

Solvent effects in the synthesis of CoAPO-5, -11 and -34 molecular sieves

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Abstract

Series of CoAPO-5, CoAPO-11 and CoAPO-34 molecular sieves have been synthesized starting from a synthesis gel varying in its amount of Co^{2+} and type of solvent molecule. Four protonic solvents have been investigated: water, ethanol, ethylene glycol and glycerol. The obtained crystalline materials were characterized with X-ray diffraction; diffuse reflectance UV–Vis–NIR spectroscopy; infrared spectroscopy; elemental analysis; electron microscopy microprobe analysis and thermo-gravimetric analysis. It was found that the type of solvent has a strong influence on the crystallization behavior and the substitution degree of Co^{2+} for Al^{3+} in the framework of microporous aluminophosphates. Ethanol, ethylene glycol and glycerol seem to be the best solvents for the synthesis of single-phase and highly crystalline Co-rich CoAPO-34, CoAPO-11 and CoAPO-5 molecular sieves, respectively. By varying the type of solvent molecule, Co content and template amount in the synthesis gel it was possible to increase the substitution degree of framework Co^{2+} in microporous aluminophosphates. In this manner, around 10%, 25% and 36% of Al^{3+} could be replaced by Co^{2+} in the framework of CoAPO-11, CoAPO-5 and CoAPO-34, respectively. These substitution degrees are substantially higher than those for CoAPO materials synthesized in the presence of water.

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1. Introduction

AlPO_4 -*n* molecular sieves consist of alternating aluminum oxygen and phosphorus oxygen tetrahedra building up an open and neutral framework structure with microporous channels and/or pores [1,2]. One of the most fascinating researches on microporous AlPO_4 -*n* materials is

the process of isomorphous substitution, in which framework Al^{3+} and/or P^{5+} ions are replaced by e.g. transition metal ions, such as Mn^{2+} [3–6], Fe^{3+} [7,8], V^{4+} [9–13], Ti^{4+} [14,15], Zn^{2+} [16,17], Nb^{5+} [18], Cr^{3+} [19–21] and Co^{2+} [22–26]. This process can generate Brønsted acid and redox sites, leading to intriguing shape-selective catalytic performances. The incorporation of Co^{2+} (d^7) can be considered as a showcase for these substituted materials since this transition metal ion not only gives the solid an intense blue color and interesting oxidation properties, but also provides convincing spectroscopic evidence for the framework substitution of Co^{2+} as obtained with e.g. diffuse reflectance UV–Vis–NIR spectroscopy,

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electron spin resonance and X-ray absorption spectroscopy [1,3,22–26].

Unfortunately, the amount of framework Co^{2+} is still relatively low for most CoAPO molecular sieves, although Stucky and co-workers have shown that the $[\text{Co}]:[\text{Al}]$ ratio in the framework of some materials with small pore openings exceeds the value of 1.0 [27,28]. From both a scientific as well as a more applied catalytic point of view, it is important to push the framework Co^{2+} content to the highest possible substitution levels. In addition, it would be advantageous if we could understand which experimental factors are governing this substitution process. In order to tackle these issues we started some years ago a research project aiming to study in a systematic way the different synthesis factors influencing the amount of framework Co^{2+} ions in microporous aluminophosphates [29,31]. In what follows, we summarize the main conclusions of this research effort and indicate the main message of the current contribution to the existing literature on this topic.

In a first study, we have investigated the hydrothermal synthesis of CoAPO-5 molecular sieves by varying the synthesis conditions and the template molecule and amount, as well as the type of Al and Co source to make the synthesis gel [29]. It was found that the highest substitution degrees were obtained from a gel made from Co acetate, pseudo-boehmite and tri-ethylamine mixed for 1 h in an ice-bath, followed by autoclaving at 190 °C. In continuation of this work, we found that the addition of mono-valent cations, such as Cs^+ , dramatically increases the amount of Co^{2+} incorporated in CoAPO-5 and CoAPO-34 molecular sieves [29,30]. We assume that Cs^+ ions are able to compensate the net negative framework charge as a result of the Co^{2+} incorporation and decreasing the framework distortion owing to a stronger Cs–O bond than the template–O bond. In line with this charge compensation principle, Feng et al. successfully synthesized a pure cobalt phosphate with the ABW framework in the presence of Rb^+ [28]. We also observed that the presence of Cs^+ in CoAPO-34 significantly inhibits the oxidation of framework Co^{2+} to Co^{3+} .

