Local Environment of Phosphorus Atoms in CoAPO$_4$-*n* Molecular Sieves: A ^{31}P NMR Study

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Abstract: A spin-echo mapping technique has been used to obtain the ^{31}P NMR spectra of various cobalt-substituted aluminophosphate molecular sieves. The technique involves recording Hahn-echo spectra at different carrier frequencies in order to observe the signal within a broad spectral region. In contrast to the more commonly used magic angle spinning (MAS) or simple Hahn-echo methods, all phosphorus nuclei could be detected, even in the case of samples with high Co contents. Resonances are usually broad and range between about −500 and 10 000 ppm/H$_3$PO$_4$, but the resolution is sufficient to access the local structure around the ^{31}P nuclei. The technique is particularly interesting since the presence of signals above 500 ppm is direct proof for the framework cobalt siting. Indeed, such signals were not observed for Co-impregnated samples and are thus characteristic of framework Co species. The different NMR lines of the spectra have been assigned to various P(nCo) environments in the structure, and their shift was found to be approximately proportional to the number of Co atoms in the first coordination sphere around P atoms. A good agreement was found between the composition of the framework of the molecular sieve deduced from NMR spectra and that obtained by chemical analysis. Moreover, it was possible to estimate the location of Co atoms in the structure and to propose or confirm an ordering in the unit cell for two of the studied samples.

Introduction

AlPO$_4$-*n* molecular sieves consist of alternating AlO$_4$ and PO$_4$ tetrahedra connected together to generate microporous frameworks (*n* denotes a specific structure type).[1] By varying the synthesis conditions and the nature of the templating molecule, a great number of structures have been reported, with pore diameters ranging from about 4 to 12 Å.[2] Pure AlPO$_4$-*n* materials do not possess interesting applications in catalysis as their framework is electrically neutral. However, the substitution of P or Al by tetra- or divalent cations, respectively, creates Brönsted and Lewis acid sites in the framework, thus providing these molecular sieves with potential catalytic applications.[3−8] MeAPO$_4$-*n*, where Me is a divalent cation that substitutes for aluminum (Me = Co, Zn, Mg, ...) represent an interesting family of materials since they were the first example of molecular sieves where divalent cations could be incorporated into the lattice.[9−14] The case of CoAPO$_4$-*n* molecular sieves is of particular interest; incorporation of Co generates both acid and

redox sites, and the coupling of acidic and redox properties may open new routes in shape-selective bifunctional catalysis.[15−20]

A great variety of techniques have been used to probe the nature and location of divalent cations in MeAPO$_4$-*n* frameworks. One of them is chemical analysis that gives an indication of the possible substitution. Indeed, if all metal cations substitute for aluminum in the framework, the sum of the indices $x + y$ in the TO$_2$ formula Me$_x$Al$_y$P$_{0.5}$O$_2$ must be equal to that of phosphorus, i.e. $x + y = 0.5$. Deviations from this value may indicate the presence of extralattice species inside the channels or on the outer surface of the crystals. Nevertheless, due to the sensitivity and precision of the method, evidence for framework substitution by chemical analysis is reliable only in the case where molecular sieves contain relatively high metal contents. Moreover, chemical analysis does not bring any information about the coordination and oxidation state of the cations. In some cases, Rietveld refinement of X-ray diffraction patterns has proved to be useful to distinguish between framework and extraframework species.[21,22] An advantage of the technique is that it is sometimes possible to determine precisely the location of metal species in the unit cell. EXAFS can also give information about the coordination of the metal

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and the nature and number of neighboring atoms in the first coordination sphere.[23] A nice example has been recently published by Barrett et al.[24] on four different CoAPO$_4$-n that shows the power of the method to access the local structure around Co atoms. Diffuse reflectance electronic absorption spectroscopy (DREAS) and electron spin resonance (ESR) have also been applied to the study of the redox properties of CoAPO$_4$-n molecular sieves.[25,26] These techniques yield oxidation state and coordination of Co species in the material. However, the discrimination between framework and extraframework species is not trivial as tetrahedrally coordinated Co species have also been observed in AlPO$_4$-n materials impregnated with cobalt salts.[27]

As both ^{31}P and ^{27}Al nuclei are very easy to detect by solid state nuclear magnetic resonance (NMR), this technique is expected to provide interesting information about the local environment around P and Al atoms in the molecular sieve. In particular, substitution of Al by a divalent cation should modify the chemical shift of neighboring phosphorus nuclei to which it is bonded. Such modifications in chemical shifts are observed in ^{29}Si MAS NMR spectra of zeolites upon incorporation of aluminum into the lattice. In this case, each Si(nAl) species has a specific chemical shift which makes possible the estimation of the Si/Al ratio from ^{29}Si NMR spectra.[28] Deng et al.[29] have reported that incorporation of Mg^{2+} cations in the AlPO$_4$-5 framework modifies the ^{31}P NMR spectrum and they attributed the different ^{31}P NMR lines to various environments of phosphorus nuclei P(nAl, 4-nMg). In a similar way, we have reported that ^{31}P NMR could be used to calculate the framework composition of Zn- and Mn-substituted aluminophosphates with the chabazite structure.[30] In the special case of CoAPO$_4$-20, Barrie et al.[31] demonstrated that magnesium is strictly ordered in the framework and they could determine the nature of this ordering from ^{31}P NMR line intensities.

For CoAPO$_4$-n molecular sieves, conventional ^{31}P NMR gives only very poor information about the nature of the framework. Indeed, even at low Co contents, ^{31}P NMR lines are broadened due to strong dipolar couplings with paramagnetic cobalt species, and numerous and intense sidebands are observed in MAS spectra. Some authors have taken the presence of these sidebands as proof for framework substitution.[32] For Chen et al.,[33] substitution of Al by Co results in a decrease in the spin–lattice relaxation time T_1 measured on static samples. However, our own experience showed that spinning sidebands and a decrease in both T_1 and T_2 relaxation times are also observed for Co-impregnated AlPO$_4$-n molecular sieves and, thus, cannot be regarded as characteristics of the presence of framework Co species. In a more detailed study, Peeters et al.[34] concluded

that incorporation of Co atoms in AlPO$_4$-n frameworks leads to "NMR-invisible phosphorus", at least in the first and third coordination spheres around the metal. As we will see later, part of the ^{31}P nuclei in CoAPO$_4$-n materials are effectively undetectable by conventional NMR techniques.

