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Distribution of cobalt in CoAPO-5 and CoAPO-11 studied by ^{31}P NMR

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Abstract

AlPO-5 and AlPO-11 containing cobalt were studied by diffuse reflectance electronic absorption spectroscopy in combination with ^{31}P NMR. Quantitative ^{31}P NMR and relaxation measurements (Carr–Purcell–Gill–Meiboom procedure) were performed on calcined samples with increasing amounts of paramagnetic cobalt on lattice positions. The isomorphous substitution of aluminium by cobalt leads to NMR-invisible phosphorus (up to 30%); at least the first and third sphere (P) have to become NMR invisible to explain the observed losses for the lowest cobalt loadings. The amount of undetectable phosphorus, however, does not increase proportionally to the cobalt content, suggesting clustering of cobalt on lattice positions, as previously reported for CoAPO-50.

The ^{31}P T_2 relaxation behaviour of NMR-detectable phosphorus is also influenced by framework cobalt. The measured T_2 decays were fitted with a biexponential Lorentzian function. Both the T_2 values, as well as the relative contributions, change with increasing amounts of lattice cobalt. Impregnated samples (containing extralattice cobalt) behave essentially like normal aluminophosphates. This is probably due to the poor dispersion of cobalt throughout the crystal in the impregnated samples.

Keywords: Clustering; CoAPO-5; CoAPO-11; diffuse reflectance electronic absorption spectroscopy; isomorphous substitution; quantitative ^{31}P NMR; relaxation behaviour.

Introduction

A few years after the introduction of AlPOs [1], Flanigen and co-workers introduced a great variety of ‘isomorphously’ substituted molecular sieves [2,3]. At present the most thoroughly investigated are, apart from the AlPOs, systems modified with silicon (SAPOs). Several review papers have been published on their syntheses, structures, absorption properties and the mechanisms of aluminium or phosphorus substitution [4–6]. However, the so-

called MeAPOs where divalent or trivalent metal ions (for instance Co, Cr, Mg) substitute for aluminium ions have been investigated only recently. These MeAPOs form an interesting group of molecular sieves since they are believed to be the first molecular sieves where bivalent cations are incorporated in the lattice. Framework substitution probably has an effect on the catalytic properties of these metals [7].

Various techniques have been applied to prove or indicate the framework position of the metals. Montes et al. [8] for example have studied VAPO-5 using electron spin resonance (ESR) spectroscopy (in combination with thermogravimetric analysis (TGA) and BET surface-area measurements) to

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prove the framework position of the vanadium metal. The observed hyperfine splitting was said to prove the isomorphous substitution. We have found, however, that impregnated AIPO-11 at low vanadium contents yields exactly the same ESR spectrum. So the observed high dispersion of the vanadium atoms is not enough proof for the framework substitution of the vanadium atoms.

Schoonheydt et al. [9] used diffuse reflectance electronic absorption spectroscopy to study the redox properties of CoAPO-5. Using this technique, they were able to study the cobalt environment (oxidation state and coordination number) in the molecular sieve and to judge how much cobalt was incorporated in the lattice. Later this technique was used by others to study the cobalt incorporation and environment in other structures [10]. However, electronic spectra of AIPO samples impregnated with cobalt salts (non-framework Co) also show that some of the cobalt atoms are in tetrahedral coordination. This is probably caused by the fact that cobalt atoms, present as cobalt oxide inside the pores of these molecular sieves, are in close interaction with the oxygen atoms of the lattice [10].

Manganese-substituted AIPO-5 and AIPO-11 were intensively characterized using conventional ESR techniques combined with electron spin-echo envelope modulation (ESEM) techniques. Recently, Levi et al. [11] showed with conventional ESR that the hyperfine splitting of Mn^{2+} species in MnAPO-5 was 90 G, equal to the observed hyperfine splitting of Mn^{2+} in octahedral coordination. In addition, ESEM showed that the isolated Mn^{2+} species, the only detectable species with this technique, interacts through weak dipolar interactions with an average of six ^{31}P nuclei at a distance of 5 Å, indicating the non-framework position of Mn^{2+} . ^2H modulation by D_2O adsorbed on MnAPO-5 could be simulated with four ^2H nuclei at a distance of 2.7 Å. Levi et al. concluded that Mn^{2+} was not isomorphously substituted in AIPO-5, not even at very low concentrations (0.2 mol%). However, Brouet et al. [12] used the same technique to study MnAPO-11 and concluded that

Mn^{2+} was interacting with two ^2H nuclei at a distance of 0.24 Å and two ^2H nuclei at a distance of 0.36 Å; this would suggest framework substitution of the Mn^{2+} . In a recent paper Brouet et al. [13] proposed preferential substitution of manganese in AIPO-11 based on ESEM measurements. The observation that two water molecules interacted with manganese, combined with the observation that manganese was not coordinated by three water molecules, made them conclude that manganese was preferentially incorporated on a 6–4 site in MnAPO-11.

To our knowledge there is only one case reported in the literature where the framework substitution of metal ions was found by NMR. Barrie and Klinowski [14] studied MgAPO-20 (sodalite structure) using ^{31}P magic angle spinning (MAS) NMR and observed several bands in the spectrum. They ascribed these resonances to $\text{P}((4-n)\text{O}-\text{Al}, (n)\text{O}-\text{Mg})$ and were able to calculate the framework composition from these spectra and to deduce from the results that the magnesium in the structure is strictly ordered [15]. MAS NMR was successful in this case because of the high level of magnesium substitution in combination with the fact that magnesium caused no broadening of the ^{31}P NMR spectral signal. Mg^{2+} is diamagnetic and its only naturally occurring NMR-active isotope has a low abundance and a very low gyromagnetic ratio.

In all other cases conventional and straightforward ^{31}P and ^{27}Al MAS NMR studies were unsuccessful [8,10,16]. Montes et al. [17] for example measured ^{31}P MAS NMR of CoAPO-5. They observed that, compared with AIPO-5, multiple and intense sidebands were present in the spectrum of CoAPO-5, generated by dipolar coupling with paramagnetic cobalt and/or increased chemical shift anisotropy (CSA). They ascribed the observed increase in anisotropy to strong dipolar couplings of phosphorus with paramagnetic cobalt, supporting the view that cobalt is primarily substituting for framework aluminium. Our own measurements, however, indicate that this increased anisotropy is also observed for AIPO-5 and AIPO-11 samples which are impregnated with a cobalt salt solution

(extraframework Co), in line with the observations of others [10].

