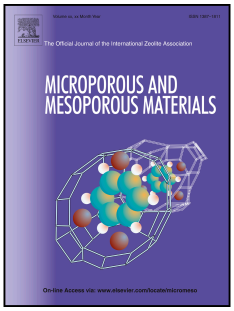

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Ionothermal Synthesis and Characterization of CoAPO-34 Molecular Sieve

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Abstract

The cobalt-doped aluminophosphate molecular sieve, CoAPO-34 (with the chabazite-type topology) was prepared under ionothermal conditions using 1-ethyl-3-methylimidazolium bromide (EMIMBr) ionic liquid in presence of 1,6-hexanediamine (HDA). The HDA is not incorporated in CoAPO-34, but is required to mediate the availability of Co^{2+} during the synthesis. The material was characterized using powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA) and solid-state NMR spectroscopy. Wideline ^{31}P NMR spectroscopy showed broad signals (~5000–10000 ppm wide), confirming that paramagnetic cobalt ions are successfully incorporated within the framework of the materials.

1. Introduction

Zeolites and related zeotype molecular sieves are inorganic materials with many industrial applications, such as gas absorption, ion exchange and catalysis. Aluminophosphates (AlPOs) are a family of zeotypes with properties similar to zeolites, and which may find use as catalysts and absorbents for molecular separation.[1,2] However, as AlPOs contain strictly-alternating AlO_4 and PO_4 tetrahedra, the materials have a neutral framework charge and, consequently, lack acid sites, meaning that they cannot be used directly as catalysts. Aliovalent substitution of Al^{3+} or P^{5+} with other heteroatoms such as Si^{4+}, Mg^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+}, *etc*. to produce silicoaluminophosphates (SAPOs) or metallo-aluminophosphates (MAPOs), respectively, introduces a negative framework charge, which is balanced by H^+ to form strong acid sites, creating potential solid-acid catalysts.[2]

AlPOs and MAPOs are mainly prepared under hydrothermal or solvothermal conditions, where a molecular liquid is used as the solvent and an organic cation as a space filler in the framework material (where the charge of the cation is offset by framework-bound fluoride or hydroxide, which is lost, along with the organocation, on calcination). In 2004, Morris and co-workers introduced the ionothermal synthesis method,[3] which has also been used to prepare AlPOs, MAPOs and other porous materials.[4] The ionothermal approach has several advantages over hydrothermal and solvothermal syntheses, predominantly that the ionic liquids (ILs) used as the solvent have a low vapour pressure, making the procedure much safer than the alternatives. The procedure has also been used to reduce the cost of preparing ^{17}O-labelled materials to an affordable level, thanks to the low volume of $H_2{}^{17}O$ required.[5] However, as the IL typically plays the role of both the solvent and the SDA, the number of frameworks so far accessed by ionothermal synthesis remains lower than for solvo- and hydrothermal syntheses.

Strategy of organic amines or quaternary ammonium ions added to ionothermal systems as cooperative structure directing agent (co-SDA) offer different chemistry to open up new vistas for synthesis of structural variety and new porous materials. Several of phosphates open-framework have been successfully formed by this experimenting. Impressively, two novel aluminophosphate materials have been discovered including the first 20-ring extra-large pore of aluminophosphate molecular sieve called as DNL-1 (with –CLO topology)[6] and 3D anionic aluminophosphate framework denoted as JIS-1 with an Al/P ratio of 6:7. [7]

Cobalt-substituted aluminophosphates (CoAPOs) are extensively studied mainly due its potential use as solid acid catalyst and redox reaction.[8] Several CoAPOs that were synthesised under ionothermal condition such as SIZ-7, SIZ-8 and SIZ-9 [9] including SIZ-13, SIZ-14 and SIZ-15 were prepared using the eutectic mixture (EM) of choline chloride and succinic acid have been reported.[10] Interestingly, cobalt-substituted aluminophosphates with -CLO structure (CoDNL-1) also was successfully synthesised under this route using 1-ethyl-3-methylimidazolium bromide (EMIMBr) in presence of 1-6 hexanediamine (HDA) as co-SDA.[11]