Many recent papers have reported the effect of paramagnetic species on the NMR signals; in most cases, large shifts are observed, attributed principally to a contact interaction between unpaired electrons of the paramagnetic ion and the observed nucleus.[35−38]

The problem of "NMR-invisible phosphorus" has also been encountered in the case of transition metal phosphates like VPO catalysts. When the solids contain significant amounts of paramagnetic V(IV) centers, part or even the totality of the ^{31}P NMR signal cannot be detected using the MAS technique.[39,40] We have previously reported that the total ^{31}P signal of these materials could be recorded using a spin-echo mapping (SEM) technique.[41,42] Indeed, in the presence of paramagnetic centers, ^{31}P NMR lines are not only broadened but also considerably shifted, and mapping is thus necessary to obtain the whole spectrum.

In the present paper, we have applied the technique of NMR SEM to the study of various CoAPO$_4$-n molecular sieves. The method and particularly its quantitative aspects are discussed in detail, and results are compared with those obtained using conventional NMR sequences. Furthermore, we have tried to assign the different ^{31}P NMR signals to various environments of phosphorus nuclei in the structure and we discuss on the possibility of estimating the framework composition and ordering from such spectra.

Experimental Section

Synthesis. CoAPO$_4$-n molecular sieves with structures 5, 20, 39, 46, and 50 and containing various amounts of cobalt have been synthesized following literature procedures.[18,23,43−46] For all samples except CoAPO$_4$-39, H$_3$PO$_4$ (85 wt %, Rhône-Poulenc), pseudoboehmite (CATAPAL B, Vista, 74 wt % Al$_2$O$_3$), and cobalt(II) nitrate (Co-(NO$_3$)$_2$·6H$_2$O, Aldrich) were the phosphorus, aluminum, and cobalt sources, respectively. For CoAPO$_4$-39, cobalt(III) acetate was used as cobalt precursor, as it yielded materials with higher purity and crystallinity.[44] The case of CoAPO$_4$-50 is different since this structural type can only be synthesized with one particular value of the Co content, corresponding approximately to the unit cell formula Co$_3$Al$_5$P$_8$O$_{32}$.3Pr$_2$-NH$_2$.[21] However this material is interesting as it can accommodate high metal contents and also because it was previously reported that part of the Co atoms are not randomly distributed in the framework but occupy specific positions. Therefore, in order to modify the Co content in this molecular sieve, mixed ZnCoAPO$_4$-50 samples have been prepared with various Zn and Co concentrations in the precursor gel. As we will see later, from the NMR point of view, Zn behaves like aluminum, as both nuclei are not paramagnetic and do not shift

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Table 1. Gel Composition and Crystallization Conditions for the Various Samples[a]

no.	sample	gel composition	T (°C)	days
1	AlPO$_4$-5	1.5Et$_3$N$-$Al$_2$O$_3$$-P_2O_5$$-$40H$_2$O	170	0.5
2	CoAPO$_4$-5	1.5Et$_3$N$-$0.25CoO$-$0.8Al$_2$O$_3$$-P_2O_5$$-$32H$_2$O	170	1
3	CoAPO$_4$-20	TMAOH$-$0.67CoO$-$0.67Al$_2$O$_3$$-P_2O_5$$-$45H$_2$O	175	0.5
4	CoAPO$_4$-39	Pr$_2$NH$-$0.2CoO$-$0.9Al$_2$O$_3$$-P_2O_5$$-$40H$_2$O	140	1
5	CoAPO$_4$-46	2Pr$_2$NH$-$0.3CoO$-$0.85Al$_2$O$_3$$-P_2O_5$$-$50H$_2$O	150	9
6	CoAPO$_4$-50	4.3Pr$_2$NH$-$0.45CoO$-$Al$_2$O$_3$$-1.47_5P_2O_5$$-11_5H_2$O	150	7
7	ZnAPO$_4$-50	4.3Pr$_2$NH$-$0.45ZnO$-$Al$_2$O$_3$$-1.47_5P_2O_5$$-11_5H_2$O	150	7
	Co$_x$Zn$_y$APO$_4$-50	2.5Pr$_2$NH$-$xZnO$-$yCoO$-$0.85Al$_2$O$_3$$-P_2O_5$$-$50H$_2$O	150	7
8	Co$_{0.2}$Zn$_{0.1}$APO$_4$-50	$x = 0.2; y = 0.1$	150	7
9	Co$_{0.1}$Zn$_{0.2}$APO$_4$-50	$x = 0.1; y = 0.2$	150	7
10	Co$_{0.05}$Zn$_{0.25}$APO$_4$-50	$x = 0.05; y = 0.25$	150	7
11	DAF-2	EDA$-$CoO$-$0.9 P$_2$O$_5$$-H_2CO_3$$-$25H$_2$O	190	3

[a] Et$_3$N = triethylamine, TMAOH = tetramethylammonium hydroxide, Pr$_2$NH = dipropylamine, EDA = ethylenediamine.

and broaden the ^{31}P NMR lines. Pure AlPO$_4$-5 was also synthesized to serve as a reference for quantitative NMR measurements. Finally, a microporous cobalt phosphate DAF-2, with a framework of strictly alternating CoO$_4$ and PO$_4$ tetrahedra, was also prepared following a recipe published by Chen et al.[47]

The chemical composition of the starting precursor gels as well as crystallization conditions for all samples are listed in Table 1. In the case of CoZnAPO$_4$-50, samples with various Co and Zn contents were synthesized by varying the concentrations of Co, Zn, and Al in the gel, keeping the (Co + Zn + Al)/P ratio constant and equal to unity.

Crystallization was performed by heating the gels in Teflon-lined stainless steel autoclaves under autogeneous pressure. After the crystallization period, autoclaves were rapidly cooled down and samples were washed several times with distilled water prior to drying overnight at 110 °C. For some of the CoAPO$_4$-n materials, occluded organics were removed by calcination in air at 550 °C for 12 h.

Coimpregnated AlPO$_4$-5 was obtained by slurring calcined AlPO$_4$-5 in an aqueous solution of cobalt(II) nitrate at 70 °C for about 3 h. The solution was then evaporated in an oven at 110 °C and the solid washed in hot water to remove the excess of Co species. It was then calcined in air at 550 °C for 12 h. The chemical composition gave 4.35 wt % Co in the calcined material.

Characterization. Al, Co, P, and Zn contents were determined by ICP after solubilization of the samples in HF:HCl solutions. X-ray diffraction patterns were collected on a Philips PW 1710 diffractometer (Cu Kα radiation) using SiO$_2$ as an external standard. Data were collected from $2\theta = 5°$ to $80°$ in $0.02°$ steps with 1 s per step.