^{51}V , ^{53}Cr and ^{59}Co MAS NMR studies are rather cumbersome in view of the rather low concentrations and the quadrupolar and paramagnetic nature of these transition metal ions. The latter property on the other hand makes it interesting to study the relaxation of ^{31}P in these systems. Preliminary experiments in our laboratories showed that the relaxation of ^{31}P is influenced by a nearby paramagnetic ion and that even the existence of NMR-invisible ^{31}P cannot be excluded. These experiments are somewhat reminiscent of the study of cadmium-containing glasses by ^{113}Cd NMR [18,19] and the ^{29}Si spin-lattice relaxation study of 2:1 phyllosilicate minerals [20].

In the literature there has been one report of ^{31}P T_2 measurements performed on AlPO-5 and SAPO-5 samples [21]. The study was performed to decide whether the broadening of the ^{31}P signal after water or methanol adsorption was caused by a decreased T_2 (homogeneous) or by a distribution in chemical shifts (inhomogeneous). It was concluded that line broadening of the ^{31}P NMR signal upon adsorption of water and methanol is caused by inhomogeneous broadening (site distribution), since the measured ^{31}P NMR linewidth was much larger than expected from the measured T_2 value. There was a substantial increase in T_2 (slower relaxation rate) upon dehydration which was ascribed to removal of the modulated dipolar coupling of ^{31}P with the water protons. Relaxation measurements performed on SAPO-5 samples with two different silicon contents gave ^{31}P T_2 values similar to those obtained from the corresponding AlPO-5 samples.

The aluminophosphates AlPO-5 and AlPO-11 both have one-dimensional pore systems: the dimensions for AlPO-11 are $6.7 \times 4.4 \text{ \AA}$ (elliptical) and $8 \text{ \AA}$ for AlPO-5 (cylindrical). A projection of the structures is drawn in Fig. 1. Table 1 lists the number of T atoms surrounding an Al site. Since the metals are supposed to be isomorphously substituting for Al, the figures listed in Table 1 also

TABLE 1

Number of T atoms surrounding a tetrahedral Al site in AlPO-5 and AlPO-11

Structure type	First sphere (P)	Second sphere (Al)	Third sphere (P)
AlPO-5	4	11	21
AlPO-11	4	11	20

represent the numbers of atoms surrounding the metals in lattice positions.

In the present paper, a contribution to the study of MeAPO-5 and MeAPO-11 by ^{31}P NMR will be presented. More particularly, quantitative ^{31}P NMR and relaxation measurements were performed. Apart from the MeAPOs, where Co, Cr or V was introduced into the mother liquor during the synthesis, also systems were studied in which the metals were incorporated a posteriori by impregnation. The differences in relaxation behaviour between the two systems are remarkable. Figures 2 and 3 may serve to illustrate these differences in spin-echo decays during Carr–Purcell–Gill–Meiboom (CPMG) experiments with CoAPO-11, containing different concentrations of cobalt, and similar differences found between MeAPO-11 samples differing in the metal species incorporated.

Experimental

Synthesis

Aluminophosphates (AlPOs) and MeAPOs were crystallized from gels with the following general composition:

$\text{P}_2\text{O}_5 \cdot (1-x/2) \text{Al}_2\text{O}_3 \cdot x\text{MeO}_y \cdot z \text{ template} \cdot \approx 40 \text{ H}_2\text{O}$
with $0.001 < x < 0.08$; $1.0 < z < 1.5$

The gels were prepared following essentially the procedures described in the patent literature [3,22]. Aluminium isopropoxide (Aldrich) or pseudo-boehmite (Condea) was added to a metal salt solution under high-shear mixing. The resulting

Fig. 1. Projection of AlPO-5 and AlPO-11 structures.

Fig. 2. ^{31}P T_2 curves of dry AlPO-11 and CoAPO-11 with different amounts of Co. Measurement method: CPGM (20 μs), 9.4 T (see Experimental section). The numbers in parentheses represent the weight percentage of metal in the samples.

viscous gel was mixed until homogeneous. Subsequently, orthophosphoric acid (Merck) was added while the temperature was controlled with a cryostat at 273 K. Finally, the template was added. Crystallization was performed by heating the gels at 463 K for 2 days under hydrothermal conditions

in teflon-lined static autoclaves (products designated MeAPO(wt% Me)). After the autoclaves were quenched, the crystals were separated from the mother liquor by sedimentation. Subsequently the samples were washed with distilled water on a filter. Calcination of the samples was performed

Fig. 3. ^{31}P T_2 curves of the different dry MeAPOs. Measurement method: CPGM (20 μs), 7.1 T (see Experimental section).

by heating the samples in a flow of dry oxygen at a rate of 5 K min^{-1} to 823 K and keeping them at the final temperature for 5 h.

Chemical analysis showed that the raw materials used for the synthesis of the aluminophosphates contained only minor amounts of contaminants; from the NMR measurements it was concluded that these contaminants did not interfere with the results. The characteristics of the prepared gels are indicated in Table 2.

Impregnated samples (designated Me(wt%)-AlPO-11) were prepared by slurrying calcined AlPO-11 in a diluted metal salt solution; the liquid (≈ 5 times the pore volume) was evaporated at 343 K. After impregnation, the samples were dried and calcined (indicated by C) as described above. After calcination the samples were slurried in water several times to remove metals from the outer surface of the crystals (indicated by W).

Chromium (III) acetate hydroxide, cobalt acetate

TABLE 2

Chemical composition of the gels, including the sources of raw materials

Sample	Al source ^a	Me source ^b	x	y	z	Template ^c
AlPO-5	B	—	—	—	1.5	TPA
AlPO-11	A	—	—	—	1	DPA
CoAPO-11	B	$\text{Co}(\text{OAc})_2$	0.001–0.08	1	1	DiPA
CrAPO-11	B	$(\text{OAc})_7\text{Cr}_3(\text{OH})_2$	0.01–0.02	$\frac{3}{2}$	1	DiPA
VAPO-11	A	VOSO_4	0.04	$\frac{3}{2}$	1	DiPA
CoAPO-5	B	$\text{Co}(\text{OAc})_2$	0.001–0.08	1	1.2	TEA

^a A, aluminium isopropoxide (Aldrich); B, pseudoboehmite (Condea).

