The first observation of 'NMR-invisible phosphorus' in cobalt-substituted aluminophosphate molecular sieves

L. Canesson and A. Tuel*

Institut de Recherches sur la Catalyse, C.N.R.S. 2 av. A. Einstein, 69626 Villeurbanne Cedex, France

A spin-echo mapping technique is used to record the total ^{31}P NMR signal of CoAPO molecular sieves for which a large proportion of phosphorus nuclei are not accessible by conventional NMR techniques.

Framework substitution of divalent cations for aluminium in aluminophosphate molecular sieves (MeAPO$_4$) has been a matter of interest over the last years as it provides AlPO materials with interesting properties in catalytic reactions.[1,2] Therefore, it is of prime importance to have an extensive characterisation of these catalysts, and to determine the nature and location of the metal ions within the channels and cavities of the structure. Among all the spectroscopic techniques that can be used, solid-state NMR is very attractive as both ^{31}P and ^{27}Al nuclei possess a natural abundance of 100%. It is expected that substitution of divalent cations for aluminium modifies the chemical shift of neighbouring ^{31}P nuclei, as observed in ^{29}Si NMR spectra of zeolites with aluminium incorporation. Up to now, the method has been successfully applied for the study of the environment of phosphorus nuclei in magnesium-substituted aluminophosphates MAPOs.[3–5] However, as far as paramagnetic transition-metal cations like Co^{2+} are concerned, conventional NMR sequences cannot be applied. NMR signals are broadened and numerous spinning side-bands are observed, due to various interactions between cobalt and phosphorus nuclei.[6] The presence of these side-bands as well as the decrease in both the T_1 and T_2 relaxation times of ^{31}P nuclei has sometimes been considered as a proof for the framework cobalt siting.[7] However, such modifications are also observed in Co-impregnated aluminophosphates, which makes the discrimination between framework and non-framework cobalt almost impossible with this technique. Peeters *et al.*[8] have shown that, when cobalt is incorporated into the AlPO framework, phosphorus nuclei in the first and third coordination spheres around the metal cannot be detected by NMR and become 'NMR-invisible'.

We report here for the first time a method that allowed us to observed these so-called 'NMR-invisible phosphorus' nuclei and to record the total ^{31}P NMR spectrum of CoAPO materials. The method is based on a spin-echo mapping technique that has been successfully applied for the characterisation of paramagnetic VPO catalysts.[9,10] Schematically, the method consists of recording a series of spectra using a Hahn echo sequence at different irradiation frequencies. For each spectrum, the intensity is corrected taking into account the relaxation of the magnetisation before acquisition of the signal. The total NMR signal is then obtained by addition of all individual spectra. Tong[11] has recently shown that, under specific conditions, the spectrum obtained by spin-echo mapping could reproduce the real line shape. Therefore, it was possible to make quantitative measurements by comparing the NMR intensities with those of pure AlPO-5. All experiments were carried out on a Bruker DSX 400 spectrometer operating at 161.9 MHz. The 90° pulse was 3 μs and the defocalisation time between the 90 and 180° pulses in the echo sequence was 20 μs. All CoAPO molecular sieves were synthesised following literature procedures.

Fig. 1 compares the ^{31}P NMR spectra of CoAPO-50 obtained under various conditions. Almost no signal is observed under MAS conditions, due to the high Co content in the sample (11 mass% Co). With a Hahn echo, a broad signal is observed at δ *ca.* −20 (ref. H$_3$PO$_4$), the intensity of which corresponds to < 10% of the total amount of phosphorus in the material. This shows that > 90% of ^{31}P nuclei are not detected under these conditions. Using the spin-echo mapping technique, a very broad signal is observed between δ *ca.* 0 and 10 000. The integrated intensity of the obtained spectrum corresponds to 98% of the phosphorus atoms present in the sample, which shows that the total signal has been recorded. In fact, most of the signal (*ca.* 85%) is shifted towards low fields, which is the reason why it could not be observed using conventional echo sequences. The invisibility of ^{31}P nuclei is thus not due to very fast relaxation processes but to the fact that the signal cannot be observed when the irradiation frequency is centred on δ 0. As for VPO catalysts, the shift probably results from an electron–nuclear dipolar-plus contact term between the electrons of Co^{2+} and ^{31}P nuclei. We have already reported that the frequency shift is proportional to a fractional contribution of the unpaired electron spin to the ^{31}P nucleus.[10] In order to obtain more information about the nature and the assignments of the NMR