All ^{31}P NMR spectra were acquired on a Bruker DSX 400 spectrometer operating at 161.9 MHz and equipped with a standard 4 mm probe head. In a typical experiment, a series of Fourier-transformed echo spectra are recorded on a static sample using a conventional Hahn-echo sequence, $90°_x - \tau - 180°_y - \tau -$ (acquisition), by incrementing the irradiation frequency with a constant step (75 kHz) below and above the ^{31}P resonance of H$_3$PO$_4$ ($\delta = 0$). The number of increments is dictated by the frequency limits beyond which the NMR signal is negligible. In practice, each spectrum is obtained with a sweep width of 5 MHz, $\tau = 20$ μs, and a 90° pulse length of 3 μs. After Fourier transformation, spectra are filtered according to a method recently reported by Tong[48] to circumvent phase problems and increase the signal-to-noise ratio of the final spin-echo mapping spectrum. For each carrier frequency, the ^{31}P T_2 relaxation time is measured by incrementing τ in the sequence between 10 and 100 μs. This allows us to correct the intensity of the echo, taking into account the loss of magnetization due to relaxation of ^{31}P nuclei before acquisition. After correction of intensities, the total ^{31}P NMR signal is obtained by adding all individual spectra. Details concerning the technique and measurements of quantitative intensities are given in the Supporting Information.

MAS spectra were obtained at 12 kHz using a one-pulse sequence with a pulse length of 3 μs and a recycle delay of 60 s.

Results and Discussion

Synthesis. All CoAPO$_4$-n molecular sieves are highly crystalline and possess the expected structure as evidenced by X-ray diffraction. The chemical composition expressed as TO$_2$ formula of as-synthesized materials is reported in Table 2. For

Table 2. Chemical Composition and Percentage of Phosphorus Nuclei Observed in the Various Samples Using a Simple Hahn-Echo Sequence (I_{HE}) and the Spin-Echo Mapping Technique (I_{SEM})

no.	sample	TO$_2$ formula	I_{HE}	I_{SEM}
1	AlPO$_4$-5	Al$_{0.48}$P$_{0.51}$O$_2$	1	0.98
2	CoAPO$_4$-5	Al$_{0.45}$Co$_{0.06}$P$_{0.51}$O$_2$	0.58	1.03
3	CoAPO$_4$-20	Al$_{0.334}$Co$_{0.175}$P$_{0.52}$O$_2$	0.25	0.96
4	CoAPO$_4$-39	Al$_{0.44}$Co$_{0.05}$P$_{0.48}$O$_2$	0.65	1.04
5	CoAPO$_4$-46	Al$_{0.32}$Co$_{0.17}$P$_{0.51}$O$_2$	0.11	0.97
6	CoAPO$_4$-50	Al$_{0.30}$Co$_{0.19}$P$_{0.48}$O$_2$	0.02	0.98
7	ZnAPO$_4$-50	Al$_{0.31}$Zn$_{0.20}$P$_{0.50}$O$_2$	0.98	0.97
8	Co$_{0.2}$Zn$_{0.1}$APO$_4$-50	Al$_{0.30}$Co$_{0.125}$Zn$_{0.062}$P$_{0.49}$O$_2$	0.16	1.01
9	Co$_{0.1}$Zn$_{0.2}$APO$_4$-50	Al$_{0.315}$Co$_{0.06}$Zn$_{0.12}$P$_{0.53}$O$_2$	0.53	1.06
10	Co$_{0.05}$Zn$_{0.25}$APO$_4$-50	Al$_{0.31}$Co$_{0.03}$Zn$_{0.16}$P$_{0.51}$O$_2$	0.76	0.99
11	DAF-2	Co$_{0.48}$P$_{0.51}$O$_2$	0.03	0.95

all samples, the (Me + Al)/P ratio (Me = Co, Zn or Co + Zn) is very close to 1, which supports the isomorphous substitution. All MeAPO$_4$-50 molecular sieves possess approximately the same metal fraction, corresponding to the unit cell formula Co$_{3-x}$Zn$_x$Al$_5$P$_8$O$_{32}$ with $0 < x < 3$. It is interesting to note that the Co/Zn ratio in the various solids agrees quite well with that of the precursor gel, indicating that neither Co nor Zn was preferentially incorporated into the aluminophosphate framework during crystallization. For DAF-2, the Co/P ratio confirms that the framework is built of strictly alternating PO$_4$ and CoO$_4$ tetrahedra.

Application to the Study of CoAPO$_4$-n Molecular Sieves. CoZnAPO$_4$-50 Samples. The ^{31}P NMR spectrum by spin echo mapping (SEM) of CoAPO$_4$-50 shows a broad signal, ranging from about -500 to 10 000 ppm/H$_3$PO$_4$ (Figure 1a). The spectrum is very different from that obtained using a simple Hahn-echo sequence (carrier frequency at 0 Hz) without mapping. In this case, only one weak line is observed around 0 ppm and most of ^{31}P nuclei are not detected. This confirms the observations of Peeters et al.,[34] who came to the conclusion that some of the ^{31}P nuclei in CoAPO$_4$-n molecular sieves are invisible using an echo sequence. However, the authors attributed the presence of "NMR-invisible phosphorus" to an extremely fast relaxation of ^{31}P nuclei in the presence of cobalt. It is clear from Figure 1 that the reason why ^{31}P nuclei are not detected is essentially due to the fact that NMR lines are shifted toward low fields, and thus not detectable using a Hahn-echo sequence with irradiation at 0 Hz.

For pure AlPO$_4$-5, both ^{31}P NMR spectra obtained by SEM and a Hahn-echo sequence are similar and composed of a single line without any signal above 250 ppm. Moreover, both spectra have the same intensity which, by comparison with the MAS

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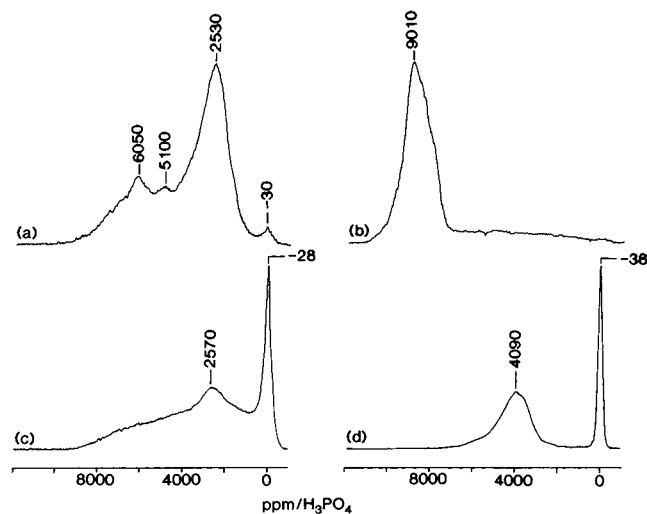(48) Tong, Y. Y. *J. Magn. Res.* **1996**, *119A*, 22.

