

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

Spectroscopic background: ^{31}P nuclei have a spin of $I = 1/2$ and, therefore, no quadrupole moment. The ^{31}P isotope has a natural abundance of 100 % and a sensitivity of 6.7×10^{-2} in comparison with ^1H 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 **tetrahedrally coordinated P(4OAl) (Q^4)** in crystalline aluminophosphates cover a chemical shift range from $\delta_{31\text{P}} = -33$ to -20 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 by silicon atoms and cause structural bridging OH-groups (Si-OH-Al) with moderate Brønsted acid strength [10, 11].

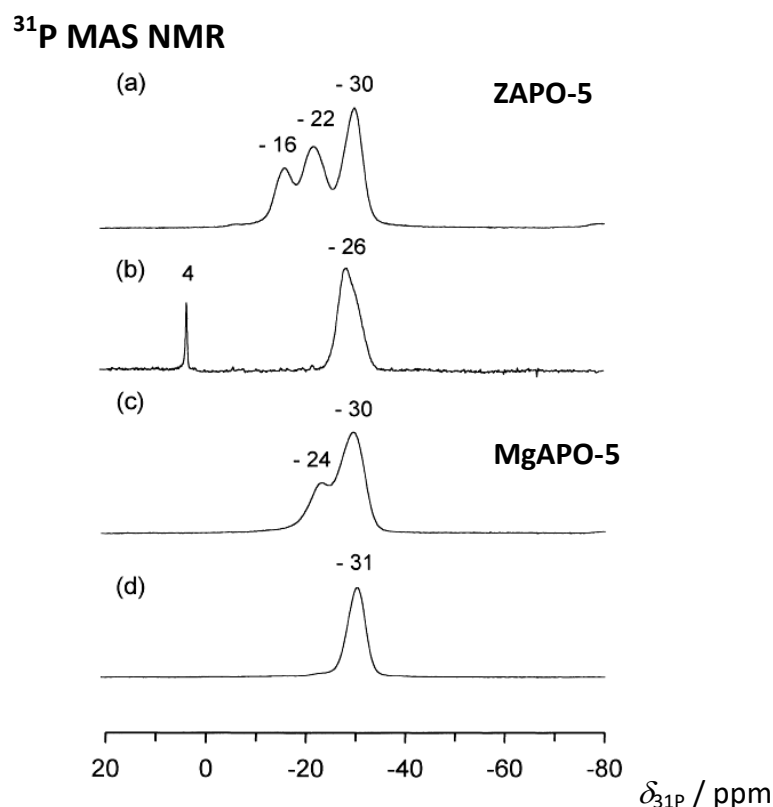


Fig. 1

For MeAPO materials, additional ^{31}P MAS NMR signals occur, due to the incorporation of metal atoms at aluminum sites causing P-O-Me bridges. For demonstration, **Fig. 1** shows the ^{31}P MAS NMR spectra of zinc- (**ZAPO-5**) and magnesium- (**MgAPO-5**) containing aluminophosphates of the structure type AFI of $\text{AlPO}_4\text{-5}$, 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 $\text{P}(n\text{OAl}, m\text{OMe})$ species, only a single signal of **P(4OAl) species** is visible at $\delta_{31\text{P}} = -31$ to -30 ppm upon the calcination (b, d) [12].

For the **magnesium-containing aluminophosphate MgAPO-20**, ^{31}P MAS NMR signals at chemical shifts of $\delta_{31\text{P}} = -34.9$ ppm, -28.0 ppm, -21.1 ppm, and -14.0 ppm due to phosphorus atoms in **P(4OAl)**, **P(3OAl,1OMg)**, **P(2OAl,2OMg)**, and **P(1OAl,3OMg) species** are observed [13]. The detailed positions of the signals of $\text{P}(n\text{OAl}, m\text{OMe})$ species depend on the mean P-O-Al angles. From a least-square treatment of the ^{31}P chemical shifts of AlPO_4 polymorphs, a mean slope of 0.57 ppm/deg (correlation: 0.988) was found [2]. 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° in their local structure [13].