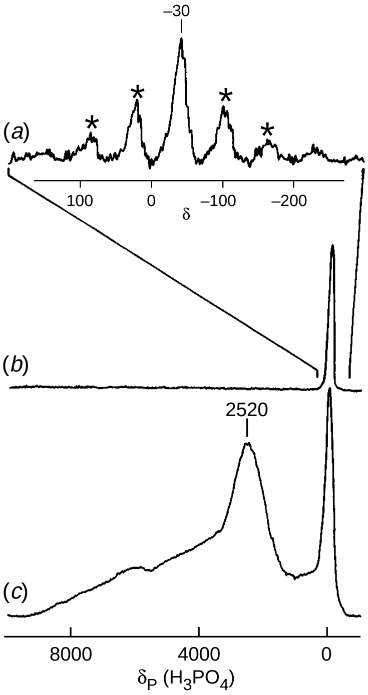

Fig. 1 ^{31}P NMR spectra of CoAPO-50. (*a*) ^{31}P MAS spectrum. Pulse length: 2 μs, recycle delay: 20 s, spinning rate: 10 kHz. 1600 scans were accumulated (asterisks denote spinning side-bands). (*b*) Spectrum obtained with a Hahn echo sequence with the irradiation frequency at 0 Hz. (*c*) Spin-echo mapping spectrum obtained by addition of 22 spectra. For each individual spectrum, 1800 FIDs were accumulated.

signals, we have recorded the spectrum of DAF-2, a cobalt phosphate made of alternating CoO_4 and PO_4 tetrahedra.[12] The signal is composed of a broad peak at δ *ca.* 9500 and corresponds to P atoms surrounded exclusively by four Co atoms. As the shift is proportional to the electron density of Co^{2+} on the ^{31}P nucleus, it is expected that it will depend on the number of Co atoms in the first coordination sphere around P. Therefore, we can suggest that the signal observed between δ *ca.* 500 and 10 000 corresponds to P atoms with at least one Co in the first coordination sphere, whilst the peak at δ *ca.* 0 corresponds to P(4A1) species. This was confirmed by studying a series of CoAPO molecular sieves with various Co contents. The relative intensity of the signal above δ 500 increases with the Co content but, in all cases, integration of the spectrum indicates that all phosphorus atoms were detected (Table 1). More details about the evolution of the line shape and intensity with the amount of Co incorporated will be given in a forthcoming paper.

CoAPO-50 clearly shows a distinct NMR peak at δ *ca.* 2500 which corresponds to approximately one quarter of the shift observed for DAF-2. We can thus assume that this line corresponds to P(1Co,3Al) units. Unfortunately, NMR lines are very broad and deconvolution of the signal into several lines corresponding to P(nCo, 4 − nAl) is not trivial. However, our assumption was supported by the study of samples containing low amounts of cobalt, like CoAPO-34 (2.95 mass% Co) or CoAPO-5 (3.05 mass% Co). For these samples, if we assume a random distribution of Co in the lattice, the relative contribution of P(2Co,2Al) species is expected to be negligible compared to that of P(1Co,3Al). Experimentally, spectra are essentially composed of two lines centred around δ 0 and 2500 without significant contribution above δ 5000. Moreover, we found that the relative intensity of the signal at δ 0 could be directly correlated with the Co content in the various samples, which makes the method very interesting not only for observing the total ^{31}P NMR signal but also to estimate the chemical composition. The line shape is slightly modified upon calcination of CoAPO materials in air (Fig. 2). As a general trend, we have noticed that the intensity in the range δ 500–1500 increases upon calcination whilst that above δ 2500 decreases, but the total intensity remained unchanged. As the observed shift strongly depends on the geometry and electronic density around P atoms, such modifications might be explained by changes in bond angles and lengths or by partial oxidation of Co^{II} to Co^{III} species upon calcination. Indeed, oxidation is expected to reduce the electronic density on the phosphorus nuclei and thus to decrease the observed NMR shift as already reported for VPO.[9]

Table 1 Percentage of phosphorus nuclei observed by ^{31}P NMR in various samples

Sample	Co (mass%)	I_E (%)[a]	I_{SEM} (%)[b]
CoAPO-50	11.7	9.5	98
CoAPO-46	7.9	17	103
CoAPO-39	2.95	71 (65[c])	101 (97[c])
CoAPO-5	3.05	67 (66[c])	99 (102[c])

[a] I_E is the percentage of ^{31}P nuclei detected using a Hahn echo with irradiation frequency at 0 Hz. [b] I_{SEM} is the percentage of ^{31}P nuclei detected with the spin-echo mapping technique. [c] Values obtained on calcined samples.

