Characterization of phosphorous-containing catalysts by ^{31}P solid-state NMR

Spectroscopic background: ^{31}P nuclei have a spin of I = 1/2 and no quadrupole moment. The ^{31}P isotope has a natural abundance of 100 % and a sensitivity of 6.6 x 10^{-2} in comparison with ^{1}H nuclei (1.0), making this isotope a very suitable candidate for NMR studies of solids. For basic principles of solid-state NMR, see lectures “Solid-State NMR Spectroscopy” for Bachelor students or PhD seminars, accessible via the link “Lectures for Students”.

^{31}P MAS NMR spectroscopy is a sensitive method for investigating the local structures of aluminophosphate- (AlPO), silicoaluminophosphate- (SAPO), and metal aluminophosphate-type zeolites (MeAPO). Typically, the ^{31}P MAS NMR signals of **P(4Al)** or **P(4OAl) tetrahedra (Q^4)** in crystalline aluminophosphates cover a chemical shift range from **δ_{31P} = -20 to -33 ppm** [1-7], depending on their mean P-O-Al angles, which is experimentally supported by Fig. 3 in Ref. [8] and Table 2 in Ref. [9]. In SAPO materials, some of the phosphorous sites are occupied and cause structural bridging OH-groups (Si-OH-Al) with moderate Broensted acid strength [10, 11] .

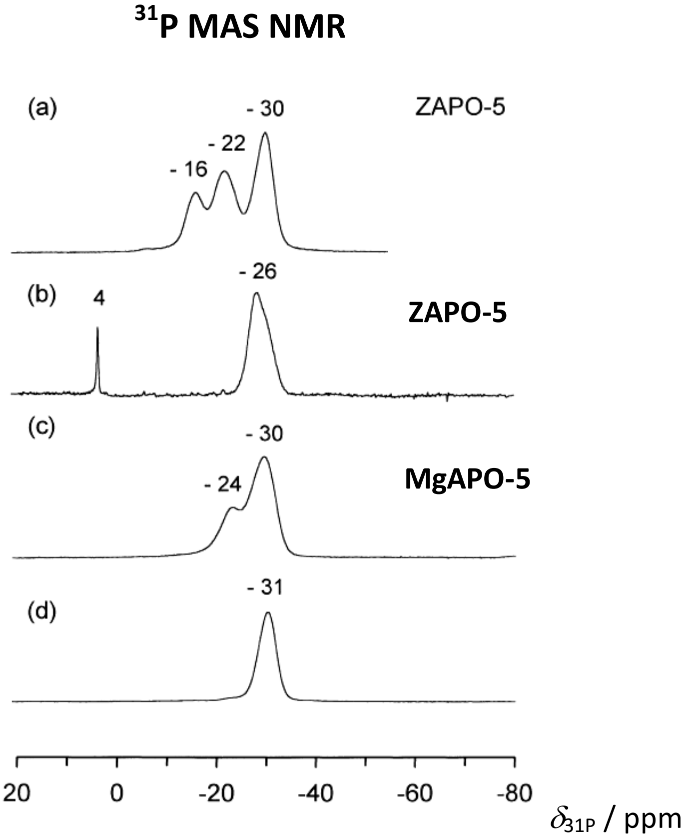

Fig. 1

For MeAPO materials, additional ^{31}P MAS NMR signals occur, due to the incorporation of the metal atoms into P-O-Me bridges at aluminium sites. For demonstration, **Fig. 1** shows the ^{31}P MAS NMR spectra of zinc- (**ZAPO-5**) and magnesium-containing (**MgAPO-5**) aluminophosphates of the structure type $AlPO_4$-5, recorded in the as-synthesized (a, c) and calcined (1073 K) state (b, d) [12]. While the spectra of the as-synthesized MeAPO-5 materials consist of signals of different P(nOAl,mOMe) species, only a single signal of **P(4OAl) species** is visible at **δ_{31P} = -31 to -30 ppm** upon the high-temperature treatment (b, d) [12].

For the **magnesium-containing aluminophosphate** MgAPO-20, ^{31}P MAS NMR signals at chemical shifts of **δ_{31P} = -14.0 ppm, -21.1 ppm, -28.0 ppm, and -34.9 ppm** due to phosphorus atoms in **P(1OAl,3OMg), P(2OAl,2OMg), P(3OAl,1OMg), and P(4OAl) units** are observed [13]. The detailed positions of the signals of P(nOAl,mOMe) species depend on the mean P-O-Al and P-O-Me angles. Therefore, the low chemical shift of the phosphorus atoms surrounded by four aluminum atoms (P(4OAl)) in MgAPO-20 was explained by the high P-O-Al bond angle of 160^{o} for this structure type [13].