Figure 1. ^{31}P NMR SEM spectra of CoAPO₄-50 (a), DAF-2 (b), CoAPO₄-46 (c), and CoAPO₄-20 (d).

spectrum, indicates that 100% of the phosphorus nuclei are detected. Therefore, this suggests that NMR signals above 250 ppm in the spectrum of CoAPO₄-50 might be assigned to ^{31}P nuclei in interaction with Co²⁺ species. Before discussing the nature of this interaction, it is of prime importance to look at changes in the NMR intensities with the Co content in the samples. As clearly shown in Figure 2, the relative intensity of signals above 250 ppm increases with the Co fraction in CoZnAPO₄-50 molecular sieves. Pure ZnAPO₄-50 shows a spectrum similar to that of AlPO₄-5, which can be explained by the absence of paramagnetism of Zn²⁺ cations. For all samples, comparison of the integrated intensity with that of AlPO₄-5 confirms that all ^{31}P nuclei are detected (Table 2). As will be discussed later, this is not the case when the MAS technique or a Hahn-echo sequence without mapping are applied.

In order to clarify the nature of ^{31}P NMR signals, we have recorded the spectrum of the Co-impregnated AlPO₄-5 sample (Figure 3). The spectrum is essentially composed of one signal around 0 ppm, and no ^{31}P NMR peaks are observed for shifts higher than 500 ppm. This observation also agrees with that of Peeters et al.,[34] who claimed the absence of "NMR-invisible phosphorus" in Co-impregnated materials. Examination of the spectrum shows that the line is broader than that of AlPO₄-5. Simultaneously, the MAS spectrum exhibits numerous sidebands that are absent from the spectrum of AlPO₄-5.

This result is very important, as it demonstrates that the presence of low field peaks in the ^{31}P NMR spectrum of CoAPO₄-*n* molecular sieves is direct evidence for the existence of framework Co species. Moreover, data obtained on Co-impregnated AlPO₄-5 show once more that line broadening and spinning sidebands under MAS conditions cannot be taken as proof for cobalt incorporation in the lattice. Figure 4 shows the evolution of the T_2 relaxation time with the carrier frequency for various CoZnAPO₄-50 molecular sieves. Actually, the evolution of ^{31}P magnetization with τ depends on the carrier frequency ω_n (see Supporting Information). On the other hand, for a given structure (structure AFY of CoAPO₄-50), it does not seem to depend on the Co content in the materials.

Typically, we observe that T_2 decreases with the ^{31}P NMR line shift, from a few ms around 0 ppm to 30−40 μs around 8000 ppm. The decrease is relatively fast between 0 and 1500 ppm and becomes slow for higher shift values. The values of T_2 measured at a carrier frequency of 0 Hz, $T_2(0)$, are comparable with those reported by Peeters et al.[34] on various
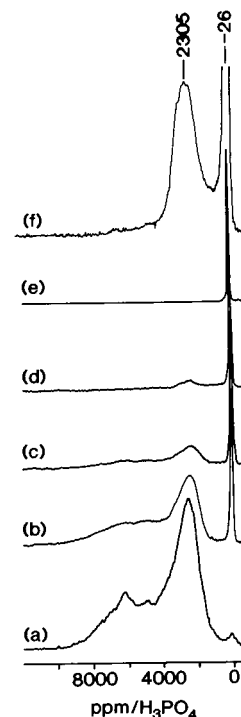

Figure 2. ^{31}P NMR SEM spectra of CoAPO₄-50 (a), Co₀.₂Zn₀.₁APO₄-50 (b), Co₀.₁Zn₀.₂APO₄-50 (c), Co₀.₀₅Zn₀.₂₅APO₄-50 (d), ZnAPO₄-50 (e), and Co₀.₀₅Zn₀.₂₅APO₄-50 after magnification (× 15).

CoAPO₄-*n* molecular sieves. In particular, we observe that T_2-(0) slightly increases when the Co content decreases, which is a direct consequence of the decrease in the number of paramagnetic centers in the framework.

From the above results, it is now possible to propose the following interpretation.

By comparison with AlPO₄-5 and Co-impregnated AlPO₄-5, the ^{31}P NMR line observed around 0 ppm in the spectra by SEM of CoZnAPO₄-50 molecular sieves can be assigned to phosphorus nuclei surrounded by four Al or Zn species. In the following, these species will be denoted P(0Co), which means that phosphorus has no Co atoms in the first coordination sphere. This line is usually broader than that of AlPO₄-5 due to dipolar interactions of ^{31}P nuclei with framework Co species.

The other peaks observed above 500 ppm are attributed to phosphorus nuclei with at least one Co atom in the first coordination sphere: P(*n*Co) with $n \geq 1$. This attribution is confirmed by the increase in the intensity of these peaks with the Co content and by the drastic difference in T_2 values compared to P(0Co) species.

In the case of VPO catalysts, we have reported that the shift of ^{31}P NMR lines results from an electron-nuclear contact term.[49] The paramagnetic shift is thus related to the atomic susceptibility of the material X_{at}:

$$\delta = (\omega - \omega_0)/\omega_0 = (H_{eff}\beta)X_{at}f \qquad (1)$$

where H_{eff} is the atomic hyperfine field for phosphorus (4.7·10² T), β the Bohr magneton, and f a fractional contribution of the unpaired electron spin of the paramagnetic species at the ^{31}P nucleus. Assuming that eq 1 can be adapted to the case of CoAPO₄-*n* molecular sieves, f probably depends not only on many structural factors like the Co−O−P bond distance and angle but also on the presence of water and templating molecules inside the channels of the molecular sieve. However, it is expected that f increases with the number of unpaired electrons

(49) Sananes, M. T.; Tuel, A. *Solid State NMR* **1996**, *6*, 157.

Table 3. Different P(nCo) Populations Deduced from ^{31}P NMR SEM Spectra (I_{NMR}) and from a Calculation Assuming a Random Distribution of Co Atoms in the Structure (I_{calc}) for the Series of CoZnAPO$_4$-50 Molecular Sieves

