoms in pyridine can contribute to the signals at 8.7 and 7.0 ppm. The rest of the line at ≈ 1.5 ppm must be assigned to inaccessible POH groups.

The total concentration of OH groups in the zeolite SAPO-5 under study is 1.0 ± 0.2 OH per 48 framework tetrahedra. A splitting procedure of the main signal with added spinning side bands gives 10% of the total concentration for OH giving rise to the signal at ≈ 1.5 ppm and 45% for each of both the 3.9 and 4.9 ppm lines, respectively.

Information about the position of OH groups in the framework is contained in the relative intensities of the spinning sidebands of the different lines. In the case of a strong heteronuclear interaction of the ^1H nucleus with nuclei in the neighbourhood, relatively intense sidebands are expected, whereas for

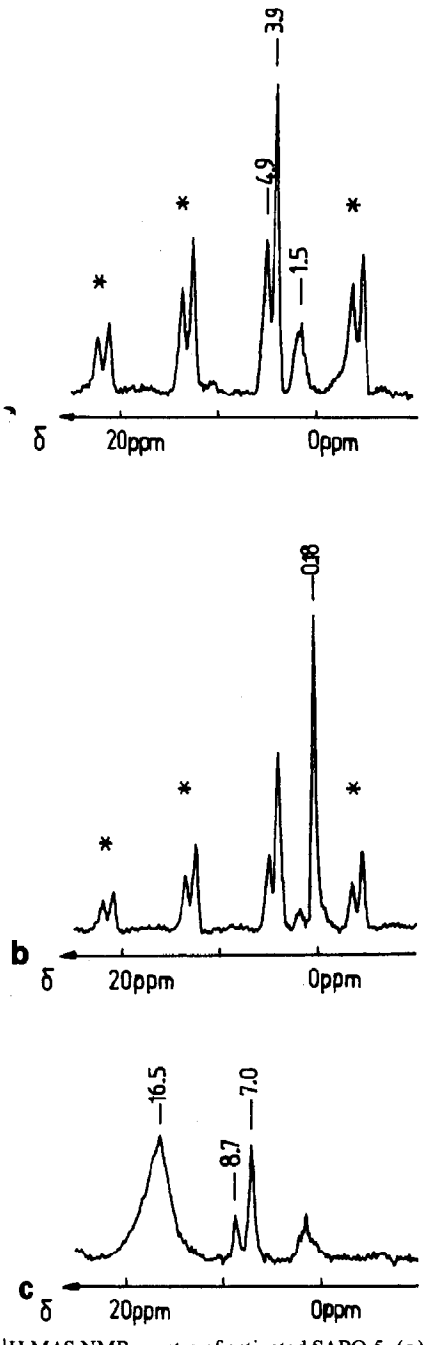
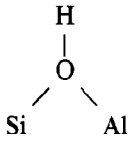


Fig. 1. ^1H MAS NMR spectra of activated SAPO-5, (a) without sorbate, (b) with sorbed methane, (c) with sorbed NC_5D_5.

weak heteronuclear coupling the intensities of the first-order spinning sidebands are already very low. For the samples under study we must consider the ^{1}H–^{27}Al or ^{1}H–^{31}P interaction. The coupling with ^{27}Al is dominant, because it gives the fivefold value for the second moment of the ^{1}H line shape in comparison with those of a ^{31}P nucleus at the same distance (cf. ref. [4]). The intensities of the spinning sidebands in fig. 1a demonstrate a strong heteronuclear interaction of ^{1}H giving rise to the lines at 3.9 and 4.9 ppm. The spectrum of a zeolite AlPO-5 shows only lines at ≈ 1.5 ppm with very weak side bands. We assign the lines at 3.9 and 4.9 ppm to bridging



groups. This parallels the high-frequency IR band ($\tilde{\nu}=3627\ cm^{-1}$) of bridging hydroxyls pointing towards the main channel, and the low-frequency band ($\tilde{\nu}=3510\ cm^{-1}$) assigned to hydroxyls in the six-membered ring in the study by Lercher and co-workers [5]. The difference of 1 ppm between the two lines is the result of an additional electrostatic interaction of the proton in the six-membered ring with the nearest oxygen atoms. For zeolites H-Y, the 3.9 and 4.9 ppm lines are the lines (b) and (c), in ref. [6], respectively.