More recently, we have observed that the addition of glycerol also enhances the degree of incorporation of Co^{2+} in the framework of CoAPO-5 molecular sieves [31]. Based on this preliminary observation, we decided

to conduct a systematic study on the effect of four different protonic solvents, namely water, ethanol, 1,2-ethanediol (ethylene glycol) and 1,2,3-propanetriol (glycerol), on the synthesis of three different Co-substituted microporous aluminophosphates. In fact, these solvents have e.g., a different dissociation constant, viscosity, dielectric constant and thermal conductivity, as summarized in Table 1 [32]. As a result, the use of protonic solvent molecules is expected to have a remarkable influence on the crystallization process of molecular sieves and on the coordination behavior of Co^{2+} in the synthesis gel.

The goal of the present paper is to explore the effect of the type and amount of protonic solvents on the crystallization degree and the substitution degree of Co^{2+} for Al^{3+} in microporous aluminophosphates. For this purpose, the synthesis of CoAPO-5, CoAPO-11 and CoAPO-34 has been investigated in detail. It will be shown that depending on the choice of solvent and the amount of template molecule, the substitution degree of Co^{2+} can be significantly increased beyond levels obtained with hydrothermal synthesis procedures. This study represents, to our best knowledge, the first systematic investigation on the influence of the solvent type on the incorporation of transition metal ions in microporous aluminophosphates and complements the preliminary work on the effect of glycerol on the synthesis of CoAPO-5 [31].

2. Experimental

2.1. Synthesis gel composition and conditions

CoAPO-5, CoAPO-11 and CoAPO-34 molecular sieves were synthesized with H_3PO_4 (85 wt.% in aqueous solution, Acros), a templating molecule (for CoAPO-5 and CoAPO-34, it was triethylamine (TEA, 99%, Acros), while in the case of CoAPO-11, it was dipropylamine (Pr_2NH , 99%, Acros)), cobalt acetate (97%, Acros), pseudo-boehmite (70 wt.% Al_2O_3 , Catapal) and a solvent, being either bi-distilled water, ethanol (99.7–100%, UCB), ethylene glycol (99+%, Acros) or glycerol (99%, Acros). The gel compositions for CoAPO-5, CoAPO-34 and CoAPO-11 were (0.7–1.4)-TEA:(0.1–0.8)CoO:(0.6–0.95) Al_2O_3 : P_2O_5 :(30–80)solvent,

Table 1
Some physicochemical properties of the protonic solvents used for preparing Co-containing microporous crystalline aluminophosphates [32]

Molecule	Dielectric constant (ϵ) at 25 °C	Thermal conductivity (W/m K) at 25 °C	Viscosity (mPa s) at 25 °C	pK _a at 25 °C
Water	80.1	0.607	0.89	13.99
Ethanol	25.3	0.169	1.07	15.50
Ethylene glycol	41.4	0.256	16.10	15.10
Glycerol	46.5	0.292	934.00	14.15