In this present work we report another ionothermal synthesis of CoAPO with CHA-type (CoAPO-34) using a EMIMBr:1,6-hexanediamine (HDA) (100 : 1.2 mole ratio) solvent system. CoAPO-34 was mostly hydrothermally prepared and the first synthesis has been reported by Union Carbide in 1985.[12] This material has a unique structure that identical to the aluminoposphate-34 ($AlPO_4$-34) with chabazite (CHA) structure [13] framework contains 8, 6 and 4 rings.[3] Fluoride atom in the structure bridging with two Al atoms (increasing Al coordination number to six) and double-6-rings (D6R) connected through to 4-membered rings, resulting in a three dimensional structure of CHA cages.[14] Therefore, CoAPO-34 with CHA-topology have found interest for their adsorptive and catalytic properties in oxidation of NO to NO_2 [15] and conversion of methanol to olefin.[16] To date there has no report arises regarding of ionothermal synthesis of CoAPO-34. These reasons as to why ionothermal synthesis was explored in this study is to provide an alternative route to prepare CoAPO-34 under low pressure instead of higher pressure which associated with hydrothermal or solvothermal condition.

Experimental

2.1 Synthesis of 1-ethyl-3-methylimidazolium bromide (EMIMBr)

EMIMBr was synthesized using a procedure modified from Ref. [17]. Under an inert atmosphere, degassed bromoethane (75.70 g, 0.7 mol, Aldrich. 98%) was added to 48.00 g (0.6 mol) of 1-methylimidazole (Aldrich, 99%) with constant stirring. This mixture was refluxed at 40 °C for 3 h then cooled to room temperature. Ethyl acetate (Fisher, 99%) was added to the solution and the product precipitated immediately. The white precipitate was recovered by filtration and washed with ethyl acetate before drying under vacuum at 40 °C for 10 h. The product was stored under an inert atmosphere. ^1H NMR (300 MHz, CD_3COCD_3) δ (ppm): 1.39 (t, 3H, CCH_3), 3.83 (s, 3H, NCH_3), 4.25 (q, 2H, NCH_2), 7.75 (d, 2H, NC(H)C(H)N), 9.06 (s, 1H, NC(H)N). ^{13}C NMR (300 MHz, D_2O) δ (ppm): 16.2 (CH_3), 36.9 (NCH_3), 45.6 (NCH_2), 123.3, 124.8 (NCCN), 138.5 (NCN). The shift values are comparable with those in the literature.[17]

2.2: Ionothermal Synthesis of CoAPO-34

CoAPO-34 was synthesised based on initial molar composition of 0.9Co: 1.7Al: 2.6PO_4: 5.7F: 88EMIMBr: 1.1HDA. A synthesis procedure was follow as: H_3PO_4 (95 wt% in H_2O, Sigma Aldrich, 0.395 g, 4 mmol), HF (48 wt% in H_2O, Alfa Aesar 0.175 g, 9 mmol), EMIMBr (26.4 g, 138 mmol), aluminium *iso*propoxide (0.547g, 2.7 mmol, Alfa Aesar, 98%) and $Co(NO_3)_2.6H_2O$ (0.3498 g, 1.2 mmol, LSR, 96%) were combined in a beaker. The reaction was stirred and heated to 110 °C for 1 h. Subsequently, 1,6-hexanediamine (HDA) (0.2 g, 1.7 mmol, Sigma Aldrich, 98%) was added into the solution and stirred for 5 minutes. This mixture was transferred into Teflon-lined autoclaves and heated in the oven at 210 °C for 2 h. The blue product was centrifuged and washed thoroughly with distilled water and methanol before being dried overnight at 110 °C.

