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Clustering of cobalt in CoAPO-5 molecular sieves

H.F.W.J. van Breukelen ^{a,*}, G.J.C. Kraaijveld ^a, L.J.M. van de Ven ^b, J.W. de Haan ^b,
J.H.C. van Hooff ^a

^a Eindhoven University of Technology, Schuit Institute of Catalysis, Department of Inorganic Chemistry and Catalysis,
P.O. Box 513, 5600 MB Eindhoven, The Netherlands

^b Eindhoven University of Technology, Schuit Institute of Catalysis, Laboratory of Instrumental Analysis, P.O. Box 513,
5600 MB Eindhoven, The Netherlands

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Abstract

The clustering of cobalt in CoAPO-5 is studied by means of quantitative ³¹P MAS NMR. To explain the amount of “NMR-invisible” P as function of the cobalt content, clusters consisting of at least five cobalt atoms have to be present inside the framework. Probably, cobalt atoms belonging to one cluster are situated in the wall of one and the same pore. © 1997 Elsevier Science B.V.

Keywords: CoAPO; Clustering; ³¹P MAS NMR; ²⁷Al DOR NMR

1. Introduction

A few years after the introduction of aluminophosphates (AlPOs) [1], Flanigen et al. introduced a great variety of “isomorphously” substituted molecular sieves [2,3]. In the early days, systems modified with silicon (SAPOs) were investigated most, but more recently, metal-substituted AlPOs (MeAPOs) have received more attention. These MeAPOs form an interesting group of molecular sieves because it is believed that these are the first structures in which bivalent cations can be incorporated in the lattice. The di- and trivalent metal ions like Co, Cr, Mn and Fe, which substitute for aluminium ions, are of special interest because of

their potential use as catalysts in gas- or liquid-phase oxidation reactions.

Various techniques have been used to prove or indicate the framework position of metals. Examples include ESR on VAPO [4] and DRUVVIS on CoAPO [5]. These techniques, however, gave no proof for incorporation in the framework, because metal-impregnated AlPOs (Me/AlPOs) gave (almost) the same results.

There is one case mentioned in the literature where the framework substitution of metal ions was found by NMR. Barrie and Kilinowski [6] studied MAPO-20 (magnesium-substituted AlPO with a sodalite structure) using ³¹P MAS NMR, and observed several bands in the spectra. They ascribed these resonances to P atoms surrounded by *n* O–Mg (*n*=0–4) and 4–*n* O–Al atoms, respectively, and were able to calculate the framework composition from these spectra in much the

* Corresponding author. Tel.: +31 40 2475028; Fax: +31 40 24455054; e-mail: tgtabb@chem.tue.nl

same way that Si/Al ratios for zeolites are calculated from ^{29}Si NMR spectra. They deduced that the magnesium in the structure is strictly ordered [7]. ^{31}P MAS NMR was successful in this case because of the high level of magnesium substitution, in combination with the fact that magnesium causes no broadening of the ^{31}P NMR signal.

In the field of MAPO-*n*, both ordered and random distributions of magnesium in the structures have been found. MAPO-5 and MAPO-34 [8] and DAF-1 [9] have a random distribution of magnesium in the framework, while in MAPO-20 [6] an ordered distribution of magnesium prevails. In MAPO-36 [10], both forms are present. Magnesium is ordered in the as-synthesised samples, while in calcined samples the magnesium is randomly distributed. One third of the magnesium has become non-framework magnesium.

For MnAPO-5 and MnAPO-44 (manganese-substituted AlPO), clustering has been determined by Lohse et al. [11]. They found with ESR that there is a Mn–O–P–O–Mn–O–P–O–Mn cluster present in MnAPO-44. In MnAPO-5 with low amounts of manganese, there is also some clustering [11,12].

A few years ago, we presented ^{31}P MAS NMR results indicating the clustering of cobalt in CoAPO-5 and CoAPO-11 [13,14]. This happened with cobalt concentrations as low as 0.042 wt.% Co for CoAPO-5 and 0.03 wt.% Co for CoAPO-11, respectively. In this article we extend our work on the clustering of cobalt in CoAPO-5 by means of extended ^{31}P MAS NMR measurements. Not only do we confirm that clustering takes place, but the form and size of the cobalt clusters in CoAPO-5 are also discussed. Furthermore, we present some ^{27}Al DOR NMR spectra of CoAPO-5 samples and discuss the results, along with previous experiments on AlPO-5 in view of recent developments regarding the structure of AlPO-5.