(1.1–2.5)TEA:(0.6–1.6)CoO:(0.2–0.7)Al₂O₃:P₂O₅:(30–80)-solvent and (0.5–2.1)Pr₂NH:(0.06–1.6)CoO:(0.2–0.97)-Al₂O₃:P₂O₅:(40–75)solvent, respectively. The gel was prepared in a beaker placed in an ice bath. The preparation procedure is as follows. First, H₃PO₄ was dissolved in the solvent, followed by the addition of cobalt acetate. Then, pseudo-boehmite was added to the solution under continuous stirring after about 30 min. Finally, the templating molecule was drop-wise added to the synthesis mixture after 20 min, and further stirred for 1 h. The resultant gel was sealed into a Teflon-lined cylindrical autoclave (with a capacity of 35 ml) and the crystallization was statically carried out under autogeneous pressure at 190 °C for the designed time. The as-synthesized samples were filtered, washed with bi-distilled water, and dried at 60 °C. It is important to mention here that many of the synthesis gels led to the formation of mixtures of amorphous and/or crystalline phases. Detailed characterization has, however, focused on single-phase crystalline materials.

2.2. Characterization of the as-synthesized solids

The relative crystallinity degree and phase purity of the as-synthesized materials were determined with a Siemens D5000 matic X-ray diffractometer with CuK α radiation. The relative crystallinity degree was estimated by comparing the area of the selected diffraction lines (for CoAPO-5, *hkl* of 100, 200, 210, 002 and 211; for CoAPO-11, *hkl* of 110, 020, 310, 002 and 240 and for CoAPO-34, *hkl* of 100 and 20(–1)) in the X-ray diffraction patterns (XRD) of the as-synthesized materials with that of a reference zeolite Y sample. Details of this method have been given elsewhere [29]. The unit cell parameters were calculated according to hexagonal (based on *hkl* of 100 and 002 lines), orthorhombic (*hkl* of 110, 020 and 002 lines) and rhombohedral (*hkl* of 100 line) symmetries for CoAPO-5, CoAPO-11 and CoAPO-34, respectively, with weighted average wavelength of CuK α and Bragg equation. The chemical compositions of the synthesis gels and final solids were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and an electron microprobe micro-analyzer (EMMA). The thermal properties of the as-synthesized samples was investigated by a Setaram thermogravimetry (TGA)–differential-thermal-analysis (DTA) 92 system at a heating rate of 10 °C using a mixture of He (60%) and oxygen (40%) as carrier gas. The diffuse reflectance (DR) UV–Vis spectra of the as-synthesized samples were recorded at room temperature by a Varian Cary 5 spectrophotometer with an integration sphere against a Halon white reference standard in the UV–Vis–NIR region of 2500–200 nm. The spectra were further deconvoluted in Gaussian components with Grams/386 software (Galactic Industries Corp.) for quantitative estimation

of the amount of tetrahedral and octahedral Co²⁺. The integrated intensity of the triplet band between 500 and 650 nm was calculated in terms of the sum of their absorbance. Details of this method have been described in previous papers [29–31]. We are fully aware that this method is qualitative in nature since at present no detailed information is available on the extinction coefficients of tetrahedral and octahedral Co²⁺ in microporous aluminophosphates. Once such knowledge is available the reported intensity ratios of tetrahedral and octahedral Co²⁺ can be transformed into true ratios of tetrahedral and octahedral Co²⁺. The potential problem of differences in scattering coefficients when comparing different samples should be minimal since it would affect both the intensities of the absorption bands of tetrahedral and octahedral Co²⁺. Infrared spectra of the as-synthesized samples in the range from 400 to 4000 cm^{–1} were measured on a Nicolet 73 Fourier-transform infrared (FT-IR) spectrometer using the conventional KBr pellet method.

3. Results and discussion

3.1. Synthesis of CoAPO-5 molecular sieves

As already indicated in the introduction, it was found in previous work that for the hydrothermal synthesis of Co-rich CoAPO-5 cobalt acetate, pseudo-boehmite and tri-ethylamine are the best cobalt source, aluminum source and template molecule, respectively [29]. The current contribution builds further on our previous studies and therefore all the synthesis batches make use of these three materials as starting reactants. Table 2 summarizes the sample notations of a selection of the as-synthesized AFI-*m*-*n*(S) materials (with *m* and *n* denoting the molar [TEA]:[P₂O₅] and [Co]:[Al] ratios in the synthesis gel, respectively, while S represents the protonic solvent, including either water (W), ethanol (E), ethylene glycol (EG) or glycerol (G)) together with the related crystallization results. It is important to mention that many of the synthesis gels gave rise to mixtures of phases.