2.3: Characterization

The powder X-ray diffraction (pXRD) patterns were collected using a STOE STADIP diffractometer operating with monochromated CuKα_1 radiation (λ = 1.5418 Å). A JEOL JSM 5600 SEM, integrated with an EDX system was used to image particle morphology and for elemental analysis. Thermogravimetric analysis (TGA) was carried out using a Netzsch STA with an atmosphere of air. Solid-state NMR spectra were recorded using Bruker Avance III spectrometers equipped with either 9.4 or 14.1 T wide-bore superconducting magnets. Samples were packed into standard 2.5 or 4 mm rotors and, for magic angle spinning (MAS) experiments, with rotation rates between 12.5 and 25 kHz. The ^{13}C MAS NMR spectrum was acquired at 14.1 T with cross polarization (CP) from ^1H using a 1 ms contact pulse (ramped for ^1H) and two-pulse phase modulation (TPPM) decoupling of ^1H ($\nu_1 \approx 100$ kHz) during acquisition. Signal averaging was carried out for 12824 transients with a recycle interval of 0.5 s. ^{27}Al solid-state MAS NMR spectra were acquired at 14.1 T with signal averaging for 1024 transients with a recycle intervals of 1 s. ^{31}P MAS NMR spectra were acquired at 14.1 T with signal averaging for 512 (as-made CoAPO) or 64 (calcined CoAPO) transients with a recycle interval of 1 s. Static ^{31}P wideline NMR spectra were recorded at 9.4 T using the spin-echo mapping approach.[18] A spin-echo pulse sequence with $\nu_1 \approx 150$ kHz and an interpulse delay of 15 µs was used. For each sub-spectrum, signal averaging was carried out for 4096 or 10240 transients for the as-made and calcined CoAPOs, respectively, with a recycle interval of 100 ms. The spectra shown are the result of the addition of 16 and 22 (for the as-made and calcined materials, respectively) sub-spectra with the transmitter frequency incremented by 600 ppm (~97 kHz) per sub-spectrum.

3: Result and discussion

Figure 1 illustrates the good match of the pXRD pattern of the as-made CoAPO-34 to the theoretical pattern of triclinic AlPO CHA, confirming that the material is isostructural with AlPO-34 (Fig. 1, inset). Upon calcination, the material should adopt rhombohedral symmetry but, as seen in Fig. 2(a), the pXRD pattern of the calcined material, after exposure to air, shows that the two different hydrated CHA phases, identified by Tuel *et al.*,[19] (both with triclinic symmetry) are present. In addition, the freshly calcined sample is blue but, upon exposure to the air, the material turns blue-green, as previously observed for CoAPO-34.[13]