^b Source of metal ions used in the synthesis.

^c DPA, dipropylamine; DiPA, diisopropylamine; TPA, tripropylamine; TEA, triethylamine.

and vanadyl sulphate were used as sources of chromium, cobalt and vanadium, respectively, for both the hydrothermally prepared and the impregnated samples.

Hydrothermally prepared samples are denoted as MeAPO-*n* (wt% Me) and impregnated samples as Me(wt%)-AlPO-*n*. All samples used in this paper were calcined. Hydration was performed by storing the samples in a desiccator with water for several days. Dry samples, used in the NMR experiments, were obtained by filling the MAS rotors with dried samples and heating the samples in the rotor (without cap) at 425 K for several hours. While the samples were still hot, the rotors were closed with tight-fitting Kel-F caps. ^{31}P MAS NMR measurements indicated that the samples stayed dry for at least 60 h in the closed rotors.

Characterization

X-ray powder diffraction data, to check the crystallinity of the molecular sieves, were collected on a Philips PW 7200 X-ray powder diffractometer using Cu K α radiation. *n*-Butane pore-volume determinations were performed on a Setaram electrobalance. Scanning electron microscopy and energy dispersive analysis by X-rays (EDAX) were done on a JEOL 840 A. Diffuse reflectance electronic absorption spectroscopy (DREAS) was performed on a Hitachi 150-20 spectrophotometer equipped with a diffuse reflectance unit.

^{31}P NMR was performed at 7.1 T on a Bruker CXP 300, or at 9.4 T on a Bruker MSL 400 spectrometer. For ^{31}P T_2 measurements, Hahn echoes as well as CPMG echo trains were used. A recycle delay of 60 s was found sufficiently long to record spectra and spin-echo decays which were unchanged at longer recycle delay times.

Hahn echos were recorded at a MAS frequency of 2.00 kHz (± 2 Hz) on a CXP-300, using rotor-synchronized pulsing, with and without external aluminium irradiation. The evolution time in the spin-echo experiment was systematically incremented with typically 10–15 values between 1 and 15 ms for dry samples and between 1 and 6 ms for

wet samples. The resulting ^{31}P NMR echo intensity was measured from the integral signal areas. Alternatively, the echo height was determined from the height of the biggest peak. Both methods gave identical results.

The CPMG procedure was applied to both stationary and spinning samples (10.0 kHz). The interval between two consecutive 180° pulses for static samples (2τ) was equal to 20 μs , unless otherwise indicated. For the CPMG measurements performed at 10.0 kHz (± 5 Hz) the interval between two consecutive 180° pulses was equal to 100 μs (one rotor period). Because of the rotor synchronization, the generation of rotational echoes is then avoided [23]. The CPMG pulse train is depicted in Fig. 4.

For the quantitative measurements $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ was used as an internal standard. The standard was thoroughly mixed with the wet samples in a ratio of 1:3 (weight). Spectra were recorded under MAS conditions (10 kHz) using a recycle delay of 600 s, because of the slow relaxation of the internal standard. High-power ^1H decoupling was applied to suppress the dipolar coupling of the protons of the crystal water with the phosphorus of the internal standard. An instrument deadtime of 5 μs was used with a 90° pulse length of 3 μs .

Results and discussion

The composition of the starting gel, the weight percentage of metal in the crystallization product and the surface composition of the crystals of some samples as determined with EDAX are listed in Table 3. Also listed in Table 3 are the metal loadings of the impregnated samples and the measured pore volumes of the samples as determined by *n*-butane adsorption. It can be concluded that the metal content of the impregnated and hydrothermally prepared samples are of the same order of magnitude (atomic absorption spectrometry (AAS) measurements).

EDAX measurements indicate that for the hydrothermally prepared samples, except CrAPO-

Fig. 4. The Carr-Purcell-Gill-Meiboom (CPMG) pulse sequence.

TABLE 3

Molar composition of the gel and characteristics of some typical products

Sample	Molar gel composition: wt% Me in product (AAS)	Surface composition (EDAX)	Pore volume (ml g ⁻¹)
AlPO-11	P ₂ O ₅ :Al ₂ O ₃ :DPA:35 H ₂ O 0 wt% Me	0 wt% Me	0.095
AlPO-5	P ₂ O ₅ :Al ₂ O ₃ :1.5 TPA:40 H ₂ O 0 wt% Me	0 wt% Me	0.130
CoAPO-11(1.0)	P ₂ O ₅ :Al ₂ O ₃ :0.04 CoO:DiPA:50 H ₂ O 1.06 wt% Co	1.4 wt% Co	0.082
CrAPO-11(1.87)	P ₂ O ₅ :Al ₂ O ₃ :0.12 Cr ₂ O ₃ :2 DiPA:40 H ₂ O 1.87 wt% Cr	9.2 wt% Cr	0.089
VAPO-11(0.85)	P ₂ O ₅ :Al ₂ O ₃ :0.04 V ₂ O ₅ :DiPA:50 H ₂ O 0.85 wt% V	0.7 wt% V	0.088
Co(0.6)AlPO-11	0.61 wt% Co	1.8 wt% Co	0.037
Cr(0.8)AlPO-11	0.76 wt% Cr	5.9 wt% Cr	0.042

Abbreviations as in Table 2.

11, the surface composition is almost equal to the bulk composition. Comparison of hydrothermally synthesized samples with those prepared by impregnation, both with low metal contents, show that the latter samples contain higher surface metal concentrations. The clear drop in pore volume of the impregnated samples, indicating pore blockage, can be caused by metal deposition in the pores and/or pore-mouth blockage. Furthermore, in agreement with literature data we found that a fraction of the cobalt atoms after impregnation are

in tetrahedral coordination, indicating the close interaction with the lattice of AlPO-11.