2. Experimental

2.1. Synthesis of AlPO-5 and CoAPO-5

AlPO-5 and CoAPO-5 were crystallised from gels with the following general composition

$\text{P}_2\text{O}_5:(1-x/2)\text{Al}_2\text{O}_3:x\text{CoO}:1.2\text{triethylamine}:50\text{H}_2\text{O}$, where $0 < x < 0.08$.

The gels were prepared following the procedures described in the patent literature [2,15]. The following procedure is a typical recipe for the synthesis of AlPO-5 and CoAPO-5. 5.4 g of cobalt nitrate hexahydrate (Acros, 97%) was added under mechanical stirring to a mixture of 66.0 g of *ortho*-phosphoric acid (Merck, 89%) and 270.0 g of demineralised water, which was cooled to 273 K. 38.7 g of pseudoboehmite (Condea, Pural SB, 75 wt.% Al_2O_3 , 25 wt.% water) was added in small portions. 20 min after addition of the pseudoboehmite, 36.4 g of triethylamine was added via a dripping funnel. After another 20 min of stirring, the gel was transferred into cooled, Teflon-lined stainless-steel autoclaves and subsequently rotated for 24 h in a preheated oven at 473 K. After quenching, the crystals were separated from the mother liquor by sedimentation. Subsequently, the crystals were washed with demineralised water, followed by drying at 353 K for 16 h. Calcination of the samples was performed by heating the samples in a flow of dry oxygen at a rate of 3 K min^{-1} to 823 K and keeping them at the final temperature for 5 h.

2.2. Characterisation

X-ray powder diffraction data were collected on a Philips PW 7200 X-ray powder diffractometer using $\text{Cu K}\alpha$ radiation. *n*-Butane pore-volume determinations were performed on a Cahn 2000 electrobalance. In order to determine the cobalt content of the molecular sieve, elemental analysis (AAS) was performed using a Perkin Elmer 3030 atomic absorption spectrophotometer. Scanning electron microscopy (SEM) was used to determine the agglomerate size of the CoAPO-5 particles.

^{31}P NMR was performed on a Bruker MSL 400 spectrometer at 9.4 T. For the quantitative measurements, Li_3PO_4 was used as an internal standard. The dried standard was thoroughly mixed with the dried samples at a ratio of 1:2 (wt./wt.). Dry samples were obtained by filling the MAS rotors with the hot mixture, dried at 393 K for 30 min, and closing the rotors with tight-fitting Kel-F caps. No increase of the mass could be observed over a

period of a week, indicating that the samples stayed dry inside the spinners. Water adsorption on hot samples indicated that at most 1 wt.% of water was adsorbed within the molecular sieve in 5 min (maximum time to fill the rotors, the actual time is less than 2 min on average).

^{31}P NMR spectra were recorded under MAS conditions (10 000 Hz) using a recycle delay of 900 s, because of the slow relaxation of the internal standard. The instrumental deadtime was 16.7 μs with a 90° pulse length of 3.0 μs .

^{27}Al DOR NMR spectra were recorded on a Bruker MSL 400 spectrometer at 9.4 T. The pulse length was 1 μs , corresponding to a flip angle of 20° . A recycle delay of 1 s was used. The outer rotor was spun at 850 Hz with the inner rotor spinning at approximately five times the speed of the outer rotor. Typically, 400–1000 pulses were accumulated. Rotor-synchronised pulsing was applied to suppress the odd-numbered spinning sidebands [16]. Rotation of the inner rotor could not be monitored directly with the present equipment. However, a sudden stop of the inner rotor during the measurement invariably results in a frequency drop of 20–30 Hz of the outer rotor. Additionally, rotation of the inner rotor could be checked after a few pulses by monitoring the length of the free induction decay (FID). The FID was significantly longer when the inner rotor was spinning compared with the case when the inner rotor was not spinning.

3. Results and discussion

All materials were crystalline and were free of crystalline impurities, and all pore volumes, measured with *n*-butane, were above 0.090 ml g^{-1} . The amount of cobalt in the molecular sieves varied between 0 and 3.15 wt.% (AAS). An agglomerate size of 30–40 μm (SEM) was usually found.