The fraction [Me] of the T-sites occupied by metal atoms Me (Me: Mg, Zn etc.) can be calculated from the relative intensities of the ^{31}P MAS NMR signals of $\text{P}(n\text{OAl}, (4-n)\text{OMe},)$ species, abbreviated $\text{P}(n\text{Al})$, via [13]:

$$[\text{Me}] = \frac{\sum_{n=0}^4 (4-n) I_{\text{P}(n\text{Al})}}{8 \sum_{n=0}^4 I_{\text{P}(n\text{Al})}} \quad (1)$$

In contrast to the **aluminophosphate AIPO-5**, which has one crystallographically equivalent phosphorous site, causing a single ^{31}P MAS NMR signal at $\delta_{31\text{P}} \cong -28$ ppm, 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. However, the ^{31}P MAS NMR spectrum of **as-synthesized VPI-5** consists of three signals of equal intensity at chemical shifts of $\delta_{31\text{P}} \cong -33$ ppm, -27 ppm, and -23 ppm [14-21]. Because the signal at $\delta_{31\text{P}} \cong -23$ ppm disappears upon thermal decomposition of the SDAs, it is explained by an effect of the structure-directing agent (SDA) on the local structure of one of the P(4OAl) tetrahedra [16].

For clarifying the signal assignment, the spatial neighbourhood of aluminum and phosphorus atoms in the framework of VPI-5 was investigated by two-dimensional <https://michael-hunger.de>

(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 interactions. 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 hydrated VPI-5 is depicted [20]. The cross-peaks observed in this spectrum indicate that each phosphorus atom ($\delta_{31\text{P}} = -33$ ppm, -27 ppm, and -23 ppm) is dipolarly coupled with tetrahedrally ($\delta_{27\text{Al}} = 41.6$ ppm and 43.6 ppm) as well as octahedrally ($\delta_{27\text{Al}} = -10.4$ ppm) coordinated aluminum atoms.