The population ratio of framework atoms in MeAPOs can be calculated from the intensities of the ^{31}P MAS NMR signals in a similar manner to that used for calculating n_{Si}/n_{Al} ratios from ^{29}Si MAS NMR spectra of zeolites. With P(nOAl,mOMe) instead of Si((4-n)OSi,nOAl) (or Si(nAl)) and using the integrated intensities $I_{P(nAl)}$ of the P(nOAl,mOMe) signals, Equ. (1) in the Section "method 6" yields the framework n_P/n_{Al} ratio [13]. Furthermore, the fraction [Me] of the T-sites occupied by the metal atom Me can be calculated via [13]:

$$[\mathrm{Me}] = \sum_{n=0}^{4} (4-n) I_{\mathrm{P}(n\mathrm{Al})} \,/\, 8 \sum_{n=0}^{4} I_{\mathrm{P}(n\mathrm{Al})} \qquad (1)$$

In contrast to the aluminophosphate AlPO-5, which has one crystallographically equivalent phosphorous site only, the structure of the aluminophosphate VPI-5 consists of two phosphorus sites located in 6-membered oxygen rings and belonging to two adjacent 4-membered rings. Therefore, the ^{31}P MAS NMR spectrum of **dehydrated VPI-5** consists of two signals at about **δ_{31P} = -26 ppm and -31 ppm** with an intensity ratio close to 2:1 [14-16]. In contrast, the spectrum of **hydrated VPI-5** reveals three lines of equal intensity at chemical shifts of **δ_{31P} = -23 ppm, -27 ppm,**

and -33 ppm [17-20]. For clarifying the signal assignment, the spatial neighborhood of aluminum and phosphorus atoms in the framework of VPI-5 was investigated by two-dimensional (2D) ^{27}Al-^{31}P HETCOR MAS NMR spectroscopy (Heteronuclear Correlation) [20]. This two-dimensional experiment (**Fig. 2a**) enables the correlation of two different kinds of nuclei via their heteronuclear dipole-dipole interaction. During the evolution period (t_1) the S- (^{27}Al) and I-spins (^{31}P) evolve under their chemical shifts and dipolar couplings. Before the acquisition of the I-spin magnetization in t_2, a second pulse sequence is applied [20].

In **Fig. 2b**, the 2D ^{27}Al-^{31}P HETCOR MAS NMR spectrum of dehydrated VPI-5 is depicted [20]. The cross-peaks observed in this spectrum indicate that each phosphorus atom (δ_{31P} = -23 ppm, -27 ppm, and -33 ppm) is dipolarly coupled with tetrahedrally (δ_{27Al} = 43.6 ppm and 41.6 ppm) as well as octahedrally (δ_{27Al} = -10.4 ppm) coordinated aluminum atoms.