no.	sample	I_{NMR}			I_{calc}		
		P(0Co)	P(1Co)	P(nCo, n>1)	P(0Co)	P(1Co)	P(nCo, n>1)
6	CoAPO$_4$-50	0.03	0.57	0.40	0.148	0.362	0.49
8	Co$_{0.2}$Zn$_{0.1}$APO$_4$-50	0.25	0.49	0.26	0.316	0.42	0.26
9	Co$_{0.1}$Zn$_{0.2}$APO$_4$-50	0.57	0.35	0.08	0.60	0.33	0.07
10	Co$_{0.05}$Zn$_{0.25}$APO$_4$-50	0.77	0.21	0.02	0.78	0.2	0.02
7	ZnAPO$_4$-50	1	0	0	1	0	0
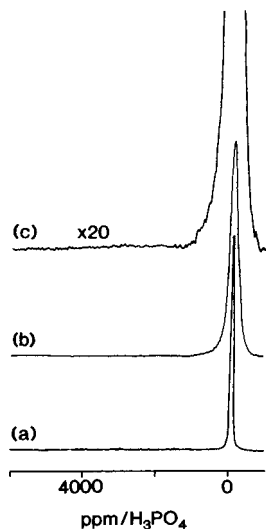
Figure 3. ^{31}P NMR SEM spectra of AlPO$_4$-5 (a), Coimpregnated APO$_4$-5 (b and c). Spectrum c was plotted with a magnitude of 20 compared to b.
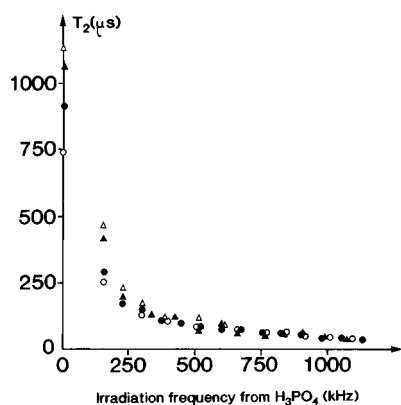
Figure 4. Evolution of the relaxation time T_2 with the carrier frequency for various CoZnAPO$_4$-50 molecular sieves: (○) sample 6, (●) sample 8, (▲) sample 9, (△) sample 10.

participating in the interaction, i.e. with the number of Co atoms in the first coordination sphere around P. Indeed, Grey et al.[37] have observed that the ^{89}Y paramagnetic shift in rare-earth pyrochlores was proportional to the number of lanthanide ions substituted for yttrium in the first coordination sphere around Y. In order to check this assumption, we have recorded the ^{31}P NMR SEM spectrum of DAF-2, a microporous cobalt phosphate in which all phosphorus atoms are surrounded by four Co atoms. The spectrum shows a single broad line around 9000 ppm, without any significant contribution below 7000 ppm, which confirms that the material contains only P(4Co) units in the structure (Figure 1b). At 300 K, the volume susceptibility of DAF-2 was found to be 121·10^{-6} (cgs) which, according to

(50) Bose, M.; Bhattacharya, M.; Ganguli, S. *Phys. Rev. B* **1979**, *19*, 72.

(51) Li, J.; Lashier, M. E.; Schrader, G. L.; Gerstein, B. C. *Appl. Catal.* **1991**, *73*, 83.

eq 1 gives $f = 6.7·10^{-3}$. This indicates that the fraction of unpaired electron transferred per Co−O−P bond is ca. 0.17%. Such a value is in good agreement with those reported for manganese and vanadium phosphates.[50,51] Considering that effects due to the molecular sieve structure are minor and that f is approximately proportional to the number of Co atoms in the first coordination sphere around P, the shift for P(nCo) species in CoAPO$_4$-n molecular sieves is expected to be

$$\delta_{P(nCo)} \text{ (ppm)} \approx 9000(n/4) = 2250n \qquad (2)$$

We have previously mentioned that it was possible in the case of Mg-containing aluminophosphate molecular sieves to estimate the framework composition by measuring the relative intensities of the different ^{31}P NMR lines corresponding to various P(nMg) environments. However, except for P(0Co) species, NMR lines are not only shifted but also drastically broadened in the presence of cobalt. This makes the deconvolution of NMR spectra into several lines corresponding to P(nCo) environments very difficult, even impossible. The ^{31}P MAS NMR spectrum of ZnAPO$_4$-50 shows five distinct peaks between −5.5 and −24.5 ppm that can be assigned to the different P(nZn) environments in the material. If we assume that Zn randomly substitutes for aluminum in the framework, then it is possible to calculate the different P(nZn) populations using the binomial theorem. Let p be the probability for an atom in the first coordination sphere around P to be Al; p can be directly deduced from the TO$_2$ formula Zn$_x$Al$_y$P$_{0.5}$O$_2$: $p = 1 - 2x$. For $x = 0.2$ (Table 2), the relative populations are given by

$$P(0Zn) = p^4 = 0.13 \qquad P(1Zn) = 4p^3(1 - p) = 0.345$$
$$P(2Zn) = 6p^2(1 - p)^2 = 0.345$$
$$P(3Zn) = 4p(1 - p)^3 = 0.154$$
$$P(4Zn) = (1 - p)^4 = 0.025$$

These populations are in good agreement with those obtained by deconvolution of the ^{31}P MAS NMR spectrum, which indicates that, in contrast to Co, Zn does not occupy preferential sites in the unit cell.

All CoZnAPO$_4$-50 molecular sieves can be regarded as Co-substituted ZnAPO$_4$-50 materials. For low Co contents, like in sample 10, the P(nCo) populations corresponding to $n \geq 2$ are probably very low. For sample 10, populations can be calculated assuming that either Co is randomly distributed on the same sites as Al or Zn or that Co atoms occupy a specific position in the structure. In the first case, the binomial theorem gives

$$P(0Co) = 0.77 \qquad P(1Co) = 0.21 \qquad P(2Co) = 0.02$$
$$P(3Co) \approx P(4Co) \approx 0$$

In the second case, we have

$$P(0Co) = 0.75 \qquad P(1Co) = 0.25 \qquad P(nCo, n>1) = 0$$

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This indicates that in both cases the spectrum should be essentially composed of two lines with relative intensities of approximately 4:1 for a random distribution and 3:1 for a material in which Co occupies a preferential site. Figure 2f shows that the ^{31}P NMR SEM spectrum of sample 10 is effectively composed of two distinct signals around 0 and 2300 ppm, respectively. Note that the position of the line at 2300 ppm corresponding to P(1Co) species is very close to that given by eq 2 and deduced from the NMR shift of DAF-2. From a quantitative point of view, the relative intensity of this line corresponds to 20% of the total intensity, which is consistent with a random distribution of Co species in the material. Moreover, in the absence of signal above 4000 ppm, it is possible to estimate the line shape corresponding to P(1Co) species. The line is rather symmetrical and can be quite well simulated by a Gaussian function with a full width at half maximum (fwhm) of 1400 ppm. This line will serve as a reference for P(1Co) species in the deconvolution of NMR spectra of the various CoZnAPO$_4$-50 samples. Since for P(nCo) species with $n > 1$ NMR lines are usually broad, we have simulated only the two first lines at ca. 0 and 2300 ppm, and we obtain the relative contribution of P(nCo) species ($n > 1$) by difference between the original spectrum and the simulation.

