A ^{31}P NMR Study of Cobalt in Cobalt–Aluminophosphate Molecular Sieves

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The incorporation of cobalt ions into the aluminophosphate framework is monitored by ^{31}P spin-lattice relaxation.

In order to increase the Brønsted acidity and catalytic activity of aluminophosphate molecular sieves, the isomorphous substitution of divalent metal cations for trivalent aluminium or tetravalent silicon for pentavalent phosphorus have been made by a number of researchers.[1–5] The incorporated metal ions may stay within the cavities or channels of the $AlPO_4$ molecular sieves as metal oxides or counter ions instead of within the framework. The determination of framework metal species is a subject of great interest and importance. The incorporation of paramagnetic cobalt ions in an aluminophosphate framework should affect the magnetic properties of P nuclei. We have investigated the ^{31}P NMR spectra of a series of partially cobalt-substituted CoAPO-5 and CoAPO-34 molecular sieves; the variation of the spin-lattice relaxation of ^{31}P nuclei is truely a function of cobalt content in the cobalt aluminophosphate framework.

The template of synthetic blue $Et_3N{\cdot}CoAPO$-5 sample was removed by calcining in a dry air flow to 823 K at a heating rate of 1 K min^{-1} and maintaining at 823 K for 20 h. The calcined sample was treated with an oxygen flow at 823 K for 10 h until green CoAPO-5(III) was obtained. This compound was cooled to room temperature and evacuated, then heated to 423 K at a heating rate of 2 K min^{-1}, from 423 K to 673 K heated at 5 K min^{-1}, and then treated with a hydrogen flow at 673 K for 3 h until blue CoAPO-5(II) was obtained. This compound could be oxidized back to green CoAPO-5(III) by using an oxygen flow at 723–823 K. The chemical compositions of samples were determined by inductively coupled plasma–atomic emission spectroscopy and were close to the results obtained from the X-ray structural analysis.[6] The ^{31}P NMR measurements were made using a Bruker MSL-200 spectrometer at 295 K. Typically 16~800 transients were accumulated using a recycle delay (D_0) of 1~100 s dependent on Co content. For the inversion–recovery experiments, the π-pulse duration was set using the sample signal itself, and a very clearly defined null signal was obtained.

Since $AlPO_4$-5 contains single types of crystallographic sites for phosphorus, one resonance is expected in its ^{31}P NMR spectrum. The ^{31}P static spectra of CoAPO-5 and $AlPO_4$-5 show a broad peak at δ −30 and the linewidth increases with increasing Co content in the CoAPO-5 samples. The ^{31}P MAS NMR spectra of CoAPO-5 and CoAPO-34 samples appear with spinning sidebands, which arise from strong interactions with paramagnetic cobalt. The cobalt substitution for framework aluminum should affect the spin-relaxation of the framework ^{31}P nuclei. Application of the usual inversion–recovery sequence does distinguish the relaxation process of ^{31}P nuclei between CoAPO, cobalt treated $AlPO_4$ and $AlPO_4$ molecular sieves. The values of time (τ) at zero intensity for ^{31}P NMR signals at the inversion–recovery sequence are given in Fig. 1 and Table 1. The value of τ is much reduced with increasing Co content for synthetic CoAPO molecular sieves, but not for Co-coated calcined $AlPO_4$-5 samples. The isomorphous substitution of cobalt for aluminum in CoAPO-5 was confirmed by a single crystal X-ray diffraction structural analysis.[6] The Co : P atomic ratio of synthetic $Et_3N{\cdot}CoAPO$-5 is 0.13 by bulk chemical analysis which is close to 0.11 obtained from X-ray analysis on a crystal from the same batch. The ^{31}P relaxation on CoAPO is mainly affected by framework cobalt ions, not by exchangeable nonframework cobalt ions which can be removed by NH_4 ion-exchange. The relaxation measurements thus provide convincing evidence that the cobalt ions are incorporated into the aluminophos-