It was found that when ethanol was used as solvent, α -cristobalite as a dense phase was formed from the synthesis gel having a molar [Co]:[Al] ratio of only 0.01. Furthermore, attempts to synthesize single-phase CoAPO-5 by increasing the molar [Co]:[Al] ratio in the synthesis gel containing ethanol led to the formation of CoAPO-34 as second crystalline phase. It was found that the relative amount of CoAPO-34 gradually increased with increasing molar [Co]:[Al] ratio in the synthesis gel. Fortunately, when water, ethylene glycol or glycerol were used as solvent molecules, highly crystalline single-phase CoAPO-5 materials could be synthesized. In addition, the molar [Co]:[Al] ratio in the synthesis gel can be increased to a value of 0.43 for

Table 2

A selection of the crystallization results for the synthesis of CoAPO-5 molecular sieves with different solvents (water (W), ethanol (E), ethylene glycol (EG) and glycerol (G)) from a $x\text{TEA}:2y\text{CoO}:(1-y):\text{Al}_2\text{O}_3:\text{P}_2\text{O}_5:40$ solvent gel

x	y	Water as solvent		Ethanol as solvent		Ethylene glycol as solvent		Glycerol as solvent	
		Sample	Crystal phase	Sample	Crystal phase	Sample	Crystal phase	Sample	Crystal phase
1.0	0.05	AFI-1.0–0.01(W)	AFI	AFI-1.0–0.01(E)	AFI + cristobalite	AFI-1.0–0.01(EG)	AFI	AFI-1.0–0.01(G)	AFI
1.0	0.10	AFI-1.0–0.05(W)	AFI	AFI-1.0–0.05(E)	AFI + CHA				
1.0	0.15	AFI-1.0–0.11(W)	AFI	AFI-1.0–0.11(E)	AFI + CHA				
1.0	0.20	AFI-1.0–0.18(W)	AFI	AFI-1.0–0.18(E)	AFI + CHA				
1.0	0.25	AFI-1.0–0.25(W)	AFI	AFI-1.0–0.25(E)	AFI + CHA	AFI-1.0–0.25(EG)	AFI	AFI-1.0–0.25(G)	AFI
1.0	0.25	AFI-1.0–0.33(W)	AFI + CHA	AFI-1.0–0.33(E)	AFI + CHA			AFI-1.0–0.33(G)	AFI
1.1	0.30							AFI-1.0–0.43(G)	AFI
1.3	0.30							AFI-1.3–0.43(G)	AFI + CHA
1.0	0.35							AFI-1.0–0.54(G)	AFI
1.0	0.40					AFI-1.0–0.67(EG)	AFI + CHA	AFI-1.0–0.67(G)	AFI + CHA
0.7	0.2	AFI-0.7–0.25(W)	AFI + cristobalite						
0.8	0.2	AFI-0.8–0.25(W)	AFI						

ethylene glycol and 0.54 for glycerol without any contamination of the CoAPO-34 phase. In the case of water, the molar $[\text{Co}]:[\text{Al}]$ ratio in the gel was, however, limited to a value of 0.25 since higher amounts resulted in the formation of pink colored solids, contaminated with the CoAPO-34 phase. All these experiments show that:

- (1) the choice of solvent markedly affects the crystallization process of CoAPO-5 molecular sieves;
- (2) ethanol is not a good solvent for the synthesis of a pure Co-rich CoAPO-5 phase and
- (3) glycerol is highly effective for the synthesis of a single-phase CoAPO-5 material.