Results corresponding to the series of CoZnAPO$_4$-50 molecular sieves are reported in Table 3. We have also listed the calculated values, assuming a random distribution of Co atoms in the ZnAPO$_4$-50 or AlPO$_4$-50 frameworks. For samples with high Co contents, particularly pure CoAPO$_4$-50, populations deduced from NMR spectra differ from the calculated ones.

The case of CoAPO$_4$-50 is of particular interest since it was previously reported that cobalt atoms do not randomly substitute for aluminum in the structure. From X-ray diffraction studies, Bennett et al.[21] concluded that 66% of Co in CoAPO$_4$-50 occupies a specific position in the framework while the remaining cobalt is randomly distributed on the same crystallographic sites as aluminum. The structure can be considered as built of sheets of six-membered rings held together by tetrahedral atoms capping each six-membered ring above and below it to form double four-membered rings. The bonds connecting the sheets together are cobalt−oxygen−phosphorus bonds, as shown in Figure 5. As a consequence, each P atom has at least one Co neighbor in the first coordination sphere and some of the four-membered rings contain only phosphorus and cobalt. We have estimated the different P(nCo) populations in CoAPO4−50 assuming that two Co atoms occupy a specific position in the unit cell along the 3-fold axes and that the remaining Co randomly substitutes for Al. Populations calculated using a Monte Carlo method on $19 \times 19 \times 19$ unit cells were

$$P(0Co) = 0 \qquad P(1Co) = 0.581 \qquad P(2Co) = 0.343$$
$$P(3Co) = 0.070 \qquad P(4Co) = 0.005$$

These populations, particularly P(0Co) and P(1Co), are very different from those corresponding to a random distribution but are in good agreement with those deduced from the ^{31}P NMR SEM spectrum of CoAPO$_4$-50 (Table 3), which could indicate a partial ordering in the structure.

A more detailed examination of the NMR spectrum (Figure 1a) shows two peaks above 4000 ppm, one at ca. 5000 ppm and the second one around 6000 ppm. As P(1Co) species are characterized by a NMR line at about 2400 ppm, we expect P(2Co) species to be observed at approximately 5000 ppm. Unfortunately, in the absence of theoretical data on the line shape in these compounds, it is almost impossible to deconvolute this part of the spectrum. Nevertheless, one of these peaks could
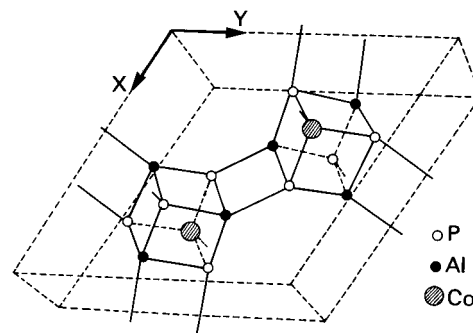

Figure 5. Structure of the unit cell of CoAPO$_4$-50. About 17% of Al atoms are Co.

be assigned to P(2Co) species with the two Co atoms in the same 4-membered ring while the other could correspond to P(2Co) species with Co atoms in different 4-membered rings. The variation in line shift could be explained by different local structures around P, particularly different bond angles and lengths. Further studies are in progress to assess the nature and assignment of these two peaks.

When the CoZnAPO$_4$-50 molecular sieve contains one Zn and two Co atoms per unit cell (sample 8), populations are also different from those calculated assuming a random distribution. However, a peak is observed around 0 ppm, which indicates the presence of P(0Co) species in the framework. This means that some of the Zn atoms are located along the 3-fold axes of the structure, at the specific positions that were occupied by Co in CoAPO$_4$-50. Indeed, if these positions were only occupied by the two Co atoms (sample 8), P(0Co) species would not be observed, as for CoAPO$_4$-50. As far as the Zn content is increased (samples 9 and 10), populations tend to equal those corresponding to a random distribution, in agreement with data obtained on pure ZnAPO$_4$-50.

Influence of the Structure of the Molecular Sieve. We have recorded the ^{31}P NMR SEM spectra of CoAPO$_4$-n molecular sieves with various structures, namely CoAPO$_4$-5, -20, -36, -39, and -46. For all samples, integration of the NMR signal shows that all phosphorus atoms are detected within experimental error (Table 2).

CoAPO$_4$-46. CoAPO$_4$-46 and CoAPO$_4$-50 have structures that can be related to each other via a sigma transformation of a double 4-membered ring into a 6-membered ring. However, while both materials possess high Co contents, the ^{31}P NMR SEM spectrum of CoAPO$_4$-46 differs from that of CoAPO$_4$-50, particularly by the presence of a peak around 0 ppm (Figure 1c). In the region above 1500 ppm, the signal is broad and relatively featureless with a more pronounced peak at about 2570 ppm. By comparison with CoAPO4−50 molecular sieve, this peak can be assigned to P(1Co) species. Moreover, the two lines around 5000 and 6000 ppm that were present on the spectrum of CoAPO$_4$-50 are not observed. Due to the broad overlapping signals at low fields, it is very difficult to calculate the various P(nCo) populations in this sample. However, assuming that the peak at −28 ppm is symmetrical and that the contribution of other signals is negligible in this region of the spectrum, it is possible to estimate the fraction of P(0Co) species. Under such conditions we find P(0Co) = 0.18 ± 0.02, and the value agrees quite well with that obtained for a random distribution. Indeed, the binomial theorem gives P(0Co) = 0.19, P(1Co) = 0.39, P(2Co) = 0.285, P(3Co) = 0.095 and P(4Co) = 0.01. The above calculation also shows that P(1Co) species are in the majority in CoAPO$_4$-46, which could explain the presence of a maximum around 2570 ppm in the NMR spectrum. Even though these observations are consistent with
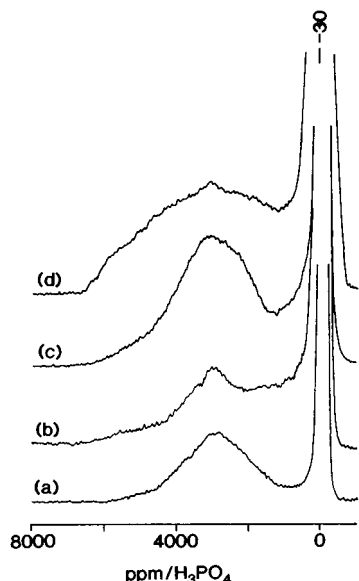
Figure 6. ^{31}P NMR SEM spectra of CoAPO$_4$-39 as-synthesized (a) and calcined (b) and CoAPO$_4$-5 as-synthesized (c) and calcined (d).