³¹P pulse NMR was performed on the hydrothermally prepared samples, as well as on the impregnated samples. The presence of the metals in the samples, in lattice or extralattice positions, did not result in the appearance of multiple peaks in either of the MAS NMR spectra. For both the hydrothermally prepared and the impregnated samples, the presence of the metals leads to the formation of intense spinning sidebands. The

occurrence of these spinning sidebands is, therefore, no indication of the incorporation of the metals in the AlPO lattice [8,10].

^{31}P T_1 measurements using the inversion-recovery technique indicated that the metals have a profound influence on the T_1 values. Table 4 depicts the T_1 values for some characteristic samples. First of all, the T_1 value strongly depends on the hydration state of the sample. Hydration of AlPO-11, for example, leads to an increase of the T_1 value by a factor of 25 to approximately 40 s. This is largely due to the exclusion of oxygen from the samples upon water absorption, because for a dry AlPO-11 sample (without oxygen) the T_1 value increases to 25 s. A large decrease of the T_1 values for wet samples is observed due to the presence of the metals, lattice and/or extralattice. In this case, the effect of metals is more explicit as there seem to be no other effective sources of longitudinal ^{31}P relaxation. The overall results, however, indicate that T_1 measurements do not allow one to make a distinction between the different samples.

Quantitative ^{31}P NMR measurements

Normally, MAS NMR on non-quadrupolar, non-disturbed nuclei, like ^{31}P , can be performed without any difficulty. Quantitative ^{31}P MAS NMR experiments, to check the amount of ^{31}P visible with MAS NMR, were performed using $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ as an internal standard. Measurements were done at a MAS frequency of

TABLE 4

T_1 values of various products

Sample	T_1 (s) (wet)	T_1 (s) (dry)
AlPO-11	40.0	1.4
AlPO-11 (N_2)	—	25
CrAPO-11(1.87)	0.5	0.42
Cr(0.8)AlPO-11	2.6	1.14
CoAPO-11(1.0)	3.0	1.5
Co(0.6)AlPO-11	23.0	2.8

10.0 kHz with a recycle delay of 600 s. The samples were measured in a fully hydrated state to suppress the abstraction of water of crystallization from the trisodium phosphate by the aluminophosphates, which would result in multiple ^{31}P NMR signals (overlapping signals) and a large anisotropy for the internal standard.

In order to obtain quantitatively meaningful determinations, the peaks visible in the ^{31}P MAS spectrum at 10 kHz, including spinning sidebands if any, were integrated. From Table 5 (column 3)

TABLE 5

Quantitative ^{31}P NMR measurements

Sample	wt% Me ^a (AAS)	Internal Standard ^b Wet	CPGM ^c	
			Dry	Wet
<i>9.4 T</i>				
AlPO-11	0	100	100	100
AlPO-5	0	100	100	100
CoAPO-11(0.03)	0.03	71	96	
CoAPO-11(0.31)	0.31	62	76	
CoAPO-11(0.63)	0.63	55	79	
CoAPO-11(1.31)	1.31	60	90	
CoAPO-11(2.2)	2.2	48	71	
CoAPO-5(0.042)	0.042	92	91	
CoAPO-5(0.33)	0.331	73	91	
CoAPO-5(0.75)	0.75	68	93	
CoAPO-5(1.54)	1.54	71	71	
CoAPO-5(2.5)	2.5	61	81	
CoAPO-5(5.0)	5.0	64	69	
<i>7.1 T</i>				
AlPO-11	0	100	100	100
Co(1.5)AlPO-11C	1.5	65		
Co(0.6)AlPO-11CW	0.61	71	101	109
Co(1.0)AlPO-11C	0.98	72		
Co(0.5)AlPO-11CW	0.49	73		
CrAPO-11(1.87)	1.87	65	55	56
CrAPO-11(1.42)	1.42	67		
Cr(1.1)AlPO-11C	1.06	94	93	107
Cr(0.8)AlPO-11CW	0.76	93		
VAPO-11(0.85)	0.85	81	83	80

^a Weight percentage of metal as determined with AAS.

^b Amount of ^{31}P visible by NMR measured with $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ as internal standard; $D_0 = 600$ s; dead time = 5 μs ; number of scans = 4; wet samples; 10.0 kHz MAS.

^c Echo height of spin-echo measurements, referenced to AlPO-11; static samples, $\tau_1 = 20$ μs ; $C = 50$ (total measurement period 1 ms).

it can be seen that all the phosphorus in AlPO-11 can be detected with MAS NMR. The hydrothermally prepared MeAPOs, however, suffer from a large loss of signal. The presence of ≈ 0.03 wt% of paramagnetic cobalt results in a decrease of the ^{31}P NMR signal by ≈ 10 –30%. The further decrease of NMR-visible phosphorus with increasing concentrations of cobalt is less pronounced. When 2% of cobalt is present in the samples, the amount of visible ^{31}P decreases to about 50%. The loss of ^{31}P NMR signal at comparable metal loadings is less for the impregnated samples, although magnetic susceptibility measurements show that these samples are equally paramagnetic.

During spin-echo measurements, the amount of phosphorus detectable by NMR has been estimated from the full signal amplitudes (extrapolated to zero deadtime) as compared to AlPO-11. Using this approach, both dry and wet samples were measured. It can be concluded that with this technique the amount of non-detectable phosphorus decreases significantly. This is probably due to the instrument's deadtime of 5 μs in straight-forward pulse NMR experiments. Especially, a large gain is achieved for the ^{31}P NMR signal of the impregnated samples. The extremely fast relaxation of the hydrothermally prepared MeAPOs, however, still makes it impossible to observe phosphorus quantitatively. The percentage of phosphorus visible in these samples is limited to approximately 70–90%.