The substitution of Co^{2+} for Al^{3+} should lead to an expansion of the unit cell of the CoAPO-5 material and this effect can be studied in a qualitative manner by investigating the X-ray diffraction pattern of the as-synthesized solids in more detail. One of the assumptions made is that extra-framework Co^{2+} in the channels does not contribute to an increase in unit cell volume. Fig. 1 shows the relationship between the unit cell volume of the as-synthesized CoAPO-5 solids prepared with different solvents and the $[\text{Co}]:[\text{Al}]$ ratio in the synthesis gel. Although the samples synthesized in ethanol contained some CoAPO-34 crystals, its maximal unit cell volume (1369.1 \AA^3) showed a comparable value to that obtained with water as solvent (1364.9 \AA^3). In contrast, the unit cell volume of CoAPO-5 synthesized with glycerol as solvent increased with increasing molar $[\text{Co}]:[\text{Al}]$ ratio in the synthesis gel up to a value of 0.54, reaching a unit cell volume of 1415.3 \AA^3 . Finally, when ethylene glycol was used as a solvent, the unit cell volume of AFI-1.0–0.25(EG) was similar to that of AFI-

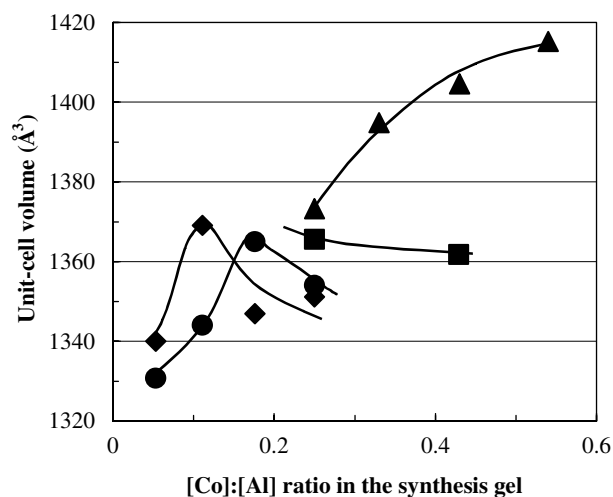


Fig. 1. Unit cell volume vs. the molar $[\text{Co}]:[\text{Al}]$ ratio in the synthesis gel for as-synthesized CoAPO-5 molecular sieves prepared with ethanol (◆), ethylene glycol (■), water (●) and glycerol (▲).

1.0–0.43(EG) with a value between 1362 and 1365 \AA^3 and a further increase of the $[\text{Co}]:[\text{Al}]$ ratio to 0.67 led to the formation of a CoAPO-34 crystalline phase. This shows that the choice of solvent not only has an effect on the type of solid obtained, but also influences the substitution degree of Co^{2+} for Al^{3+} in the framework of CoAPO-5. The maxima in unit-cell volume observed in Fig. 1 indicates that in a high molar $[\text{Co}]:[\text{Al}]$ ratio synthesis gel not all Co^{2+} is taken up by the growing solid.

All the as-synthesized CoAPO-5 samples have a blue color, although some of them contained pink spots. The latter samples were not phase-pure and contained some amorphous material as well. The blue color of the well

crystalline CoAPO-5 materials is consistent with the presence of tetrahedrally coordinated Co^{2+} , which was evidenced by DR UV–Vis–NIR spectroscopy. This technique is generally believed to give spectral evidence for the isomorphous substitution of Co^{2+} for Al^{3+} in the lattice [33]. It was found that an intense and well-resolved triplet band between 500–650 nm appeared in the DR UV–Vis–NIR spectra of almost all the as-synthesized materials. This triplet band is attributed to the $^4\text{A}_2\text{--}^4\text{T}_1$ (P) transitions of high-spin Co^{2+} (d^7) in tetrahedral coordination [33,34]. The integrated intensity of the triplet band can be used as a measure for the determination of framework Co amount in the as-synthesized Co-containing molecular sieves as shown in previous work [29–31]. It was found that the integrated intensity of AFI- m - n (G) samples increased with increasing molar $[\text{Co}]:[\text{Al}]$ ratio in the gel up to a value of 0.54, while for the as-synthesized AFI- m - n (W) samples, it increased with the molar $[\text{Co}]:[\text{Al}]$ ratio in the gel only up to 0.18. In spite of this, the AFI-1.0–0.43(EG) sample had a similar integrated intensity to the AFI-1.0–0.25(EG) material, although both samples were pure CoAPO-5 materials. This is in accordance with the above-described XRD measurements. With respect to the as-synthesized AFI- m - n (E) samples, the intensity of the triplet band monotonically increased with increasing molar $[\text{Co}]:[\text{Al}]$ ratio in the gel.