Figure 7. Sodalite cage of CoAPO$_4$-20 showing the specific positions occupied by Co atoms.

a random distribution of Co atoms in the structure, such a conclusion should be speculative due to the poor resolution of the spectrum. Comparison between CoAPO$_4$-46 and CoAPO$_4$-50 also suggests that the relatively good resolution of NMR lines in CoAPO$_4$-50 probably arises from the ordering of some of the Co species in the framework.

CoAPO$_4$-5 and CoAPO$_4$-39. For all these materials, the Co content is low and close to 3 wt %, and corresponds to ca. 1 Co atom per unit cell in CoAPO$_4$-5. Therefore, we expect ^{31}P NMR SEM spectra to be composed of essentially two lines corresponding to P(0Co) and P(1Co) species, respectively. Actually all spectra show an intense band around -30 ppm and a weak and broad signal in the range of 500$-$5000 ppm (Figure 6). Due to the position of the broad peak it is reasonable to assign it to P(1Co) species in both samples. However, Figure 6 clearly shows that the lineshape is complex, particularly for CoAPO$_4$-5, where a shoulder is observed at ca. 2000 ppm. Nevertheless, in the absence of additional data on this sample, assignment of this shoulder was not possible and all NMR signals above 500 ppm were considered to arise from P(1Co) species. The relative areas of the resonance at -30 ppm, obtained experimentally assuming that the line is symmetrical, are 0.65 ± 0.1 and 0.6 ± 0.1 for CoAPO$_4$-39 and CoAPO$_4$-5, respectively. Unfortunately, such low Co contents did not permit conclusions to be drawn about the distribution of Co species in the structure. Indeed, for CoAPO$_4$-39, a random distribution gives P(0Co) = 0.655 and P(1Co) = 0.29 while a completely ordered framework leads to P(0Co) = 0.6 and P(1Co) = 0.4. Due to the low intensity and signal-to-noise ratio of NMR signals between 500 and 5000 ppm, the difference between experimental and calculated populations is within error limits for both configurations. No significant differences in line shift corresponding to P(1Co) species are observed for the two samples and maxima are comprised between 2800 and 3100 ppm. This shows the limitation of the method for structure determination. Such determination is possible in the case of nonparamagnetic systems where ^{31}P NMR lines are narrow and sensitive to very small perturbations. In the case of CoAPO$_4$-*n* molecular sieves, the spectrum is dominated by the electron-nuclear interactions, which are at least 2 orders of magnitude higher than those due to structure modifications. However, these examples show that it is possible to detect phosphorus species
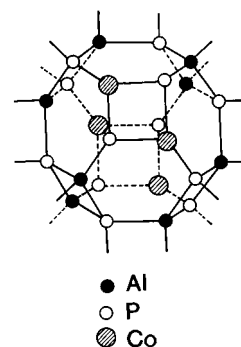
with Co ions in their coordination sphere, even in the case where the Co fraction in the solid is relatively low.

CoAPO$_4$-20. CoAPO$_4$-20 is a cobalt-substituted aluminophosphate with the sodalite structure, whose unit cell is a truncated octahedron built of eight 6-membered and six 4-membered rings. The TO$_2$ formula of the material, Co$_2$-Al$_4$P$_6$O$_{24}$, shows that CoAPO$_4$-20 contains exactly two Co atoms per unit cell, which means that 33% of Al atoms are replaced by Co. The ^{31}P NMR SEM spectrum of CoAPO$_4$-20 shows two major peaks at about -30 and 4100 ppm, with relative intensities of 0.3 and 0.6, respectively, together with a weak signal around 6000 ppm (Figure 1d) The spectrum is not consistent with a random distribution of cobalt species in sodalite cages, which suggests that CoAPO$_4$-20 possesses a relatively well-ordered framework. If we consider that the line at ca. 4100 ppm corresponds to P(1Co) species, this leads to P(0Co) = 0.3, P(1Co) = 0.6, and P(*n*Co, *n*>1) = 0.1. However, it is impossible to find an ordering in the sodalite cage consistent with such populations. Another possibility is that the line at 4100 ppm corresponds to P(2Co) species. In this case, we have P(0Co) = 0.3, P(1Co) ≈ 0, P(2Co) = 0.6, and P(*n*Co, *n*>2) ≈ 0.1. This corresponds to the unit cell given in Figure 7, where the two Co atoms share a 4-membered ring. The comparatively small shift for P(2Co) species with respect to other CoAPO$_4$-*n* molecular sieves could be due to the large T$-$O$-$T bond angles commonly found in sodalite structures.

A completely ordered framework has also been observed by Barrie et al.[31] for MAPO$_4$-20, the magnesium-substituted aluminophosphate. However, in the case of Mg, ^{31}P NMR intensities indicated that Mg atoms share only 6-membered rings, yielding relative populations P(1Mg) = 0.67 and P(2Mg) = 0.33. The difference between Mg and Co-substituted AlPO$_4$-20 is very interesting and underlines the importance of the nature of the divalent cation in the crystallization of MeAPO$_4$-*n* molecular sieves.

NMR Spectra of Calcined Molecular Sieves. The nature, coordination, and oxidation state of cobalt species in calcined CoAPO$_4$-*n* molecular sieves are still a matter of debate. For Berndt et al.,[52] the change in color upon calcination of CoAPO$_4$-*n* molecular sieves does not necessarily mean oxidation of Co(II) species. In fact, the proportion of cobalt readily oxidized in CoAPO$_4$-5 or CoAPO$_4$-11 would be very small. This is also the conclusion of Barrett et al.,[24] at least for CoAPO$_4$-5 and CoAPO$_4$-36. From EXAFS data, these authors observed that calcined samples probably contain both Co(III) and unoxidized Co(II) species. Indeed, the mean Co$-$O distance and the coordination number of Co atoms are intermediate between those of a fully oxidized material (CoAPO$_4$-18) and as-synthesized samples.

(52) Berndt, H.; Martin, A.; Zhang, Y. *Microporous Mater.* **1996**, *6*, 1.

Upon oxidation, Co(II) looses an electron (3d^6 configuration) and the Co−O distance is decreased about 5% with respect to that observed in as-prepared samples. Therefore, it is difficult to predict the effect of calcination on the position of the ^{31}P NMR lines.