The incorporation of cobalt in aluminophosphates can be studied by DREAS. The incorporation of cobalt in the lattice of the aluminophosphates gives the samples an intense blue colour (tetrahedral coordination). The intensity of this colour (converted to the Kubelka–Munk function [24]) is proportional to the amount of cobalt incorporated. Although non-framework cobalt (impregnated) shows a much less pronounced absorption at 500–650 nm, the intensity of the DREAS signal should be considered to be the upper limit of the amount of framework cobalt. Both the CoAPO-5 and the CoAPO-11 samples were characterized using this technique. It

is clear that the amount of cobalt that may be incorporated into the AlPO-5 structure is somewhat higher than for the AlPO-11 structure under comparable conditions. For CoAPO-5 the linear relationship between the intensity of the DREAS bands and the weight percentage of cobalt exists up to approximately 2 wt%, while for CoAPO-11 deviation from this relationship begins already at 1–1.5 wt% (Fig. 5). Furthermore, the integrated DREAS intensity for the CoAPO-11 samples are lower at the same weight percentage of cobalt, indicating that there is probably a small fraction of the cobalt not incorporated in the lattice, but present in the pores of the molecular sieve.

As regards the amount of ^{31}P visible with NMR, using the full signal amplitude (extrapolated to zero deadtime) obtained from the CPMG measurements reveals some remarkable features (Table 5, column 4). The amount of ^{31}P which becomes NMR invisible is considerable, even for the lowest cobalt concentrations. To explain the large loss of ^{31}P signals, as measured with the CPMG procedure, at least the first and second phosphorus spheres (first and third spheres) (see Table 1) have to become NMR invisible, and probably additional ^{31}P nuclei as well. Furthermore, if two of the phosphorus spheres become NMR invisible, one would expect that, with approximately 2 mol% cobalt, phosphorus would become completely undetectable by NMR. In Fig. 6 the percentage of ^{31}P visible with NMR as a function of the DREAS intensity is displayed. Since this DREAS intensity is correlated with the amount of tetrahedrally incorporated cobalt, Fig. 6 gives the correlation between the amount of lattice cobalt and the remaining ^{31}P NMR signal. The line drawn in this graph is the expected loss of ^{31}P NMR signal as a function of the DREAS intensity, assuming random distribution of cobalt and the invisibility of the two nearest phosphorus spheres. The observed loss of ^{31}P signal for both samples is smaller than the expected loss. A possible explanation is clustering of the cobalt atoms, which would result in a smaller loss of ^{31}P NMR signal, since an overlap in the first and/or third coordination spheres with

Fig. 5. Integrated intensity of DREAS spectra as a function of the weight percentage of cobalt.

Fig. 6. Percentage of NMR visible ^{31}P as a function of the integrated intensity (DREAS). Symbols as in Fig. 5.

random cobalt incorporation would occur only for lattice concentrations larger than about 2 wt%.

The structure of CoAPO-50, an aluminophosphate with a 12-ring pore opening and one-dimensional channels, has been solved by single-crystal X-ray studies [25]. Up to 25% of the aluminium could be replaced by cobalt, suggesting the existence of Co–O–P–O–Co sequences. From the data it could be concluded that four-membered rings existed, consisting of two cobalt and two phosphorus atoms. The existence of this type of unit, even at low cobalt contents, could be a possible explanation of the ^{31}P NMR observations for CoAPO-5 and CoAPO-11.

Despite the large variation in the amount of phosphorus detectable by NMR, it seems clear that the clustering of cobalt is more pronounced for the CoAPO-5 samples. AAS measurements indicated that the uptake of cobalt in the aluminophosphate crystals of CoAPO-5 is higher than the fraction in the gel, indicating preferential incorporation of cobalt.

Spin-echo measurements

^{31}P spin-echo measurements were carried out on stationary samples using a CPMG procedure. In all cases the resulting time constants of the decay curves depend on the length of the τ_1 period (see Fig. 4). These time constants will henceforth

be denoted as T_2 values. The dependence of the T_2 values upon τ_1 is understandable since, during the interpulse period, the relaxing nuclei evolve under the influence of a Hamiltonian which is a combination of chemical-shift and dipolar influences. The latter effect will become relatively smaller for small pulse interval times [19]. The influence of the magnitude of τ_1 upon the T_2 components is shown explicitly for AlPO-11 in Table 6. This sample shows the slowest overall relaxation, so the τ_1 period can in practice be varied over a rather broad range. The long τ_1 value of 200 μs is incorporated in order to enable a comparison with experiments carried out under conditions of MAS (see below). In this study, comparisons between T_2 values of different samples will be made only between results obtained with one τ_1 value, *i.e.* 20 μs . Decreasing the value of τ_1 of course leads to an increase of the observed T_2 values.

MAS reduces the homonuclear and heteronuclear dipolar interactions and is likely to have an influence on both T_1 and T_2 relaxation times. The influence of MAS was investigated by applying the CPMG procedure to dry AlPO-11. The τ_1 period was chosen to be 200 μs . This allowed the measurements to be performed at 0, 5 and 10 kHz (0, 1, 2 rotor periods). The results are listed in Table 7. MAS results in a drastic increase of the observed T_2 values. The largest changes are, how-

TABLE 6

Influence of τ on the measured relaxation of AlPO-11 using the CPMG method (static samples); total measurement period $C\tau_1 = \tau$

Hydration state	C^a	$\tau_1(\mu\text{s})$	Slow component		Fast component	
			Amplitude	T_2 (ms)	Amplitude	T_2 (ms)
Dry	50	20	90.2	248	9.9	18.8
Dry	30	33.3	85.5	197.3	14.5	16.9
Dry	5	200	17.0	9.9	168.6	1.5
Wet	50	10	45.1	23.2	58.4	7.6
Wet	25	20	33.8	14.5	73.4	4.6
Wet	30	33.3	35.4	9.2	92.5	3.2
Wet	10	50	78.6	4.0	92.1	0.95

^a Number of τ_1 intervals in the T_2 measurement cycle.

TABLE 7

Influence of the MAS frequency on ^{31}P T_2 measurements of dry AlPO-11

MAS frequency (kHz)	Slow component		Fast component	
	Amplitude	T_2 (ms)	Amplitude	T_2 (ms)
0	17.0	9.9	168.6	1.5
5.0	86.7	159.3	15.0	19.8
10.0	82.6	166.9	19.2	26.0

CPGM procedure; $\tau_1 = 200 \mu\text{s}$; 7.1 T.

ever, observed going from 0 to 5 kHz; the slow component gains importance (increases from 17% to 87%) and the corresponding T_2 value increases from 10 to 160 ms. The differences between 5.0 and 10.0 kHz are only minor.