The presence of cobalt in the samples resulted in the appearance of multiple peaks in some of the ^{31}P MAS NMR spectra or a broad signal in other spectra (Fig. 1). Conventional and straightforward ^{31}P and ^{27}Al MAS NMR studies on cobalt-substituted APOs (CoAPOs) could not be used in the same way as for MAPO-20 [4, 17, 18].

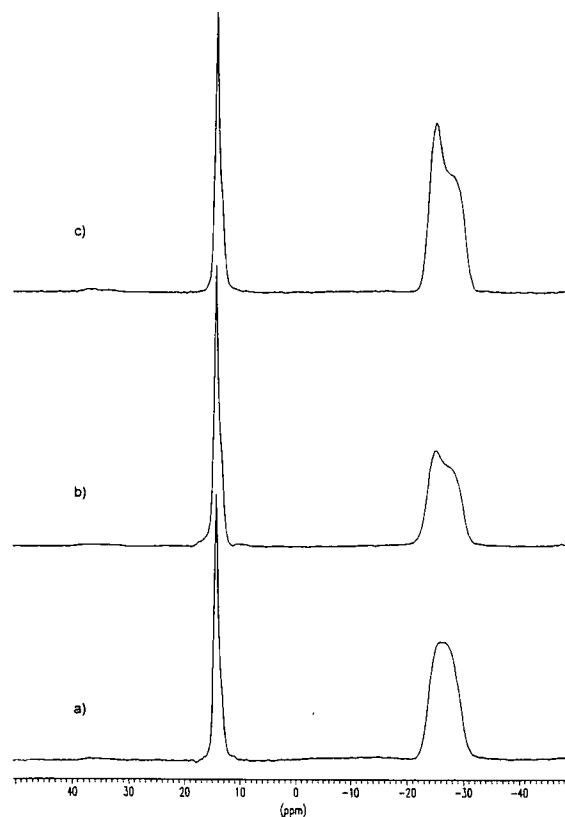


Fig. 1. Three typical ^{31}P MAS NMR spectra of AIPO-5 (a), CoAPO-5 (b, 0.0041 wt.%) and CoAPO-5 (c, 0.0012 wt.%). The line at about 14 ppm is due to the internal standard (lithium phosphate).

Montes et al. [4, 19], 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. They ascribed the observed increase in anisotropy to strong dipolar couplings of phosphorus with paramagnetic cobalt, supporting the view that cobalt primarily substitutes for framework aluminium. Measurements on Co/AIPO-5 (cobalt-impregnated AIPO-5) and Co/AIPO-11, however, also showed an increased anisotropy [13, 14, 18], so in the case of CoAPOs, chemical shift anisotropy in ^{31}P MAS NMR as such cannot be used to prove the framework incorporation of cobalt.

In the present case, no intense spinning sidebands were detected, in contrast to the work of Peeters et al. [13, 14], Prakash et al. [20, 21], Chen

et al. [22], Kraushaar et al. [18] and Montes et al. [4,19]. For CoAPSO-34 and CoAPSO-44 [23] and CoZnPO-SOD [24] and CoMnAPO-34 [25], intense sidebands were also found.

In the case of low loadings of cobalt, CoAPO-5 apparently does not show numerous sidebands [19]. The samples synthesised for the present study contain 0–3 wt.% cobalt, which is the complete range in which CoAPO-5 can be made without any extra-framework cobalt [13,26]. For CoAPO-11, no intense sidebands were found by Prasad et al. [27].

Prakash et al. [21] suggest that the broad peak for CoAPSO-46 is caused by the presence of a P(3 Al,1 Co) peak as well as the P(4 Al) peak. Although three different aluminium species were detected in ^{27}Al DOR NMR spectra, and at least two different phosphorus species in ^{31}P MAS NMR for both AlPO-5 and CoAPO-5 [13,14], we prefer not to ascribe this to signals due to P(3 Al,1 Co) groups. In our view, these signals are broadened and/or displaced beyond detection in our spectral window by interference with the nearby paramagnetic cobalt ions. The phosphorus signals are moved over very large distances in the spectra and cannot be excited and observed when the irradiation frequency is centered on $\delta=0$ ppm, as was shown recently by Canesson and Tuel for CoAPOs [28] and others for VPO catalysts [29–32]. They showed that at about $\delta=2500$ ppm, a signal for P(3 Al,1 Co) is found, and for every additional cobalt as a direct neighbour to a phosphorous atom, about 2500 ppm should be added to find a NMR signal for the phosphorous atom in question. Preliminary spin echo mapping experiments on our CoAPOs show the large displacements and typical lineshapes obtained by Canesson and Tuel [28], thus showing framework positioning of cobalt atoms in the lattice. The presence of extra-framework cobalt would not give these displacements and lineshapes.