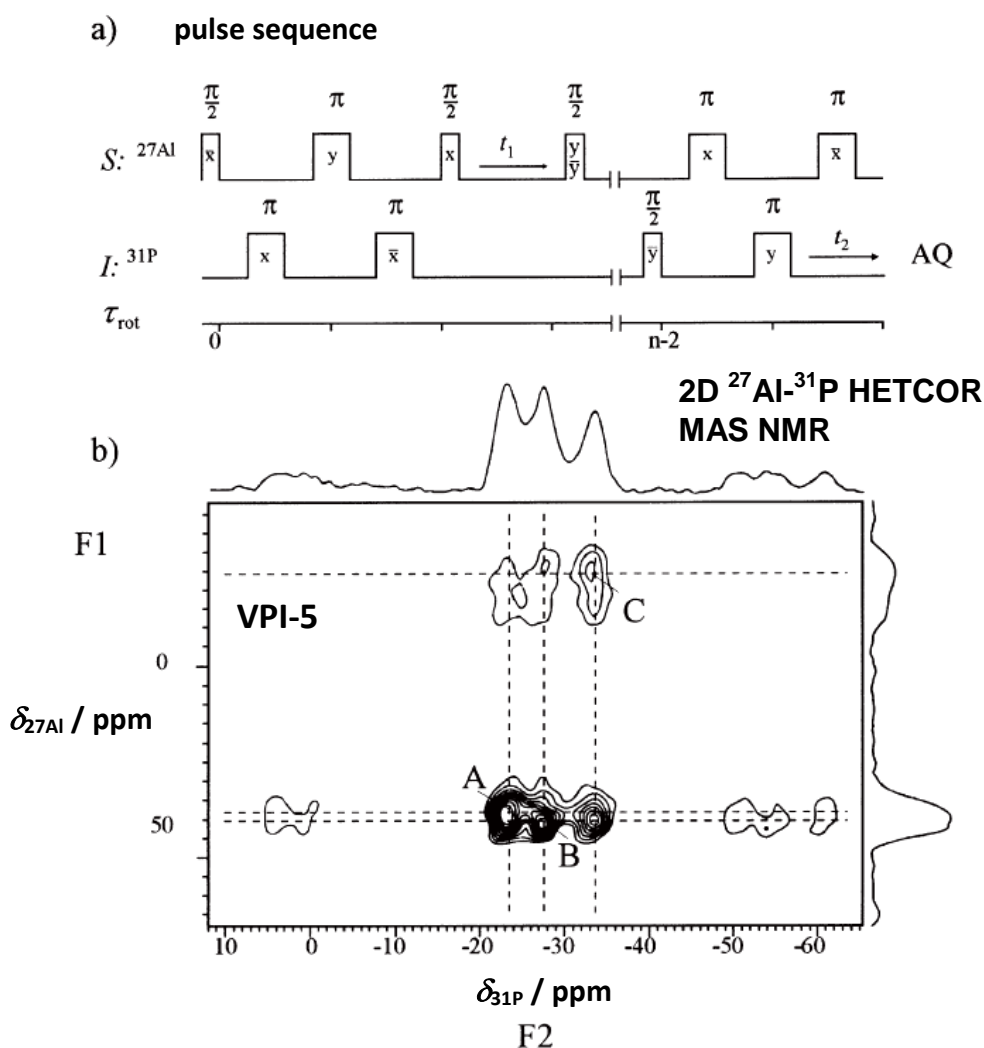


Fig. 2

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 AIPO-8 [14, 18, 19, 21]. The ^{31}P (left) and ^{27}Al MAS NMR spectra (right) were obtained for as-synthesized VPI-5, dried at $T = 333\text{ K}$ overnight (a), VPI-5, evacuated at $T = 327\text{ K}$ overnight and calcined at $T = 523\text{ K}$ overnight (b), AIPO-8, transformed from VPI-5 by calcination at $T = 673\text{ K}$ overnight (c), and hydrated AIPO-8 (d) [14]. The asterisks denote MAS sidebands.