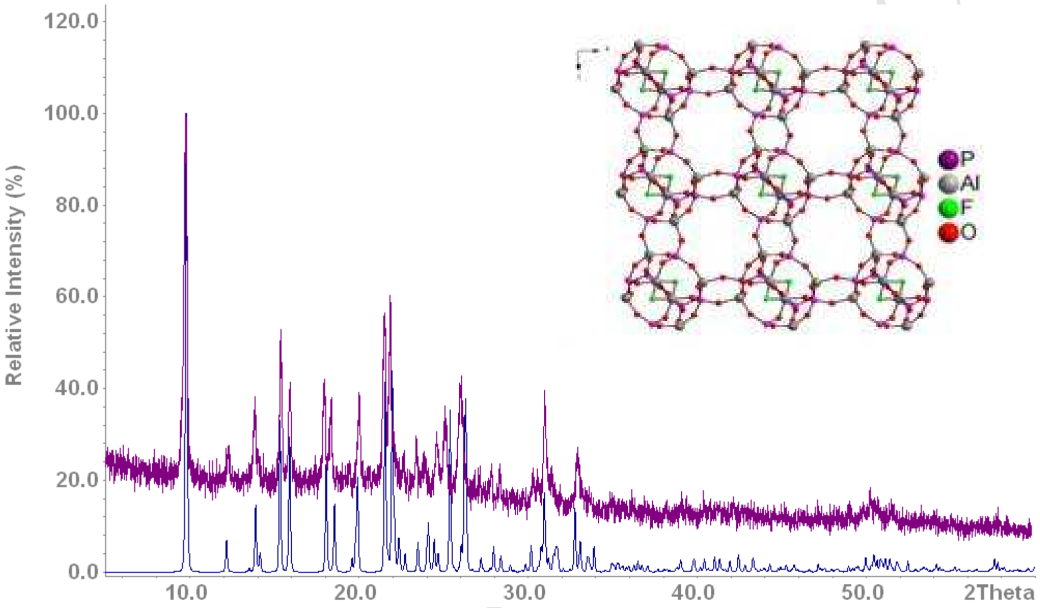

Fig. 1. PXRD pattern of the as-made CoAPO-34 with triclinic CHA structure and simulated pattern for triclinic CHA-type AlPO-34. The inset shows the structure of AlPO-34.

^{13}C NMR spectroscopy was used to determine whether the HDA was present in the pores of CoAPO-34. Fig. 2 (a) shows the ^{13}C NMR spectra of EMIMBr and HDA in D_2O and Fig. 2(b) shows the ^{13}C CP MAS NMR spectrum of the as-made CoAPO-34. While the presence of the paramagnetic Co^{2+} (and the inherently lower resolution of solid-state NMR spectroscopy) leads to broader resonances in the solid-state spectrum of the CoAPO, the six resonances from the $EMIM^+$ can clearly be observed at positions that are very similar to the solution-state spectra. However, there is no evidence of any of the resonances expected for HDA in the ^{13}C CP MAS NMR spectrum of CoAPO-34, indicating that $EMIM^+$ is the only organic species occluded in the pores. Based on previous ionothermal syntheses of CHA-type AlPOs,[3,17] and the structure of hydrothermal CoAPO-34,[13] it can be assumed that two $EMIM^+$ are present in each pore, with their charge balanced by two F^- bound to the Al (or Co), giving a general formula of $[Co_xAl_{1-x}PO_4]_6F_{2-x}.R_2$, where R is the SDA (here $EMIM^+$). Although HDA was not present as a template in the final material, it plays an important role as a co-SDA in the synthesis and, when absent, white crystals of AlPO-11 (AEL framework type) are preferentially formed instead of blue crystals of CoAPO-34. There are two possible explanations for this observation: either the Co^{2+} is too soluble in the IL and remains in solution while the $AlPO_4$ framework crystallises, or it is not sufficiently soluble and is never in the correct form to be incorporated into the AlPO framework. The addition of the HDA appears to alter the crystallisation of reaction to allow the formation of CoAPO-34. The incorporation of Co^{2+} into the CoAPO-34 framework was confirmed with ^{31}P spin-echo mapping NMR experiments (discussed below).