In another study, Tuel et al. [25] claim to see a P(3 Al,1 Me) signal for Me=Zn and Mn in MeAPO-34, while for CoAPO-34 this peak is not found. For Me=Zn this is in our view a definite possibility since it is not paramagnetic, but for Me=Mn or Co (both are paramagnetic) we do not expect such a signal. Quite remarkably, Tuel

et al. [25] have shown that there is a difference of at least a factor of 50 in T_1 relaxation times between ZnAPO-34 on the one hand and MnAPO-34 and CoAPO-34 on the other.

At first sight, the two articles of Tuel et al. [25,28] seem to present somewhat diverging views as far as the existence of P(3 Al,1 Me) signals are concerned. Prakash et al. [21] proposed a similar assignment of signals for CoAPSO-46 (see above). Judging from the fact that more than one ^{31}P NMR signal is found in the “ $\delta=0$ ppm region”, there are differences among T-sites in CoAPSO-46 and MnAPO-34, and all are attributed to P(4 Al,0 Me). (See Note added in proof, below.)

3.1. Quantitative ^{31}P NMR measurements

According to Canesson and Tuel [28], the intensities of the signals at about $\delta=0$ ppm are still directly correlated to the cobalt content of the different samples. In previous ^{31}P MAS NMR investigations on CoAPOs in our group, it was noted that some of the phosphorus atoms become “NMR-invisible” for CoAPOs in the $\delta=0$ ppm region. In the present study, quantitative ^{31}P MAS NMR experiments were performed to check the amount of ^{31}P visible with MAS NMR using lithium phosphate as an internal standard. Measurements were performed on dried samples at an MAS frequency of 10 000 Hz with a recycle delay of 900 s.

In order to obtain quantitatively meaningful determinations, the peaks in the ^{31}P MAS NMR spectrum (MAS rotation at 10 000 Hz) were integrated. From Table 1 it can be seen that all the phosphorus atoms in AlPO-5 can be detected with MAS NMR. Recently, Hong et al. [33,34] found using ESR that there are some paramagnetic defect centres present in dehydroxylated AlPO-5. These can influence the amount of NMR-visible phosphorous in AlPO-5, although they found only four defect centres on 1000 unit cells for samples which were refluxed in water for 4 h. The number of defect centres for samples which are exposed to atmospheric moisture is lower. This will probably cause a decrease in the NMR signal of less than 0.5%. The error is even smaller for CoAPO-5, where the number of paramagnetic sites is

Table 1
Results of quantitative ^{31}P NMR measurements as a function of the cobalt content of CoAPO-5

Sample	wt.% Co (AAS) ^a	% NMR-visible P ^b
AlPO-5	0	100
CoAPO-5	0.0010	97
CoAPO-5	0.0012	92
CoAPO-5	0.0020	93
CoAPO-5	0.0041	96
CoAPO-5	0.0120	94
CoAPO-5	0.0490	93
CoAPO-5	0.0850	77
CoAPO-5	0.1400	99
CoAPO-5	0.6300	80
CoAPO-5	1.2100	56
CoAPO-5	1.2400	70
CoAPO-5	1.2800	62
CoAPO-5	1.5600	60
CoAPO-5	1.6300	64
CoAPO-5	2.3100	46
CoAPO-5	2.4200	50
CoAPO-5	3.1500	42

^aWeight percentage of cobalt as determined using AAS.

^bAmount of ^{31}P visible by NMR measured with Li_3PO_4 as internal standard: $D_0=900$ s, dead time = 16.7 μs , number of scans = 4, dry samples, 10 000 Hz MAS.

restricted by the presence of cobalt. Therefore, a substantial decrease in ^{31}P MAS NMR signals for AlPO-5 and CoAPO-5 due to the presence of paramagnetic defect centres under our experimental conditions is unlikely.