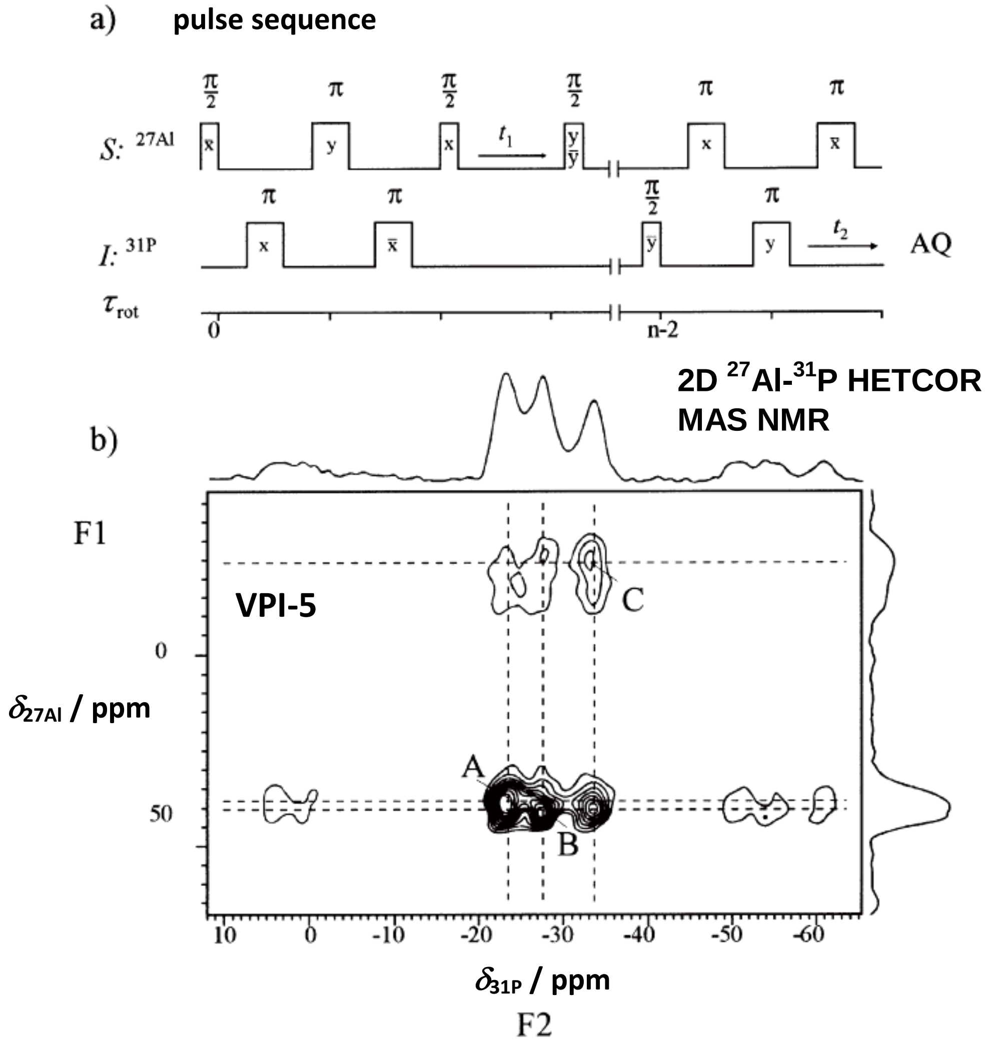

Fig. 2

Fig. 3 demonstrates the potential of ^{31}P MAS NMR spectroscopy for studies of the **structural transformation of aluminophosphates**. These solid-state NMR spectra evidence the thermal transformation of VPI-5 to AlPO-8 [14, 18, 19, 21]. The ^{31}P (left) and ^{27}Al MAS NMR (right) spectra were obtained for VPI-5 dried at 333 K overnight (a), VPI-5 evacuated at 327 K overnight and calcined at 523 K overnight (b), AlPO-8, transformed from VPI-5 by calcination at 673 K overnight (c), and hydrated $AlPO_4$-8 (d) [14]. The asterisks denote MAS sidebands.