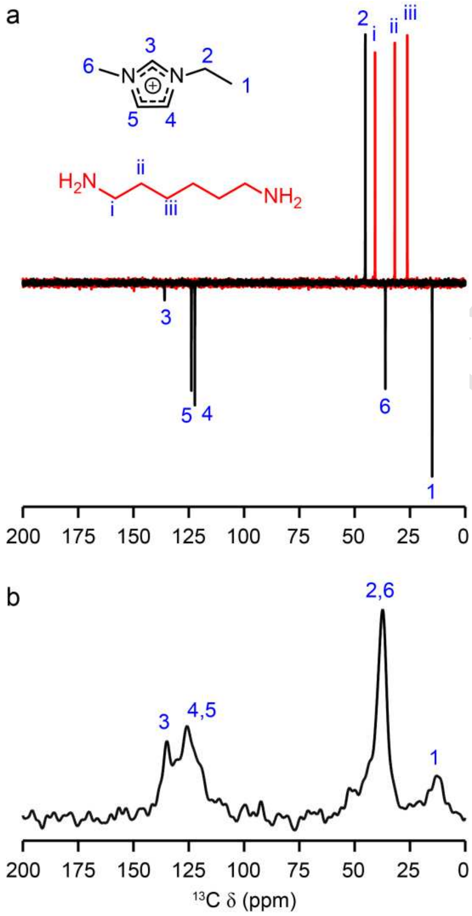

Fig. 2. (a) ^{13}C (7.05 T, D_2O, DEPTQ) NMR spectra of EMIMBr (black) and HDA (red). (b) ^{13}C

(14.1 T, 12.5 kHz CP MAS) NMR spectrum of as-made CoAPO-34. In both parts, peak assignments are indicated in blue text using the numbering scheme shown in part (a).

In this study, EDX analysis (shown in Fig. 3(a)) showed that the cobalt content of CoAPO-34 was ~0.75 mol%. Therefore, the empirical formula of this material can be written as $[Co_{0.05}Al_{0.95}PO_4]_6F_{1.95}.R_2$, where R = EMIM. The TGA curve of as-made CoAPO-34 (Fig. 4) shows an initial mass loss of about 4.4% between 25 ^{o}C and 320 ^{o}C, which can be attributed to physisorbed water.[20] The remaining mass loss between 320 ^{o}C and 550 ^{o}C of 20.7% corresponds to the loss of one equivalent of EMIM fluoride per $[Co_{0.05}Al_{0.95}PO_4]_6$ formula unit (calc. 23 %).[3,20]

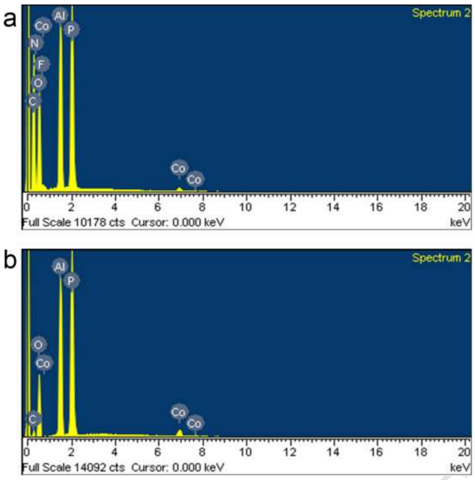

Fig. 3. EDX spectra of (a) as-made and (b) calcined CoAPO-34.

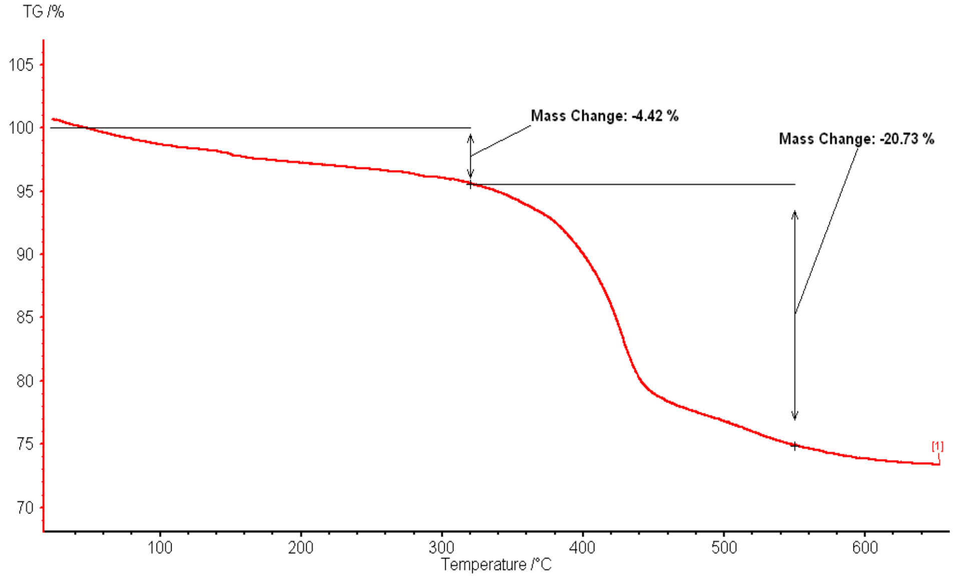

Fig. 4. The TGA plot for as-made CoAPO-34.