The DR UV–Vis–NIR spectra of CoAPO-5 molecular sieves can be deconvoluted into four Gaussian components in the range of 400–800 nm. The area of the three bands between 500 and 650 nm represents the amount of tetrahedral Co^{2+} ($[\text{Co}^{2+}]_{\text{tetra}}$), whereas the area of the band at about 480 nm is representative for the amount of octahedral Co^{2+} ($[\text{Co}^{2+}]_{\text{octa}}$). Thus, the molar $[\text{Co}^{2+}]_{\text{tetra}}:[\text{Co}^{2+}]_{\text{octa}}$ ratio can be calculated to confirm the quality of the as-synthesized CoAPO-5 samples. The larger this ratio, the higher the incorporation degree of Co^{2+} . Fig. 2 summarizes the molar $[\text{Co}^{2+}]_{\text{tetra}}:[\text{Co}^{2+}]_{\text{octa}}$ ratios of the as-synthesized CoAPO-5 samples as a function of the molar $[\text{Co}]:[\text{Al}]$ ratio in the synthesis gel. It is clear that the molar $[\text{Co}^{2+}]_{\text{tetra}}:[\text{Co}^{2+}]_{\text{octa}}$ ratio of hydrothermally synthesized molecular sieves sharply decreased with increasing molar $[\text{Co}]:[\text{Al}]$ ratio in the synthesis gel, and reduces to a value around 3.5 when the molar $[\text{Co}]:[\text{Al}]$ ratio in the gel reached a value of 0.25. This reveals that more than 20% of the Co^{2+} ions present in the AFI-1.0–0.25(W) sample were octahedrally coordinated, or in extra framework positions, assuming that the extinction coefficient of both Co^{2+} species are equal. Most probably, the amount of octahedrally coordinated Co^{2+} is higher since it is generally known that the extinction coefficient of tetrahedrally coordinated Co^{2+} is higher than that of octahedrally coordinated Co^{2+} . Unfortunately, there is no information on the exact values of the extinction coefficients for both species in microporous aluminophos-

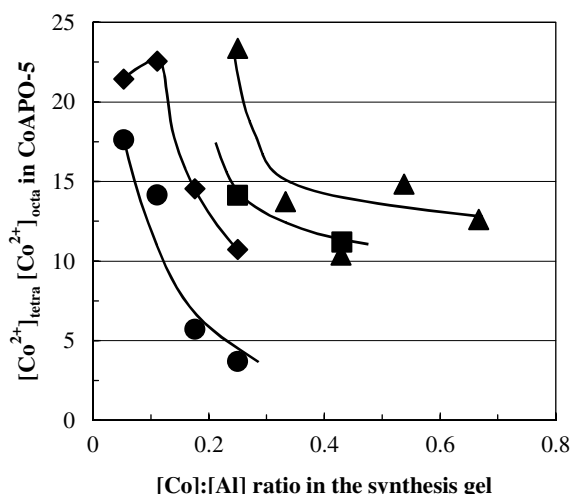


Fig. 2. Relationship between the molar $[\text{Co}^{2+}]_{\text{tetra}}:[\text{Co}^{2+}]_{\text{octa}}$ ratio as determined with UV–Vis–NIR spectroscopy in as-synthesized CoAPO-5 molecular sieves prepared in ethanol (♦), ethylene-glycol (■), water (●) and glycerol (▲) and the molar $[\text{Co}]:[\text{Al}]$ ratio in the synthesis gel.

phates and as a consequence the reported ratios should only be considered as a qualitative measure of the amount of framework Co^{2+} . A further increase of the molar $[\text{Co}]:[\text{Al}]$ ratio in the gel to 0.33 led to the formation of appreciable amounts of pink materials, showing that extra framework Co^{2+} was indeed present.