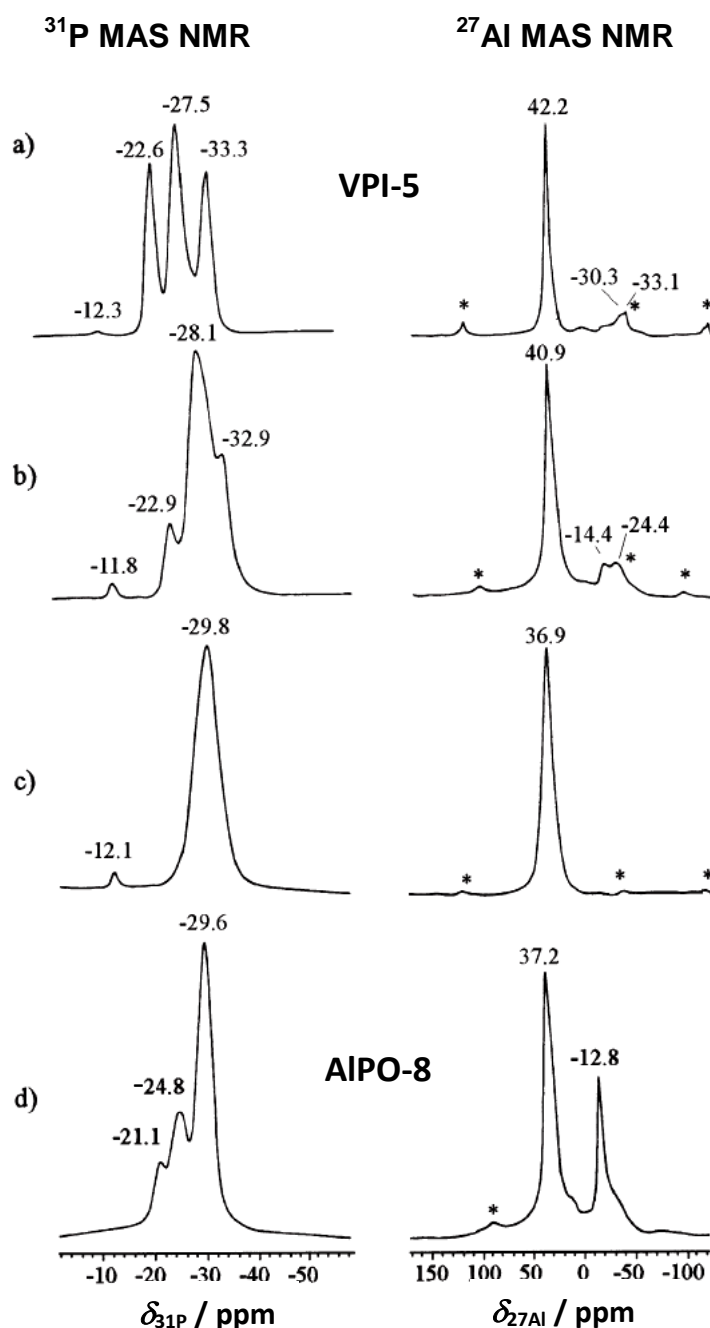


Fig. 3

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

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

Table 1 gives a survey on the ^{31}P solid-state NMR parameters of the above-mentioned and some additional zeolites.

Materials	P Species	$\delta_{31\text{P}}$ / ppm	Refs.
as-synthesized VPI-5	P(4OAl)	-33.3, -27.5, -22.6	[14, 17-20]
calcined AIPO-5	P(4OAl)	-27.8	[1]
calcined AIPO-8	P(4OAl)	-29.6, -24.8, -21.1	[14]
calcined AIPO-11	P(4OAl)	-30.2, -23.3	[1]
calcined AIPO-14	P(4OAl)	-32.0, -27.1, -21.9	[4]
calcined AIPO-17	P(4OAl)	-34.5, -29.0	[6]
calcined SAPO-5	P(4OAl)	-30.7	[5]
calcined SAPO-11	P(4OAl)	-30.2	[3, 11]
calcined SAPO-17	P(4OAl)	-34.5, -29.0	[6]
calcined SAPO-18	P(4OAl)	-27.0	[11]
calcined SAPO-31	P(4OAl)	-30.5	[5, 11]
calcined SAPO-34	P(4OAl)	-30.3	[5, 24]
calcined SAPO-37	P(4OAl)	-26.0	[24]
as-synthesized ZAPO-5	P(4OAl)	-30	[12]
	P(3OAl,1OZn)	-22	[12]
	P(2OAl,2OZn)	-16	[12]

calcined ZAPO-5	P(4OAl)	-26	[12]
as-synthesized MgAPO-5	P(4OAl)	-30	[12]
	P(3OAl,1OMg)	-24	[12]
calcined MgAPO-5	P(4OAl)	-31	[12]
as-synthesized MgAPO-20	P(4OAl)	-34.9	[13]
	P(3OAl,1OMg)	-28.0	[13]
	P(2OAl,2OMg)	-21.1	[13]
	P(1OAl,3OMg)	-14.0	[13]
partially hydrolyzed P atoms	P(n OAl, m H ₂ O)	-18 to -14	[24, 25]

Table 1

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

³¹P MAS NMR studies: ³¹P MAS NMR measurements were carried out utilizing, e.g., a Bruker Avance III 400WB spectrometer at a resonance frequency of $\nu_0 = 161.9$ MHz with a 4 mm MAS NMR probe and a sample spinning rate of $\nu_{\text{rot}} = 10$ kHz, upon single pulse $\pi/2$ excitation, with a repetition time of at least 30 s, and high-power proton decoupling (HPDEC). For the parameters of 2D ²⁷Al-³¹P HETCOR MAS NMR <https://michael-hunger.de>

measurements, see Ref. [20]. Chemical shifts are referenced to 0.85 M H_3PO_4 ($\delta_{31\text{P}} = 0$ ppm).

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