The ^{27}Al MAS NMR spectrum of the as-made CoAPO-34 shows resonances at 41.5 and –7.5 ppm, as shown in Fig. 5(a). These can be assigned to tetrahedral $Al(OP)_4$ and octahedral $Al(OP)_4F_2$, respectively.[13,14] The fluoride ions present in the material framework are to balance the charge of protonated organic molecule which is located in the CHA cage of the material.[19] Upon calcination (Fig. 5(b)) the resonance from the octahedral Al disappears and only one tetrahedral resonance is observed (at *ca.* 40 ppm), typical of calcined $AlPO_4$ frameworks.[14]

The ^{31}P MAS NMR spectrum of as-made CoAPO-34, shown in Fig. 6(a) contains three distinct resonances at –7.5, –23.0 and –29.0 ppm, which correspond to the three different tetrahedral $P(OAl)_4$ sites of triclinic AlPO-34.[3,20] The resonance at –7.5 ppm is due to the phosphorus nearest the fluoride bridges in the structure.[3,14] Fig. 6(b) shows that the ^{31}P MAS NMR spectrum of the calcined CoAPO-34 has a single resonance at –30 ppm, consistent with the rhombohedral symmetry of the calcined CHA structure.[21]

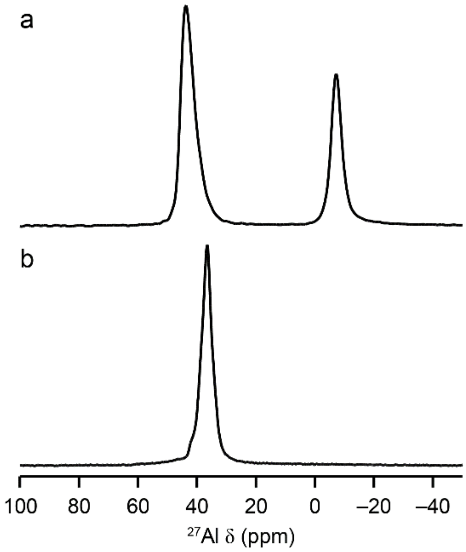

Fig. 5. ^{27}Al (14.1 T) MAS NMR spectra of (a) as-made and (b) calcined CoAPO-34 with MAS rates of (a) 20 and (b) 25 kHz.