Reported here are measurements with a τ_1 period of 20 μs . The decrease of the echo height was fitted with a two-exponential curve of the following shape (Lorentzian):

$$I(t) = I(0) \exp(-t/T_2) + I(0)' \exp(-t/T_2')$$

The use of three exponents did not give any further improvement of the fit.

The absence of an efficient averaging of the spin interactions in solids often leads to a free-induction decay (FID) signal given by a more complicated time function, which can be approximated by the Gaussian function [26]

$$I(t) = I(0)/\sqrt{(\pi T_{2s})} \exp(-t/T_{2s})^2$$

The observed decay in the present study can, however, not be satisfactorily described by these inverted S-shaped curves. Therefore, the ^{31}P signal of AlPO-11 probably consists of several overlapping Lorentzian-shaped signals.

The results are summarized in Tables 8 and 9 and Figs 2, 3, 7 and 8. It should be emphasized that the following discussion pertains to that part of the ^{31}P nuclei that remain visible by NMR. In our view, this excludes the ^{31}P nuclei in the first and third coordination spheres around the metal ions in hydrothermally prepared samples. Figure 7 shows that the T_2 values of dry AlPO-11, impreg-

TABLE 8

 ^{31}P T_2 measurements of dry samples

Sample	Slow component		Fast component	
	Amplitude	T_2 (ms)	Amplitude	T_2 (ms)
7.1 T				
AlPO-5	97.1	332	4.5	6.3
AlPO-11	90	250	10	18.8
CrAPO-11(1.87)	28	34	78	3.1
CoAPO-11(1.0)	80	136	21	11.0
VAPO-11(0.85)	75	115	27	10.9
Co(0.6)AlPO-11	88	335	11	15.0
Cr(0.8)AlPO-11	78	200	22	14.5
V(1.4)AlPO-11	98	495	3.3	4.7
9.4 T				
AlPO-11	93	319	6	22.0
	97	282		
CoAPO-11(0.03)	97	269	3	0.4
CoAPO-11(0.30)	89	200	11	15.8
CoAPO-11(0.50)	87	196	13	15.2
CoAPO-11(1.0)	84	172	16	14.5
CoAPO-11(1.95)	79	145	21	13.9
AlPO-5	90	349	9	14.7
	94	301		
CoAPO-5(0.042)	92	373	7	17.7
CoAPO-5(0.33)	85	184	15	17.5
CoAPO-5(0.63)	72	120	28	17.8
CoAPO-5(1.31)	65	145	34	15.7
CoAPO-5(2.2)	66	93	33	13

CPGM procedure; 20 μs ; static samples.

TABLE 9

 ^{31}P T_2 measurements of wet samples

Sample	Slow component		Fast component	
	Amplitude	T_2 (ms)	Amplitude	T_2 (ms)
7.1 T				
AlPO-11	35.1	15.3	81.2	5.0
CoAPO-11(1.0)	10.7	113	96.8	7.3
CrAPO-11(1.87)	22.5	46.0	88.7	2.3
VAPO-11(0.85)	66.4	10.1	55.5	2.9
Co(0.6)AlPO-11	33.0	14.8	72.5	4.7
Cr(0.8)AlPO-11	51.3	10.1	57.1	3.4

CPGM procedure; 20 μs ; static samples.

Fig. 7. ^{31}P T_2 curves of dry AlPO-11, Co(0.6)AlPO-11 and Cr(0.8)AlPO-11 (impregnated samples). Measurement method: CPMG ($20\ \mu\text{s}$), 7.1 T, static samples.

Fig. 8. ^{31}P T_2 curves of dry AlPO-5 and CoAPO-5 with different amounts of Co. Measurement method: CPMG ($20\ \mu\text{s}$), 9.4 T, static samples.

nated dry $\text{Co}(0.6)\text{AlPO-11}$ and $\text{Cr}(0.8)\text{AlPO-11}$ are of the same order of magnitude. In other words, impregnation of AlPO-11 samples with these paramagnetic ions does not result in a significant decrease of the T_2 relaxation time. On the other hand, the hydrothermally prepared MeAPOs show a significant decrease of the T_2 values compared with the AlPOs. The curves in Fig. 2 show that the T_2 values of CoAPO-11 decrease strongly with increasing amounts of incorporated cobalt. For AlPO-11 the T_2 value changes from approximately 320 ms (monoexponential) to a biexponential decay with T_2 values of 145 ms (80%) and 14 ms (20%) for CoAPO-11(1.95). The sample with the lowest concentration of cobalt, CoAPO-11(0.03), seems to be unaffected by the presence of the cobalt ions. Nearly the same results are obtained with the CoAPO-5 samples (Fig. 8). Here, the lowest concentration of cobalt apparently leads to a small increase of the T_2 values. Increasing amounts of cobalt also lead to a monotonic (not linear) decrease of the T_2 values. From Fig. 3 it can be seen that the same effects are observed with other MeAPOs (for instance Cr, V).

Wetting of the samples in all cases leads to drastic changes in the measured overall T_2 behaviour. Both the T_2 values and their relative contributions change. For CrAPO-11(1.87), the system with the shortest relaxation time in the dry state, the changes are only minor. The T_2 value of the largest component changes from 3.1 to 2.1 ms. Remarkably, this is the only system where wetting of the samples causes an increase of one of the contributing T_2 values (small contribution). All other samples show a significant decrease of the T_2 values. The T_2 values of AlPO-11 for example decrease from 220 to 8 ms. The presence of paramagnetic chromium acts as an efficient relaxator; the increase of the relaxation rate by water cannot further accelerate this process.

It should be noted that wetting of the AlPO-11 samples causes a change of the crystal symmetry [27] which can be monitored by X-ray diffraction and ^{31}P NMR. The ^{31}P MAS NMR spectrum of dry AlPO-11 (three crystallographically different

sites [28]) shows only one signal while the spectrum of wet AlPO-11 exhibits two signals (five crystallographic sites) in a ratio of 4:1. It is, however, not possible to assign the two T_2 components in the AlPO-11 ^{31}P MAS NMR spectrum to the two T_2 components measured. This becomes immediately evident upon comparing the results of the dry and wet samples.