As a general trend, we observe that ^{31}P NMR lines of calcined CoAPO$_4$-*n* molecular sieves are comparatively broader than those of as-synthesized materials (Figure 6). This is particularly evident for the line assigned to P(1Co) species. However, the integrated intensity of the spectra is the same as that of as-synthesized samples, which shows that all phosphorus nuclei are also detected for calcined samples. It has been widely reported that most of CoAPO$_4$-*n* molecular sieves are not very stable upon heating at high temperature and that thermal treatment results in a slight decrease in the crystallinity. This probably increases the distribution of bond lengths and angles in the structure and, consequently, the NMR line width. For all samples, the position of the maximum of the line assigned to P(1Co) species is not drastically modified, but we observe an increase of the signal intensity in the region between 1000 and 2000 ppm (Figure 6). This could be attributed to the oxidation of a small fraction of Co(II) species from the framework. Indeed, calcination reduces the electronic density around Co and, thus, the fractional contribution of the unpaired electron spin, *f* (eq 1). However, as oxidation also modifies the Co−O bond length, this interpretation needs to be confirmed, particularly by studying CoAPO$_4$-18, where most of the Co(II) species are oxidized upon calcination.[24]

Relation between ^{31}P NMR Signals and "NMR-Invisible Phosphorus". As we have clearly shown, all ^{31}P NMR lines in the range of 500−10 000 ppm cannot be detected using a Hahn-echo sequence with irradiation frequency at 0 Hz. This can represent a considerable proportion of ^{31}P nuclei, particularly in the case of materials with high Co contents like CoAPO$_4$-50 or CoAPO$_4$-20. However, some of the signal corresponding to P(0Co) species can also be undetectable. Indeed, the NMR signal is totally observed when the line width is smaller than that of the spectrum of the RF pulse, which is about 80 kHz (500 ppm) in our case. Considering a CoAPO$_4$-*n* molecular sieve with the framework composition Co$_x$Al$_{1-x}$PO$_4$, the percentage (by weight) of cobalt is

$$W = 59x/(32x + 122)$$

and

$$x = 122W/(59 - 32W)$$

For low Co contents, the fraction of P(0Co) species can be approximated by

$$P(0Co) = (1 - x)^4 \approx 1 - 8.3W \qquad (3)$$

which means that the fraction of phosphorus nuclei with no Co atoms in the first coordination sphere is proportional to the Co weight content. The percentage of phosphorus nuclei observed using a Hahn-echo sequence without mapping (carrier frequency at 0 Hz) versus the Co content in the molecular sieve is reported in Figure 8. For all samples, the intensity was corrected by taking into account the decrease in magnetization due to relaxation before acquisition. For comparison, the relative intensity of the ^{31}P NMR line assigned to P(0Co) species in the SEM spectrum is also plotted. For low Co contents (<5 wt %), both curves follow approximately the theoretical variation given by (eq 3). Whilst for samples with low Co contents a simple Hahn-echo is sufficient to observe all P(0Co) species, a deviation is observed for high Co contents (COAPO$_4$-46, sample
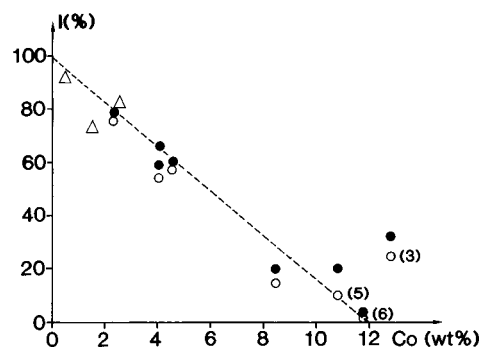

Figure 8. Evolution of the intensity of the NMR signal obtained using a simple Hahn-echo sequence (○) and of the percentage of P(0Co) species (●) with the Co content in the various samples. P(0Co) was obtained by deconvolution of the SEM spectrum. The dashed line corresponds to the theoretical value given by eq 3. Numbers in parentheses refer to samples in Table 2. (△) data taken from ref 34.

5). The intensity of the NMR signal obtained with a simple echo represents only 60−70% of the P(0Co) species, due to the exceptionally large width of the P(0Co) NMR line in this sample. The case of CoAPO$_4$-20 (sample 3) is particular as most of the P(0Co) species can be detected with a standard echo sequence despite a high level of aluminum substitution. This results from the ordering of Co atoms in the unit cell, which reduces the distribution of bond lengths and angles in the framework and, thus, decreases the ^{31}P NMR line width.

Conclusion

^{31}P NMR spectra of cobalt-substituted aluminophosphate molecular sieves have been recorded using a spin echo mapping sequence. By selecting the appropriate mapping increment and correcting the intensities of individual spectra to account for the relaxation of ^{31}P magnetization before acquisition, it was possible to observe all phosphorus nuclei in the materials, even when they possessed high Co contents. This contrasts with conventional methods generally used to characterize MeAPO$_4$-*n* materials like the MAS technique or a simple Hahn-echo sequence with irradiation frequency at 0 Hz, for which a large proportion of ^{31}P nuclei were not detected. ^{31}P NMR spectra of CoAPO$_4$-*n* materials are broad, and the signal is observed in the range of −500 to 10000 ppm/H$_3$PO$_4$. The NMR line around 0 ppm has been assigned to P atoms surrounded by four Al, whereas lines with shifts higher than 500 ppm were attributed to P atoms with at least one Co species in the first coordination sphere. Indeed, no signal above 500 ppm was observed on Co-impregnated aluminophosphates.

The different ^{31}P NMR lines have been assigned to various P(*n*Co) environments in the structure. The NMR line shift, which depends on a fraction of the unpaired electron density of Co^{2+} being on phosphorus nuclei, is approximately proportional to the number of Co atoms around P. The framework composition of various CoAPO$_4$-*n* molecular sieves was estimated from the various P(*n*Co) populations obtained by deconvolution of the spectra and was found to be in good agreement with chemical analysis data.

Comparison of P(*n*Co) populations with those calculated using a binomial theorem showed that Co does not randomly substitute for Al in CoAPO$_4$-50 and CoAPO$_4$-20. For CoAPO$_4$-50, populations correspond to a framework where about 66% of Co atoms occupy special positions while the remaining Co is randomly distributed on the same sites as Al. Such partial ordering in CoAPO$_4$-50 had already been suggested by Bennett et al.[21] from X-ray diffraction studies. For CoAPO$_4$-20, the

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framework is probably completely ordered and NMR data suggested that the two Co atoms share a 4-membered ring in the sodalite cage.

^{31}P NMR spectra of calcined samples are slightly different from those of as-prepared materials, especially in the range of 1000−2000 ppm. We observed an increase in the signal intensity in this region upon calcination, but the interpretation is difficult due to the fact that calcined samples probably contain both Co(III) and unoxidized Co(II) species. However, as in the case of as-synthesized materials, comparison of the integrated intensity with that of pure AlPO$_4$-5 showed that all phosphorus species were detected.

The spin echo mapping technique seems to be a very interesting technique to study paramagnetic materials for which NMR lines are shifted and broadened. In particular, it could be extended to the characterization of various microporous transition-metal phosphates whose syntheses have been recently reported in the literature.

Supporting Information Available: Mathematical derivation of the spin-echo mapping technique (3 pages). See any current masthead page for ordering and Internet access instructions.