In this study, the CoAPO-34 product was deep blue, typical of the incorporation of tetrahedral Co^{2+} in an AlPO framework.[22-25] The presence of intense spinning sidebands in the ^{31}P MAS NMR spectra of CoAPOs can also sometimes be considered proof of the presence of Co in the AlPO framework.[22,23,26] As shown in Fig. 6(c) and (d), the ^{31}P MAS NMR spectra of both as-made and calcined CoAPO-34 contain intense spinning sidebands, indicative of a larger paramagnetic shift anisotropy rather than the negligible diamagnetic chemical shift anisotropy typically observed for tetrahedrally-coordinated P in AlPOs.[27] However, these sidebands mainly arise from longer-range through-space paramagnetic interactions, which are also observed for AlPOs impregnated with a cobalt salt solution (*i.e.*, extra-framework Co species can cause a similar effect).[28-30] To confirm that the cobalt in CoAPO-34 has truly been incorporated into the framework, evidence of the presence of Co-O-P linkages is required. The interaction of unpaired electrons from the paramagnetic Co^{2+} or Co^{3+} with ^{31}P nuclei in $P(OAl)_{4-n}(OCo)_n$ environments can lead to both very large isotropic shifts and very broad resonances (owing to paramagnetic shift anisotropy and relaxation effects).[31] Thus, the resulting ^{31}P signal cannot be detected by conventional MAS NMR experiments. To overcome this issue, static spin-echo mapping can be used to record the very broad line in a stepwise fashion, with the final spectrum being the sum of the individual frequency-stepped spectra. This method has previously been applied to characterise other paramagnetic catalysts, including vanadyl phosphates, CoAPO-5 and MAPO-34 with M = Ni, Co, Fe and Mn.[18,30-34] Figures 7(e) and (f) show the static spin-echo-mapped ^{31}P NMR spectra for the as-made and calcined CoAPO-34. The “sharp” resonance at $\delta \approx 0$ ppm in Fig. 6(e) is the overlap of the static lineshapes of the three inequivalent P species observed in the ^{31}P MAS NMR spectrum in Fig. 6(a), while the signal at $\delta \approx 0$ ppm for the calcined sample (shown in Fig. 6(f)) comes from the single P species in the ^{31}P MAS NMR spectrum in Fig. 6(b). The broad ^{31}P signals (*ca*. 1000–5000 ppm for the as-made CoAPO and *ca*. 1000–10000 ppm for the calcined CoAPO) are due to $P(OAl)_{4-n}(OCo)_n$ species. Typically, the position of the broad ^{31}P signal depends on the number of Co atoms in the second coordination sphere of the P nucleus, following the order of $P(OAl)(OCo)_3 > P(OAl)_2(OCo)_2 > P(OAl)_3(OCo)$, *i.e.*, proportional to the number of unpaired electrons interacting with the P nucleus.[30,31] Canesson and Tuel reported a shift of *ca*. 2000-3000 ppm per additional cobalt ion in the second coordination sphere of P in CoAPO-5,[30] which was confirmed by a shift of 9500 ppm for $P(OCo)_4$ in DAF-2 (a cobalt phosphate containing alternating CoO_4 and PO_4 tetrahedra[35]). Therefore, as the maximum in the spectrum in Fig. 6(e) is around 2500 ppm, it can be assumed that this signal arises mainly from $P(OAl)_3(OCo)$. The ^{31}P lineshape of CoAPOs changes upon calcination, although, while Canesson and Tuel suggested that the intensity in the region between 500 and 1500 ppm typically increases relative to that above 2500 ppm,[30] Mali *et al.* showed that, for CoAPO-34, the signal actually broadens and a greater proportion of the intensity is observed at higher shifts.[31] This is observed here for the ^{31}P spectrum of the calcined CoAPO-34 shown in Fig. 6(f). The change in lineshape will depend on the bond geometry (*i.e.*, electron and spin density) around the P atoms, and so might be explained by changes in bond angles and lengths or by partial oxidation of Co(II) to Co(III) upon calcination. Oxidation on calcination has previously been attributed to changes in the ^{31}P lineshape for CoAPOs [30] and vanadyl phosphates.[34] Even though using the static-spin echo-mapped ^{31}P NMR technique is successfully prove the incorporation of Co into AlPO framework for both materials, however, it unable to provide an evidence of absence for extra-framework species. Therefore, the existence of extra-framework Co species in the CoAPO-34 material are possibly present.