The CoAPO-5s in this study, however, suffer from a loss of ^{31}P MAS NMR signal intensity (Table 1 and Fig. 2). Repeated measurements on a selected number of samples indicate an experimental standard deviation of 1.65%. Taking this spread into account, there is a monotonous decrease of the ^{31}P NMR signal with increasing cobalt concentration.

Charge compensation by extra-framework cobalt has been checked by ion exchange experiments, and a loss of not more than 2.1% of the total amount of cobalt after stirring in an 0.01 M zinc nitrate solution indicates that the presence of appreciable amounts of cobalt in extra-framework positions is unlikely. This exchangeable cobalt must be formed during the calcination of the as-synthesised CoAPO-5, because zinc-ion exchange of as-synthesised CoAPO-5 only results

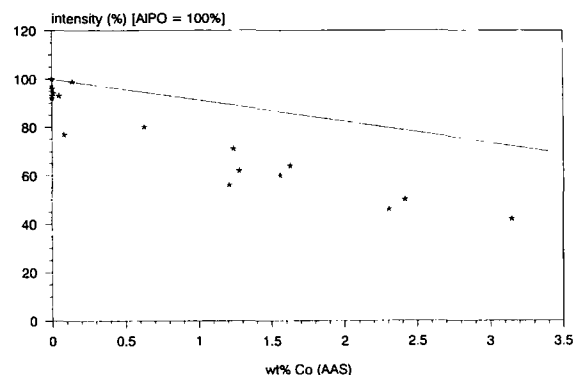


Fig. 2. Quantitative ^{31}P NMR measurements (*), and calculations for random distribution of cobalt when the first (solid line) and second (dashed line) phosphorus shells are invisible by NMR.

in a loss of cobalt of less than 0.01%. Therefore, clustering of two cobalt atoms, positioned in a four-membered ring (like that shown in Fig. 3(a)) with one extra-framework cobalt for charge compensation is not likely. Also, in the literature it is generally accepted that (almost) all cobalt is incorporated into the framework [35,36]. Therefore it is very unlikely that one third of the cobalt is present as extra-framework cobalt for charge compensation. The excess negative charge of the framework must be compensated by template molecules or, after calcination, by protons [37,38]. From these data it can be deduced that 9.5–10.8 “NMR-

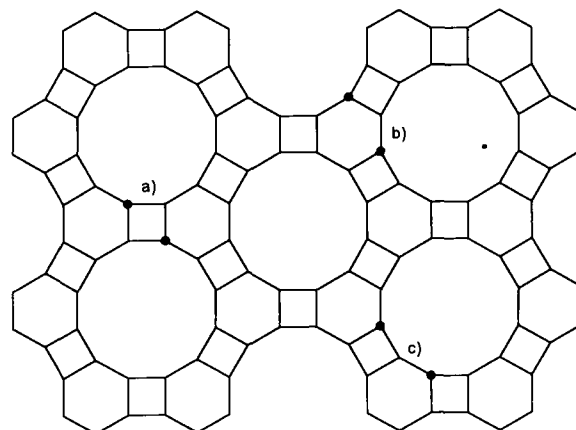


Fig. 3. Different ways for two clustered cobalt atoms to be placed in CoAPO-5: two cobalt atoms in (a) a four-membered ring, (b) a six-membered ring, and (c) a twelve-membered ring.

invisible” phosphorus atoms per cobalt atom are needed to explain the observed decrease in signal intensity.

In the present paper, as in previous studies [13,14], and also in line with Tuel’s concept [28], it is assumed that ^{31}P NMR signals are either shifted beyond detection at the original position or are completely visible. The amount of “NMR-invisible” phosphorus cannot be explained by assuming that only ^{31}P NMR signals of nuclei in the first coordination sphere of cobalt become broadened or displaced beyond detection, because the observed signal intensity is much lower than expected on this basis (there are four phosphorous atoms surrounding every cobalt atom when cobalt is randomly built into the framework).