Using Sanderson's concept of intermediate electronegativity, Jacobs and Mortier [7] related the acid strength of bridging OH groups to the compound composition. The average electronegativity of $AlPO_4$ compounds is intermediate between those of $HAlSiO_4$ and SiO_2 [8]. We therefore expect to find the chemical shift of the large channel bridging OH in SAPO-5 between the values of bridging hydroxyl groups in H-X (3.8 ppm) and H-ZSM-5 (4.3 ppm, cf. ref. [6]).

In zeolite AlPO-5, lines only at ≈ 1.5 ppm are observed. Therefore, the line at ≈ 1.5 ppm in SAPO-5 should be assigned to non-acidic POH groups, but a small amount of non-acidic SiOH or AlOH groups cannot be excluded. All zeolites contain non-acidic hydroxyl groups on framework defects (including a relatively small portion of hydroxyls terminating at the outer surface of the crystallites), which give rise to signals in this region (line (a) in ref. [6]).

Our assignment is confirmed by comparison of the intensities of spinning sidebands: The strongest ^{1}H–^{27}Al interaction exists for protons in the six-membered ring (strong coupling with one Al plus additional coupling with the further two Al nuclei in the ring). Only a relatively weak ^{1}H–^{31}P interaction exists for protons in POH groups.

The total concentration of bridging OH groups is 0.8 ± 0.2 OH per 48 framework tetrahedra. That means that in the hypothetical AlPO framework $\frac{1}{30}$ of the phosphorus must be substituted by silicon resulting in Brønsted acid sites.

The ^{29}Si MAS NMR spectrum in fig. 2a gives further information about the incorporation of silicon into the zeolite framework. We assign the line at -92 ppm to silicon four-coordinated with aluminium (cf. ref. [9]). Only this line is enhanced upon cross-polarization (cf. fig. 2b). This is because bridging OH groups are in the neighbourhood of the silicon incorporated in the framework on P sites. There is no line which could correspond to Si(1 Al)(3 Si) or Si(1 P)(3 Si) coordination of silicon. Also, no signal can be found for SiOH in the CP spectrum. Therefore, the spectra support neither the incorporation of silicon pairs for Al+P nor the SiO_2 cluster on non-framework positions which are terminated by OH groups. The line at -112 ppm must be explained by a small amount of crystalline SiO_2 in the zeolite powder. This explanation of the ^{29}Si spectrum is in agreement with the results of Martens et al. [10].

The conclusion that $\frac{1}{60}$ of framework tetrahedra is occupied by single Si (four-coordinated with OAl) and $\frac{1}{120}$ of framework tetrahedra by SiO_2 (four-coordinated to OSi) agrees with the results of ^{1}H and ^{29}Si MAS NMR and the composition determination by chemical analysis.

The ^{27}Al NMR spectra (cf. figs. 2c and 2d) contain two lines: The 38 ppm line must be ascribed to aluminium tetrahedrally OP-coordinated. The line at -12 ppm is in the region of chemical shifts for six-coordinated non-framework aluminium. The increase of this line in the cross-polarization spectrum confirms the assumption that it is due to $AlO_4(OH_2)_2$ complexes which arise in a non-ideal synthesis. Chemical analysis also shows the excess of aluminium in the product. The asymmetry of the 38 ppm