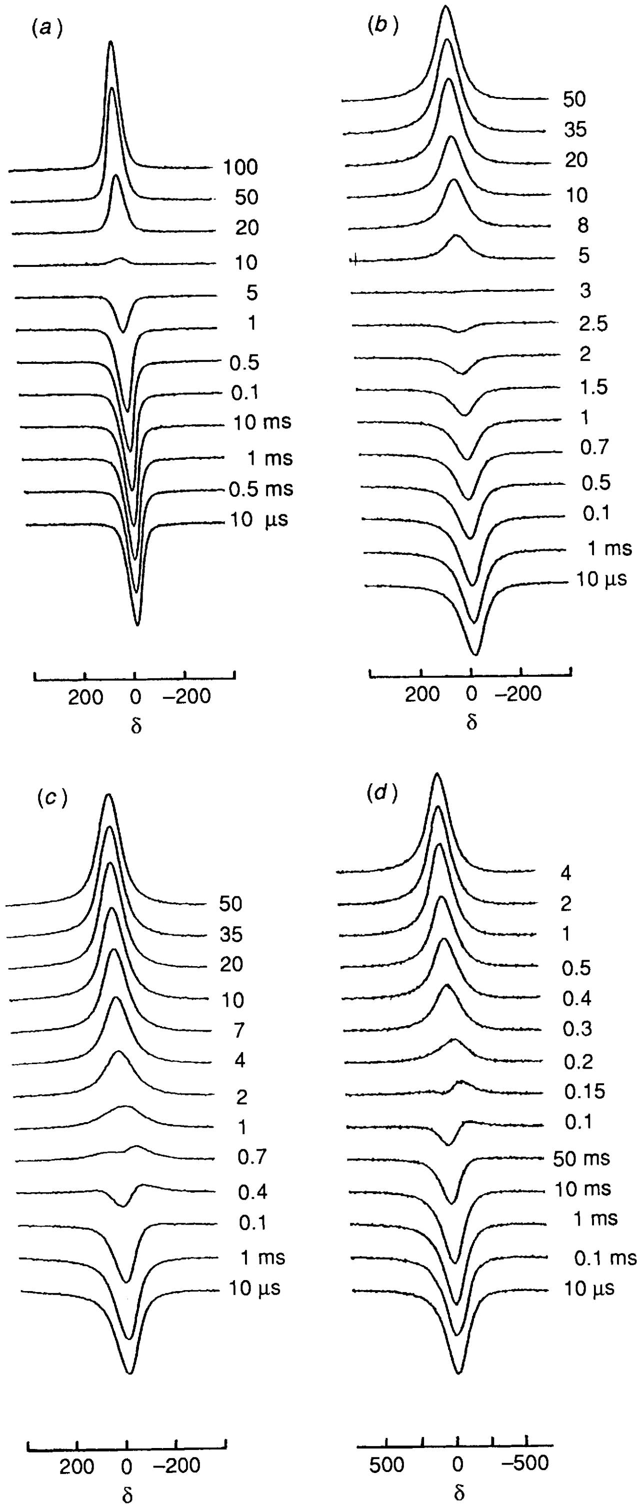

Fig. 1 Application of the inverstion–recovery sequence to synthetic $AlPO_4$-5 and CoAPO-5 and Co-coated $AlPO_4$-5 samples. (*a*) $Pr_3N{\cdot}AlPO_4$-5, (*b*) $AlPO_4$-5 + $CoSO_4$(Co : P = 13%), (*c*) $Et_3N{\cdot}$CoAPO-5(5%) and (*d*) $Et_3N{\cdot}$CoAPO-5(13%). Time/s unless otherwise stated.

Table 1 Spin-lattice relaxation rates of molecular sieves

	^{31}P NMR (static)		
Molecular sieve	Co : P (atomic ratio)	$\Delta\nu_{1/2}$	τ^{a}/s
Hydrated state			
$Pr_3N{\cdot}AlPO_4$-5	~0	60	9
$Et_3N{\cdot}$CoAPO-5(5%)	0.05	105	0.5
$Et_3N{\cdot}$CoAPO-5	0.10^{b}	—	0.23
$Et_3N{\cdot}$CoAPO-5(13%)	0.13	178	0.13
$Et_3N{\cdot}$CoAPO-34	0.22	219	0.04
$AlPO_4$-5	~0	68	4.5
$AlPO_4$-5/$CoSO_4$(5%)^{c}	0.05	64~68	2~2.3
$AlPO_4$-5/$CoSO_4$(13%)^{c}	0.13	97~102	2~3
CoAPO-5(II)	0.13	222	0.31
HCoAPO-5^{d}	0.10^{b}	—	0.39
Dehydrated state			
CoAPO-5(III)	0.13	173	1
CoAPO-5(II)	0.13	180	0.9
CoAPO-5(II′)^{e}	0.13	189	0.9

[a] Time of zero intensity at the inversion–recovery sequence. [b] Reactant molar ratio. [c] $CoSO_4$ was impregneted on calcined $AlPO_4$-5 at room temp., then the sample was dried at 60 °C. [d] Deammoniated form of $NH_4{\cdot}$CoAPO-5 obtained by exchanging CoAPO-5(II) with NH_4Cl solution. [e] Reduced form of CoAPO-5 after three redox cycles.

phate framework in CoAPO-5 and CoAPO-34. Besides, both dehydrated CoAPO-5(II) and CoAPO-5(III) give the same τ value for ^{31}P NMR longer than that of their hydrated precursor $Et_3N{\cdot}$CoAPO-5. According to the ^{31}P NMR results, we suggest that both framework Co^{II} and Co^{III} might be in high spin states.

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