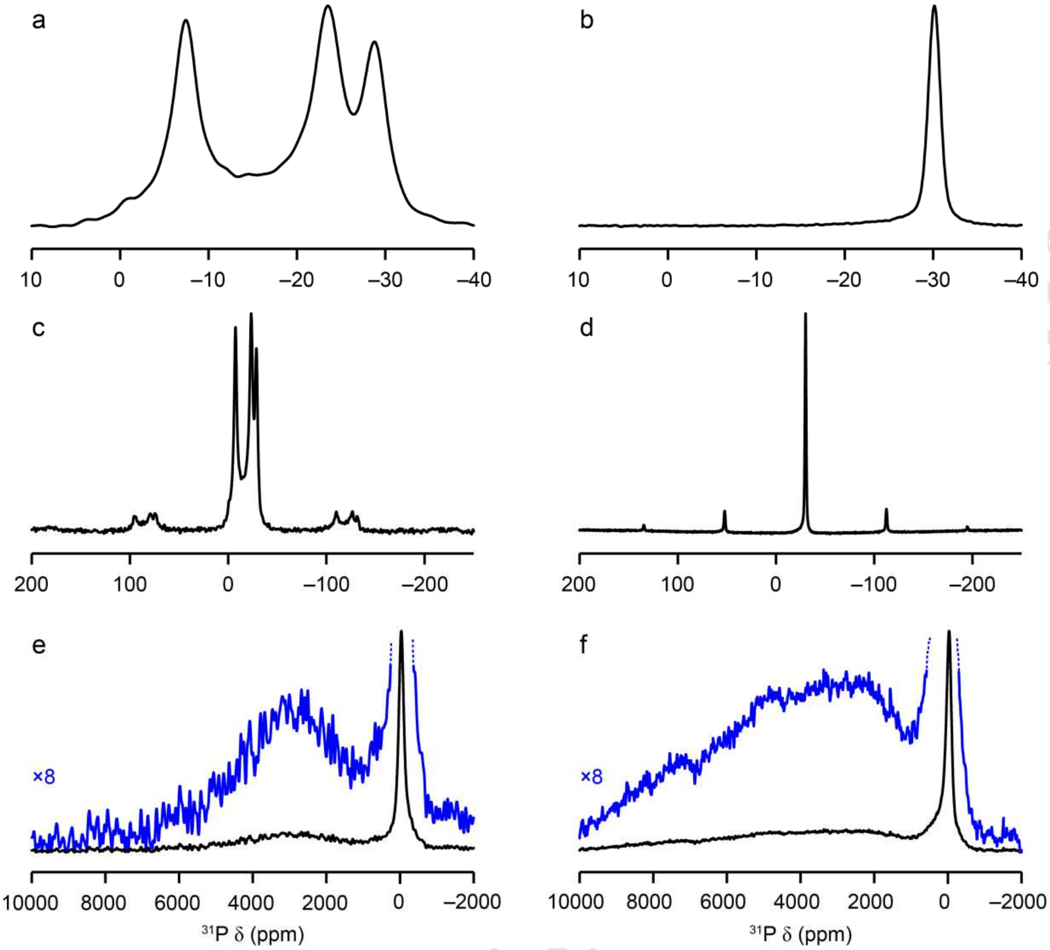

Fig. 6. (a and c) ^{31}P (14.1 T, 25 kHz MAS) NMR spectrum of as-made CoAPO-34, (b and d) ^{31}P (14.1 T, 20 kHz MAS) NMR spectrum of calcined CoAPO-34. The spectra in (a) and (b) are expansions of the isotropic regions of the spectra in (c) and (d), respectively. Static ^{31}P spin-echo mapped NMR spectra (9.4 T) of (e) as-made and (f) calcined CoAPO-34. The blue lines show a vertical expansion (by a factor of 8) of the spectra shown in black.

4: Conclusion

CHA-type CoAPO-34 was successfully prepared under ionothermal conditions using EMIMBr as the solvent, in the presence of HDA. The as-made material contains only EMIM$^+$ within the pores of the framework, whereas the role of the HDA is to make the dissolved cobalt suitably available for the crystallisation of CoAPO-34. Wideline ^{31}P NMR spectroscopy confirmed the presence of $P(OAl)_{4-n}(OCo)_n$ species with covalent P-O-Co linkages, providing direct evidence of the incorporation of cobalt ions into the CoAPO-34 framework.

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Highlight for review

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