In contrast, when alcohols were used as solvents, the molar $[\text{Co}^{2+}]_{\text{tetra}}:[\text{Co}^{2+}]_{\text{octa}}$ ratio of the samples synthesized with the synthesis gel having a molar $[\text{Co}]:[\text{Al}]$ ratio less than 0.25 was larger than 10. As expected this ratio decreases in intensity with increasing amount of Co^{2+} in the gel. However, this ratio remained above 10 when glycerol was used as solvent even for a molar $[\text{Co}]:[\text{Al}]$ ratio of 0.54. This indicates that a large fraction of the Co^{2+} ions in the samples synthesized with alcohol as solvent possesses a tetrahedral coordination. As a consequence, alcohols are much more effective than water for the incorporation of Co^{2+} in the aluminophosphate framework. Furthermore, the molar $[\text{Co}^{2+}]_{\text{tetra}}:[\text{Co}^{2+}]_{\text{octa}}$ ratio increases in the sequence: ethanol < ethylene glycol < glycerol.

FT-IR spectroscopy of the as-synthesized AFI- m - n (G) samples shows that the main bands attributed to asymmetric stretching region, symmetric stretching region and T-O bonds shifted to lower wavenumbers with increasing molar $[\text{Co}]:[\text{Al}]$ ratio in the synthesis gel. This further confirmed that more Co^{2+} is isomorphously substituted for Al in the lattice. Finally, Table 3 summarizes the chemical composition of a selection of CoAPO-5 samples prepared with either water or glycerol as solvent. It was found that sample AFI-1.1–0.43(G) is a single-phase CoAPO-5, possessing the highest amount of framework Co^{2+} . The molar $[\text{Co}]:[\text{Al}]$ ratio in this

Table 3

Chemical composition of a selection of the as-synthesized CoAPO-5 molecular sieves with water and glycerol as solvent molecule

Sample	Color	Molar [Co]:[Al] ratio in the solid
AFI-1.0–0.05(W)	Blue	0.044
AFI-1.0–0.11(W)	Blue	0.081
AFI-1.0–0.18(W)	Blue	0.136
AFI-1.0–0.25(W)	Blue + pink spots	0.162
AFI-1.0–0.25(G)	Dark blue	0.150
AFI-1.0–0.33(G)	Dark blue	0.241
AFI-1.0–0.43(G)	Dark blue	0.383
AFI-1.0–0.54(G)	Dark blue + pink spots	0.535

solid was 0.383, nearly triple the ratio of the best sample made with water as solvent (sample AFI-1.0–0.18(W)).

3.2. Synthesis of CoAPO-34 molecular sieves

It has been previously shown that compared with CoAPO-5, Co^{2+} ions are more easily incorporated in the lattice of CoAPO-CHA (CoAPO-34/CoAPO-44) [27,30,35]. In the hydrothermal synthesis, Feng et al. reported that the molar [Co]:[Al] ratio in the synthesis gel could be increased to 0.5 with triethylamine as template [27]. A further increase of the molar [Co]:[Al] ratio in the gel was achieved by using 1,6-hexanediamine and 1-(2-aminoethyl)piperazine as templating molecules, and more than 23% of Al^{3+} sites in the framework could be substituted for Co^{2+} . Hill et al. found that using $[(\text{CH}_3\text{CH}_2)_4\text{N}]_2\text{CoCl}_4$ and tetraethylammonium hydroxide (TEAOH) as cobalt source and additional templating agent led to the incorporation of about 30% of Co^{2+} in the lattice [35], while the other usually used cobalt sources are not so effective. This brief literature survey shows that up to now, CoAPO-CHA with a

maximum substitution degree of 30% has been synthesized for hydrothermal systems by adjusting the choice of template molecule and cobalt source. Taken this as a starting point, we have investigated the influence of the type of protonic solvent on the incorporation of Co^{2+} in CoAPO-34 solids.