On the other hand, if one assumes that the presence of cobalt in the third coordination sphere (the second coordination sphere consists of aluminium) also causes invisibility of the ^{31}P NMR signal, then the extent of NMR-invisible phosphorus becomes too high. In that case there are 25 phosphorus atoms surrounding one cobalt atom (four phosphorous atoms in the first shell and 21 phosphorous atoms in the third shell). The only way to explain the observed decrease of the signal intensity of about ten phosphorus atoms per cobalt atom then becomes the assumption that cobalt is not incorporated randomly, but that clustering of cobalt takes place. The lines in Fig. 2 have been determined by calculation of the weight percentage of cobalt from a theoretical amount of cobalt, aluminium and phosphorus in a random distribution (see also Refs. [13,14]).

According to Bennett and Marcus [39], in CoAPO-50 two cobalt atoms are incorporated into one four-membered ring, as depicted in Fig. 3(a) for CoAPO-5, and these clusters are randomly distributed in the framework of CoAPO-50. This kind of clusters, however, is not large enough to explain the observed loss of the ^{31}P NMR signal. In the case of CoAPO-5 there are four possible ways to build cobalt pairwise into the framework: (1) in a four-membered ring, (2) and (3) in two six-membered rings, and (4) in a twelve-membered ring. The cobalt atoms thus have an effect on 16, 17, 17 and 18.5 phosphorus atoms per cobalt atom,

respectively, in the two phosphorus coordination spheres surrounding the cobalt atoms.

When three or four cobalt atoms are linked together via phosphate bridges, the number of possibilities for building-in increases significantly. None of the formed clusters this way can explain the amount of phosphorus which is invisible. Obviously, even larger cobalt clusters are necessary to explain the observed decrease in the NMR signal.

With clusters containing five or more cobalt atoms, there are structures which can explain the observed loss of the signal. The number of invisible phosphorous atoms for clusters containing 5–9 cobalt atoms are presented in Table 2. For the structures with five cobalt atoms, which can explain the observed loss, all cobalt atoms are in one or two planes, perpendicular to the *c*-axis of the AFI structure, filling at least one six-membered ring or one four-membered ring (see Fig. 4). Only one structure with six cobalt atoms was found to meet these demands and at the same time fulfil requirements regarding the number of phosphorus atoms surrounding one cobalt atom.

The other structures which can explain the observed loss of ^{31}P NMR signal have the

Table 2
Maximum and minimum number of phosphorus atoms around cobalt atoms in clusters in the CoAPO-5 framework

Number of Co atoms ^a	Minimum number of P atoms ^b	Maximum number of P atoms ^c
1	25.00	25.00
2	16.00	18.50
3	13.00	16.33
4	11.00	15.00
5	9.80	13.60
6	9.00	12.50
7	8.43	12.14
8	7.75	11.88
9	7.56	11.67
— ^d	9.50	10.75

^aNumber of cobalt atoms in cluster.

^bMinimum number of phosphorus atoms per cobalt atom in a cluster of *n* cobalt atoms.

^cMaximum number of phosphorus atoms per cobalt atom in a cluster of *n* cobalt atoms.

^dMinimum and maximum amount of phosphorus to explain the observed loss of the signal.

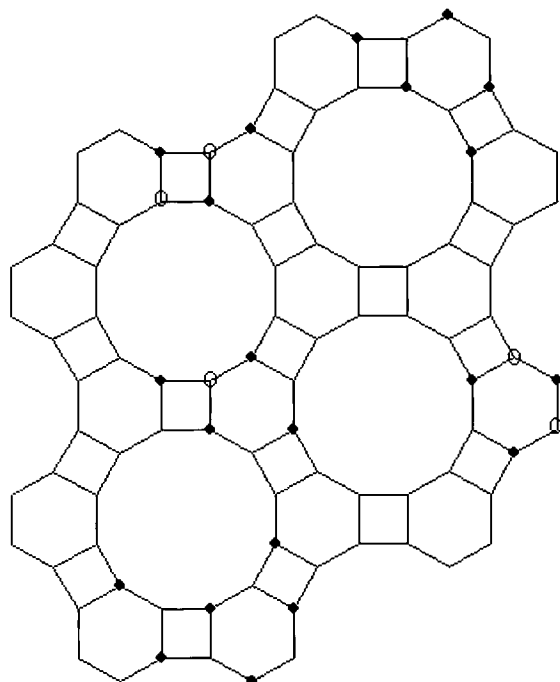


Fig. 4. Two-dimensional representation of structures with five or six cobalt atoms which have cobalt atoms in more than one twelve-membered ring. The dots are in the plane of the paper and the open circles are underneath the plane of paper, both representing cobalt atoms.