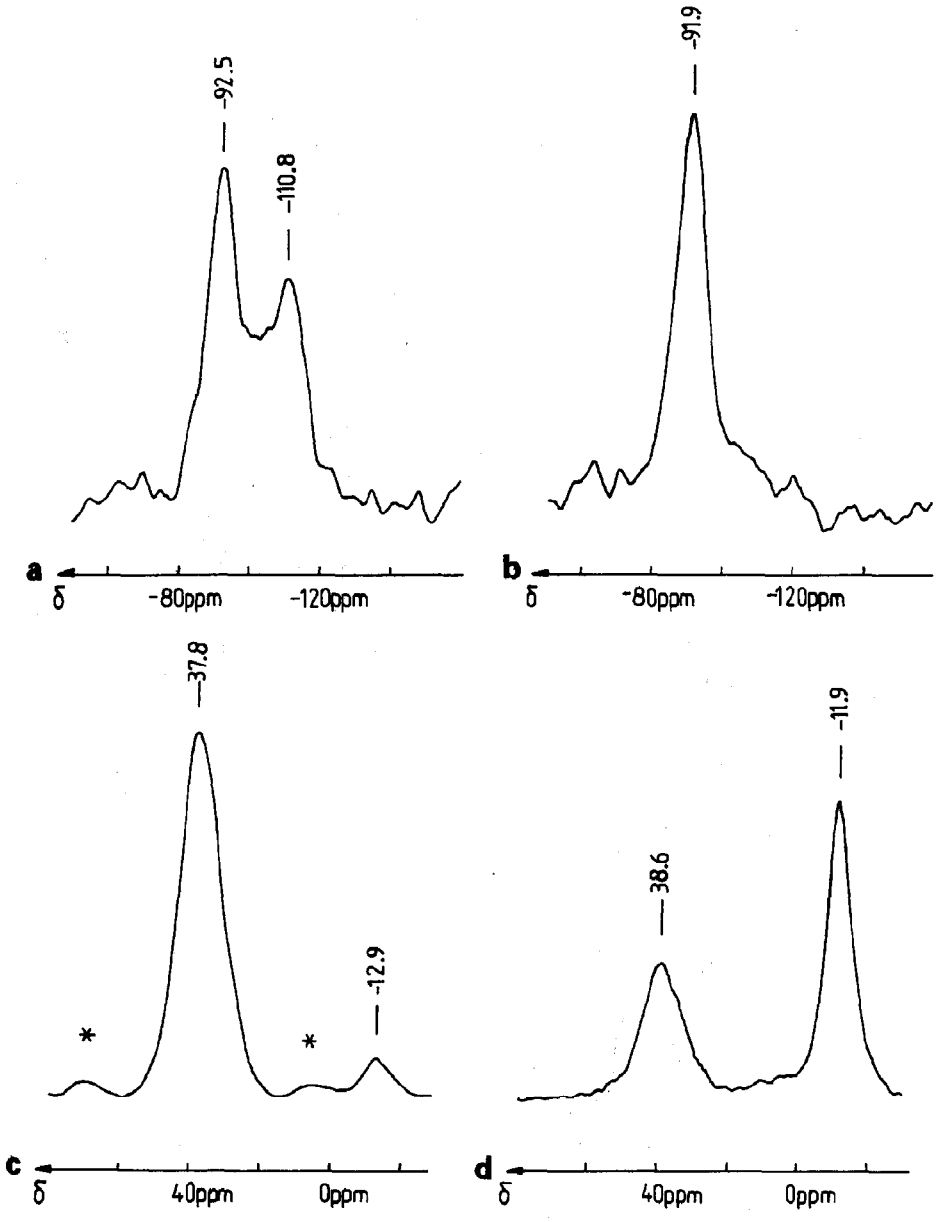


Fig. 2. ^{29}Si and ^{27}Al MAS NMR spectra of SAPO-5. The asterisk denotes spinning sidebands.

line in the ^{27}Al spectrum may be caused by second-order quadrupole interaction. Regarding a quadrupole-induced correction of the ^{27}Al chemical shift ($e^2qQ/h = 2.3$ MHz) the observed chemical shift value of 38 ppm corresponds to the expected value of 40 ppm for AlPO-5 [11]. The ^{31}P NMR chemical shift of SAPO-5 (−29 ppm) agrees with that measured for AlPO-5 [11].

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