We feel, however, that the decrease of T_2 upon water adsorption is not caused by dipolar coupling with water protons as supposed in Ref. [21] but, to a large extent, by the change in symmetry of the system. The dipolar coupling of ^{31}P with water can be eliminated with high power ^1H decoupling. The decoupling of the water protons in wet samples leads to a small increase of the T_2 value but the resulting value is still much shorter than the T_2 obtained from the corresponding dry sample. The results of these measurements are listed in Table 10 and displayed in Fig. 9.

The observed biexponential decay for dry AlPO-5 and AlPO-11 cannot be explained by the presence of different P sites or a small amount of water. All T sites in dry AlPO-5 are equivalent while dry AlPO-11 has three different sites in a ratio 1:2:2. It is clear that the observed fast decay (approximately 10%) cannot be due to the presence of different sites on the basis of this ratio. The effect of water can be excluded on the basis of the CPMG measurements done at 10.0 kHz. In these experiments, complete FIDs were recorded after varying numbers of echoes, allowing the study of the two peaks independently (MAS conditions). Both signals in wet samples turn out to exhibit a biexponential behaviour with approximately equal relative contributions of slow- and fast-relaxing components. Therefore, we think that the observed biexponential decay is due to the τ_1 value chosen at the given magnetic field. The T_2 decay of the AlPO-11 sample behaves almost monoexponentially at 9.4 T while, with the same conditions at 7.1 T, the behaviour is clearly biexponential.

For the CoAPO samples with different cobalt contents a gradual increase of the fast-relaxing component is observed, together with a decrease

TABLE 10

Effect of ^1H decoupling on the T_2 values of wet and dry samples

Sample	Slow component		Fast component		Conditions
	Amplitude	T_2 (ms)	Amplitude	T_2 (ms)	
AlPO-11	67.7	10.3	40	3.2	^1H decoupling Dry
	80.1	19.7	22.3	6.1	
	90.0	250	10	18.8	
CrAPO-11(1.87)	23.1	41.4	89.8	2.2	^1H decoupling Dry
	27.5	36.2	79.6	2.7	
	38.0	34	78	3.1	
Cr(0.76)AlPO-11	51.3	10.1	57.1	3.4	^1H decoupling Dry
	70.8	16.1	33.0	4.6	
	78	200	22	14.5	

CPGM procedure; 20 μs ; static samples. Fig. 9. Effect of ^1H decoupling on the relaxation of wet samples. Measurement method: CPMG (20 μs), 7.1 T, static samples.

of the T_2 value of the slow-relaxing component. This indicates that the cobalt also has a large influence on the phosphorus which can be detected with the CPMG procedure. The gradual increase of the fast-relaxing fraction with the cobalt content is a strong indication that the observed biexponen-

tial decay is realistic and not due to the choice of the τ_1 value.

Hahn echoes were performed on the same samples at a MAS frequency of 2.00 kHz. The period between the $\pi/2$ pulse and the π pulse (τ) was increased by typically 0.5 ms (one rotor period)

between 1 and 15 ms. The observed echo heights could be fitted with a single exponential decay. The results of these experiments are listed in Table 11 and Figs 10 and 11. The observed trend in the CPGM measurements on static samples is also found here. The differences between the different samples are, however, smaller. This is probably caused by the long period (at least 0.5 ms) before the first echo can be measured. During this period, a large fraction of the fast-relaxing phosphorus has relaxed, and the signal is lost before

the measurement starts. What remains is a larger fraction of the phosphorus which is unaffected by the incorporated metals. Therefore, the observed differences between the samples become smaller. Relaxation of ^{31}P is enhanced by external ^{27}Al irradiation, in line with the findings reported by van Eck et al. [29].

The remaining question is how the large influences of paramagnetic metals on a spin $\frac{1}{2}$ nucleus can be explained. One possibility could be the anisotropic dipolar coupling of ^{31}P and the

TABLE 11

Results of ^{31}P T_2 experiments

Sample	Dry sample		Wet sample	
	T_2 (ms)	T_2 irr. ^a (ms)	T_2 (ms)	T_2 irr. ^a (ms)
<i>7.1 T</i>				
AlPO-11	7.7	0.62	2.90	0.37
CrAPO-11(1.87)	4.03	0.16	2.26	0.54
Cr(0.71)AlPO-11	6.83	0.67	2.90	0.29
CoAPO-11(1.0)	6.97	1.03	3.3	0.31
Co(0.6)AlPO-11	8.0	0.45	2.2	0.270

Hahn echo; 2.0 kHz.

^a Value when external ^{27}Al irradiation is applied. Fig. 10. ^{31}P T_2 curves of some dry MeAPOs. Measurement method: Hahn echoes, 2.00 kHz, 7.1 T.

Fig. 11. ^{31}P T_2 curves of some wet MeAPOs. Measurement method: Hahn echoes, 2.00 kHz, 7.1 T.

unpaired electrons of the paramagnetic metal ion, resulting in a decreased T_2 value. This interaction is strongly dependent upon the distance between the two interacting species. In hydrothermally prepared samples, where the metal ion is assumed to substitute for aluminium, the shortest distance between ^{31}P nuclei and the metal ions is approximately equal to the sum of the P–O and Al–O bond length: $\approx 3.2 \text{ \AA}$. If the metal ion after impregnation is located in the pores of the molecular sieve, the distance would be maximally equal to half of the longest pore diameter: $\approx 3.2 \text{ \AA}$. It is immediately clear that this effect is unable to explain the experimental data. This fact, together with the surface enrichment measured with EDAX, indicates that after impregnation the metals are not homogeneously dispersed throughout the crystals, but concentrated at the outer region of the crystals. The observed strong influence of the metals in the hydrothermally prepared samples indicates a distribution of metal nuclei throughout the crystals, suggesting isomorphous substitution of aluminium. At higher loadings, clustering of cobalt in lattice positions occurs (see above). Supposedly, the bonding between metals and aluminophosphates is ionic after hydrothermal synthesis

and coordinative after impregnation. The influence of the metals on ^{31}P relaxation may well be different in the two cases.

Conclusions

Strong indications of isomorphous framework substitution of cobalt in AlPOs can be obtained by DREAS. The observed pore volumes and the special redox properties of cobalt in this environment are supporting evidence.