following in common: they have the clustering cobalt atoms in one twelve-membered ring, divided over several planes, filling the six-membered rings parallel to the *c*-axis of the AFI structure. An example of clustering with six cobalt atoms is given in Fig. 5, but structures with seven, eight and nine or even more cobalt atoms, which can

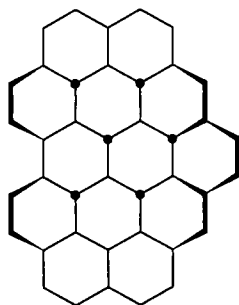


Fig. 5. Two-dimensional representation of clustering of cobalt atoms in CoAPO-5 in one twelve-membered ring parallel to the *c*-axis of the AFI structure. The dots represent cobalt atoms.

explain the observed loss in NMR signal, are also possible.

From the above, it follows that cobalt in CoAPO-5 probably forms clusters of at least five atoms. Our results do not require the presence of only one kind of cluster in CoAPO-5. Combinations of cobalt clusters (e.g. 3+7, 4+6, 1+8 or 2+9) can also explain the observed loss in the signal, but the requirement of forming clusters of at least five cobalt atoms is valid in any situation.

Canesson and Tuel [28] describe in their papers ^{31}P NMR spin echo mapping effects of the paramagnetic metal nuclei on immediately neighbouring ^{31}P nuclei. Our previous and current results [13,14] indicate that odd-electron delocalisation extends to the second phosphorus shell.

There is a structure known of cobalt phosphate, DAF-2 [40], which is built from tetrahedrally surrounded cobalt oxide and phosphate groups, thus resulting in the structure depicted in Fig. 6. In DAF-2 with a Co/P ratio approaching unity, cobalt is totally clustered by definition. Our expectation would be that there will be no visible phosphorus signal in ^{31}P MAS NMR. Indeed, the signal around $\delta=0$ ppm is now displaced to much higher frequencies (“downfield”), and is found at $\delta=10\,000$ ppm [28].

3.2. ^{27}Al DOR NMR on AlPO-5 and CoAPO-5

In 1993 some of us described ^{27}Al DOR NMR and ^{31}P MAS NMR spectra of AlPO-5 in which

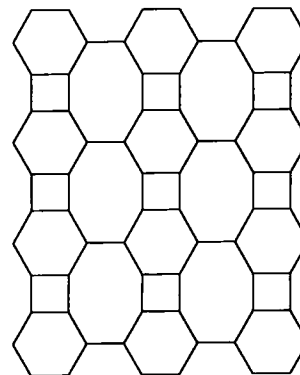


Fig. 6. The framework structure of DAF-2 depicting only atoms (Co or P) viewed along either the [100] or the [010] direction.

three different T-sites were found [13,41]. Earlier diffraction studies [42–44] showed that there should be only one type of aluminium and phosphorus site present in AlPO-5 (space group P6cc), until Mora et al. [45] determined a structure of calcined AlPO-5 using high-resolution X-ray and neutron powder diffraction. They found that the structure is most adequately described using a Pcc2 or Ccc2 space group, i.e. groups with a lower symmetry. The Pcc2 space group, however, results in six different aluminium and phosphorus sites (two slightly different twelve-membered rings), each with a C_2 axis. The NMR results are probably not compatible with those six different sites, unless three “pairs” were formed accidentally, which is highly unlikely. The Ccc2 space group with three different sites in the structure (all 12-membered rings are the same) appears far more probable. Theoretical studies [46] showed, however, that this structure is less stable than the Pcc2 and P6 unit cell, albeit with a difference smaller than kT . The peak-splitting in X-ray diffraction is not quite described correctly [45]. The Pcc2 space group, however, does not account very well for the weak peaks [45], just as in the case of the Ccc2 space group [45,46].

Recent theoretical studies showed unit cells belonging to space groups Cc [47], Pcc2 and P6 [46], all using the same potentials determined by van Beest et al. [48]. Other calculations yielded space groups P6, P6cc [49] and P6, P31c and P6cc [50]. A major difference between some of the studies is the presence or absence of a template for XRD and NMR. In theoretical studies the influence of the template is not taken into account. The template may cause thermally induced phase transitions [51], pointing to subtle differences in structure induced by the template.