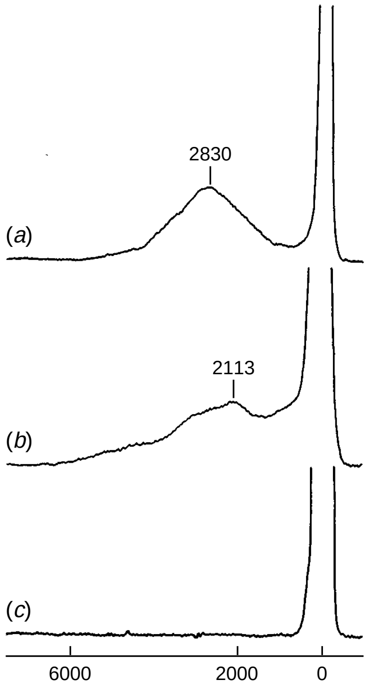

Fig. 2 ^{31}P NMR spectra by spin-echo mapping of as-synthesised CoAPO-5 (*a*), calcined CoAPO-5 (*b*) and cobalt impregnated AlPO-5 (*c*)

Finally, we have studied a CoAPO-5 sample (10 mass% Co) obtained by impregnation of calcined AlPO-5 with cobalt(ii) nitrate followed by calcination in air at 500 °C. As previously reported,[8] numerous spinning side bands are observed in the MAS NMR spectrum and T_1 and T_2 relaxation times considerably decrease with respect to pure AlPO-5. However, no signal is detected in the range δ 500–10 000 using the spin-echo mapping technique. This strongly suggests that the presence of an NMR signal in this region is characteristic of the incorporation of Co in the AlPO framework. The presence of Co–O–P bridges is probably necessary to delocalise the unpaired electrons of the metal on ^{31}P nuclei.

All these experiments show that the spin-echo mapping technique is a rapid and very powerful method to characterise CoAPO molecular sieves and to prove the incorporation of the metal in the framework. A detailed attribution of the different signals as well as the possibility of applying the method to the characterisation of other transition-metal substituted molecular sieves is in progress.

References

1 B. Akolekar, *J. Catal.*, 1993, **143**, 227.
2 J. Chen and J. M. Thomas, *J. Chem. Soc., Chem. Commun.*, 1994, 603.
3 F. Deng, Y. Yue, T. Xiao, Y. Du, C. Ye, L. An and H. Wang, *J. Phys. Chem.*, 1995, **99**, 6029.
4 J. P. Barrie and J. Klinowski, *J. Phys. Chem.*, 1989, **93**, 5972.
5 A. Tuel, I. Arcon, N. Novak Tušar, A. Meden and V. Kaucic, *Microporous Mater.*, 1996, **7**, 271.
6 C. Montes, M. E. Davis, B. Murray and N. Narayana, *J. Phys. Chem.*, 1990, **94**, 6431.
7 S. H. Chen, S. P. Sheu and K. J. Chao, *J. Chem. Soc., Chem. Commun.*, 1992, 1504.
8 M. P. J. Peeters, J. L.M. Van de Ven, J. W. de Haan and J. H. C. van Hooff, *Colloids Surf. A: Physicochem. Eng. Aspects*, 1993, **72**, 87.
9 M. T. Sananes, A. Tuel, G. J. Hutchings and J. C. Volta, *J. Catal.*, 1994, **148**, 395.
10 M. T. Sananes and A. Tuel, *Solid State Nucl. Magn. Reson.*, 1996, **6**, 157.
11 Y. Tong, *J. Magn. Reson.*, 1996, **119**, 22.
12 J. Chen, R. H. Jones, S. Natarajan, M. B. Hursthouse and J. M. Thomas, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 639.

Received, 8th November 1996; Com. 6/07603C