Quantitative aspects of direct-pulsed NMR and of NMR spin-echo measurements proved to be rather useful methods to distinguish framework substitution from extraframework depositions. Framework substitution of aluminium by cobalt, chromium or vanadium influences a major part of the ^{31}P in the crystal. At least the first and the third coordination spheres (P) around the metal nuclei become NMR invisible. Extralattice metals do not seem to have a significant effect. EDAX indicates that large portions of the metals are located in the outside region of the particles after impregnation.

DREAS confirmed the framework substitution of cobalt for the CoAPO-5 and CoAPO-11 samples. However, ^{31}P NMR indicated that increased amounts of framework cobalt had only a small effect on the amount of ^{31}P visible. This would suggest clustering of cobalt, earlier proposed for CoAPO-50.

The ^{31}P T_2 relaxation of visible phosphorus in MeAPOs is strongly influenced by the presence of isomorphously substituted paramagnetic ions. An increase of the amount of substitution has two effects: the contribution of the fast T_2 increases and the T_2 value of the slow decay decreases. Impregnation of samples with the metal salts followed by calcination does not have such a great impact. This is explained by the poor dispersion and/or the absence of chemical bonding in the latter case.

The existence of several ^{31}P signals in single-pulse experiments for dry CoAPO, where the metal is paramagnetic, is not expected.

Straightforward ESR and ESEM may yield information on the surrounding of the metals. ESR and ESEM measurements are planned.

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References

- 1 S.T. Wilson, B.M. Lok, C.A. Messina, T.R. Cannan and E.M. Flanigen, *J. Am. Chem. Soc.*, 104 (1982) 1146–1147.
- 2 B.M.T. Lok, B.K. Marcus, L.D. Vall, E.M. Flanigen, R.L. Patton and S.T. Wilson, European Patent 159,624, 1985.
- 3 S.T. Wilson and E.M. Flanigen, U.S. Patent 4,567,029, 1986.
- 4 J.A. Martens, C. Janssens, P.J. Grobet, H.K. Beyer and P.A. Jacobs, in P.A. Jacobs and R.A. van Santen (Eds), *Zeolites, Facts, Figures, Future*, Elsevier, Amsterdam, 1989, pp. 215–225.
- 5 J.A. Martens, P.J. Grobet and P.A. Jacobs, *J. Catal.*, 126 (1990) 299–305.
- 6 P.P. Man, M. Briend, M.J. Peltre, A. Lamy, P. Beaunier and D. Barthomeuf, *Zeolites*, 11 (1991) 563–572.
- 7 S. Prasad and I. Balakrishnan, *Catal. Lett.*, 11 (1991) 105–110.
- 8 C. Montes, M.E. Davis, B. Murray and M. Narayana, *J. Phys. Chem.*, 94 (1990) 6425–6430.
- 9 R.A. Schoonheydt, R. de Vos, J. Pelgrims and H. Leeman, in P.A. Jacobs and R.A. van Santen (Eds), *Zeolites, Facts, Figures and Future*, Elsevier, Amsterdam, 1989, pp. 559–568.
- 10 B. Kraushaar-Czarnetzki, W.G.M. Hoogervorst, R.R. Andréa, C.A. Emeis and W.H.J. Stork, *J. Chem. Soc. Faraday Trans.*, 87(6) (1991) 891–895.
- 11 Z. Levi, A.M. Raitsimring and D. Goldfarb, *J. Phys. Chem.*, 95 (1991) 7830–7838.
- 12 G. Brouet, X. Chen and L. Kevan, *J. Phys. Chem.*, 95 (1991) 4928–4929.
- 13 G. Brouet, X. Chen, C.W. Lee and L. Kevan, *J. Am. Chem. Soc.*, 114 (1992) 3720–3727.
- 14 P.J. Barrie and J. Klinowski, *J. Phys. Chem.*, 93 (1989) 5972–5974.
- 15 P.J. Barrie, M.E. Smith and J. Klinowski, *Chem. Phys. Lett.*, 180 (1991) 6–12.
- 16 D. Goldfarb, *Zeolites*, 9 (1989) 509–515.
- 17 C. Montes, M.E. Davis, B. Murray and M. Narayana, *J. Phys. Chem.*, 94 (1990) 6431–6435.
- 18 D.R. Franke and H. Eckert, *J. Phys. Chem.*, 95 (1991) 331–336.
- 19 D.R. Franke, R. Maxwell, D. Lathrop and H. Eckert, *J. Am. Chem. Soc.*, 113 (1991) 4822–4830.
- 20 P.F. Barron, P. Slade and R.L. Frost, *J. Phys. Chem.*, 89 (1985) 3305–3310.
- 21 I. Kustanovich and D. Goldfarb, *J. Phys. Chem.*, 95 (1991) 8818–8823.
- 22 E.M. Flanigen, B.M.T. Lok, R.L. Patton and S.T. Wilson, U.S. Patent 4,759,919, 1988.
- 23 E.T. Olejniczak, S. Vega and R.G. Griffin, *J. Chem. Phys.*, 81(11) (1984) 4804–4817.
- 24 P. Kubelka, *J. Opt. Soc. Am.*, 38(5) (1948) 448–457.
- 25 J.M. Bennet and B.K. Marcus, in P.J. Grobet, W.J. Mortier, E.F. Vansant and G. Schulz-Ekloff (Eds), *Innovation in Zeolite Materials Science*, Elsevier, Amsterdam, 1988, pp. 269–279.
- 26 G. Engelhardt and D. Michel, *High Resolution Solid State NMR of Silicates and Zeolites*, John Wiley & Sons, Chichester, 1987, p. 18.
- 27 N.J. Tapp, N.B. Milestone, M.E. Bowden and R.H. Meinholt, *Zeolites*, 10 (1990) 105–110.
- 28 J.M. Bennet, J.W. Richardson, J.J. Pluth and J.W. Smith, *Zeolites*, 7 (1987) 160.
- 29 E.R.H. van Eck, R. Janssen, W.E.J.R. Maas and W.S. Veeman, *Chem. Phys. Lett.*, 174(5) (1990) 428–432.