In our ^{27}Al DOR NMR measurements on CoAPO-5 with low loadings of cobalt, we found the same type of spectra as for AlPO-5 (Fig. 7). Samples with cobalt loadings up to 0.15 wt.% still show the same kind of spectra with three types of aluminium sites. With higher loadings, the spectra only show one signal due to line broadening caused by the presence of paramagnetic cobalt. This structure is obscured by line broadening as a consequence of interactions between the aluminium

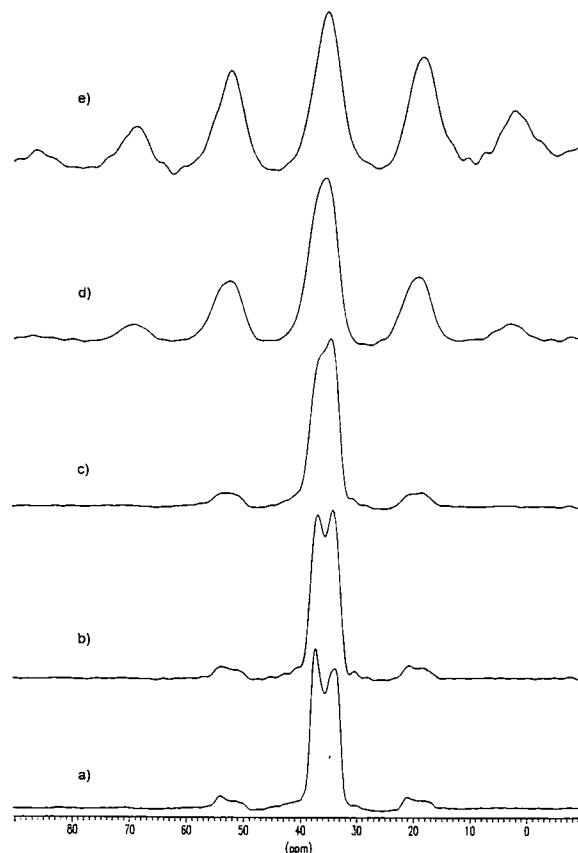


Fig. 7. ^{27}Al DOR NMR spectra of AlPO-5 (a), CoAPO-5 (b, 0.0041 wt.%), CoAPO-5 (c, 0.14 wt.%), CoAPO-5 (d, 1.56 wt.%) and CoAPO-5 (e, 3.15 wt.%).

nuclei and the unpaired electron(s) of the incorporated metal. It is quite feasible, however, that part of the ^{27}Al NMR signal is shifted in a manner analogous to ^{31}P NMR.

4. Conclusions

In CoAPO-5, the presence of paramagnetic cobalt causes a decrease in the ^{31}P MAS NMR signal intensity. Both the first and the second phosphorus shells are “NMR-invisible” due to the presence of paramagnetic cobalt. The observed loss of the signal can only be explained by assuming clustering of the cobalt atoms in groups of at least five atoms.

In our spectra of CoAPO-5, no P(3 Al,1 Co)

peak could be observed near $\delta \approx 0$, in contrast with the interpretation of Prakash et al. [21] and Tuel et al. [25], who claim the presence of such signals for CoAPO-46 and MnAPO-34, respectively.

For CoAPO-5, molecular sieves with low loadings of cobalt (<0.15 wt.% Co) the ^{27}Al DOR NMR spectra are very similar to the ^{27}Al DOR NMR spectrum of AlPO-5. For higher loadings of cobalt, the spectra show one signal with an intense manifold of spinning sidebands.

5. Note added in proof

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From recent measurements on $\text{NH}_4[\text{MeGa}_{2-x}\text{P}_3\text{O}_{12}(\text{H}_2\text{O})_2]$ (Me = Co or Mn) in these laboratories (A.R. Overweg, personal communication, unpublished data), it appears plausible that cobalt and manganese have quite different properties of transmitting (unpaired) electron density towards phosphorus atoms two bonds away in a lattice. See also a recent paper by Tuel et al. [52] in which the electron-nuclear-dipolar-plus-contact term is described explicitly. These factors may explain the different behavior of cobalt and manganese with respect to shifting the P(3Al,1Me) resonance to higher frequencies (deshielding) and justify Tuel's assignments [25].

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