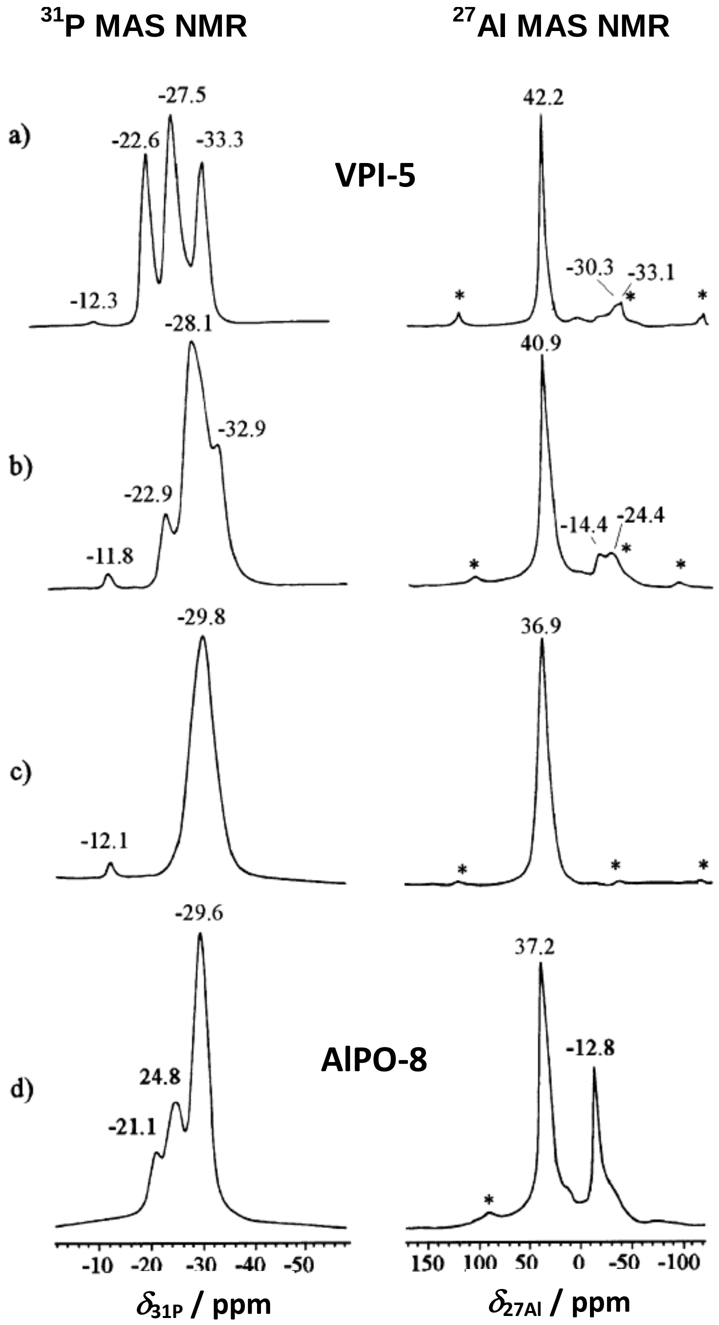

Fig. 3

The ^{31}P MAS NMR spectrum of hydrated **AlPO-8** in **Fig. 3d** consists of three signals at about **δ_{31P} = -21 ppm, -25 ppm, and -30 ppm** with an intensity ratio of 1:2:6. AlPO-8 has the structure type AFG with three crystallographically non-equivalent T-positions in the ratio 1:1:2 [22]. Simultaneously, the center of gravity of the ^{27}Al MAS NMR signal of tetrahedrally coordinated framework aluminium atoms is shifted from about δ_{27Al} = 42 ppm (VPI-5) to about δ_{27Al} = 37 ppm (AlPO-8).

In the case that structural changes of solid phosphates are induced or accompanied by a **hydrolysis of oxygen bridges**, **Q^4 units are transformed into Q^3, Q^2** etc. units. Such structural changes lead to a **low-field resonance shift** (higher chemical shift values) of the ^{31}P MAS NMR signals **by $\Delta\delta_{31P}$ = 5 to 15 ppm** (see Fig. 4 in Ref. [23]).

Catalyst preparation: Depending on the purpose of the solid-state NMR studies, hydrated as well as dehydrated catalyst samples are investigated by ^{31}P MAS NMR. The dehydration of the solid catalyst is performed inside a „sample tube system 1“ at „vacuum line 1“ (see link “*In Situ* Solid-State NMR Techniques”) is performed. The activation starts with an evacuation at room temperature for ca. 10 minutes followed by a temperature ramp from room temperature to 393 K within 2 hours. At this temperature, the sample is dehydrated for 2 hours. Subsequently, the temperature is increased up to 723 K within 3 hours and evacuated at this temperature for 12 hours. After this treatment, the sample tube system is closed via the vacuum valve and disconnected from „vacuum line 1“ after this line was ventilated with air.For solid-state NMR studies of dehydrated samples, their transfer into the MAS NMR rotor is performed without air contact, e.g. in a mini glove box purged with dry nitrogen gas (see Section “mini glove box” via link “*In Situ* Solid-State NMR Techniques”).

^{31}P MAS NMR studies: ^{31}P MAS NMR measurements were carried out using, e.g., utilizing a Bruker Avance III 400WB spectrometer at a resonance frequency of 161.9 MHz using a 4 mm MAS NMR probe with a sample spinning rate of 10 kHz, upon single pulse $\pi/2$ excitation, with a repetition time of at least 30 s, and with high-power proton decoupling (HPDEC). For the parameters of 2D ^{27}Al-^{31}P HETCOR MAS NMR measurements, see Ref. [20]. Chemical shifts are referenced to 0.85 M H_3P0_4 (δ_{31P} = 0 ppm).

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