Table 4 illustrates the crystallization results for the synthesis of CoAPO-34 molecular sieves in the presence of the four protonic solvents under study. The sample notation is the same as that for the CoAPO-5 molecular sieves. Here again, some synthesis mixtures give rise to the formation of mixtures of phases. Clearly, pure CoAPO-34 crystalline phase could be synthesized with ethanol as solvent when the molar [Co]:[Al] ratio and the [TEA]:[P_2O_5] ratio in the synthesis gel were larger than 0.43 and 1.3, respectively. However, when the molar [Co]:[Al] ratio in the synthesis gel was increased to a value larger than 1.5, a pink material was formed. XRD showed that the unit cell volume of the as-synthesized CHA-*m*-*n*(E) samples increased with increasing [TEA]:[P_2O_5] ratio in the synthesis gel up to a certain value, which depends on the Co^{2+} amount in the synthesis gel. This is shown in Fig. 3. While the molar [Co]:[Al] ratio in the synthesis gel was in the range from 0.43 to 0.67, the molar [TEA]:[P_2O_5] ratio in the gel was 1.3, whereas for the gel having a molar [Co]:[Al] ratio of 1.0 and 1.5, the molar [TEA]:[P_2O_5] ratio in the gel was 1.5 and 1.9, respectively. Fig. 3 also shows that the unit cell decreases in volume when the molar [Co]:[Al] ratio in the gel was larger than 0.67. The maximum value of 837.7 \AA^3 corresponded to the CHA-1.3–0.67(E) sample.

When glycerol was used as solvent, single-phase CoAPO-34 was only formed when the molar [Co]:[Al] ratio in the synthesis gel was larger than 2.33 (Table 4). Unfortunately, such high Co content resulted in the

Table 4

A selection of the crystallization results for the synthesis of CoAPO-34 molecular sieves with different solvents from a $x\text{TEA}:2y\text{CoO}:(1-y):\text{Al}_2\text{O}_3:\text{P}_2\text{O}_5:40\text{solvent}$ gel

<i>x</i>	<i>y</i>	Ethanol as solvent			Ethylene glycol as solvent		Glycerol as solvent		
		Sample	Crystal phase	Crystal degree (%)	Sample	Crystal phase	Sample	Crystal phase	Crystal degree (%)
1.8	0.2	CHA-1.8–0.25(E)	CHA + AFI	–					
1.0	0.3	CHA-1.0–0.43(E)	CHA + AFI	–					
1.3	0.3	CHA-1.3–0.43(E)	CHA	74					
1.5	0.3	CHA-1.5–0.43(E)	CHA	63					
1.0	0.4	CHA-1.0–0.67(E)	CHA	53					
1.3	0.4	CHA-1.3–0.67(E)	CHA	73					
1.5	0.4	CHA-1.5–0.67(E)	CHA	59					
1.5	0.5	CHA-1.5–1.00(E)	CHA	86			CHA-1.5–1.00(G)	CHA + AFI	–
1.8	0.5	CHA-1.8–1.00(E)	CHA	46					
2.1	0.5	CHA-2.1–1.00(E)	CHA	47	CHA-2.1–1.00(EG)	CHA + AFI			
1.9	0.6	CHA-1.9–1.50(E)	CHA	73			CHA-1.9–1.50(G)	CHA + AFI	–
2.1	0.6	CHA-2.1–1.50(E)	CHA	72	CHA-2.1–1.50(EG)	CHA + AFI	CHA-2.1–1.50(G)	CHA + AFI	–
2.3	0.6	CHA-2.3–1.50(E)	CHA	62			CHA-2.3–1.50(G)	CHA + AFI	–
2.1	0.7				CHA-2.1–2.33(EG)	CHA + AFI	CHA-2.1–2.33(G)	CHA	86

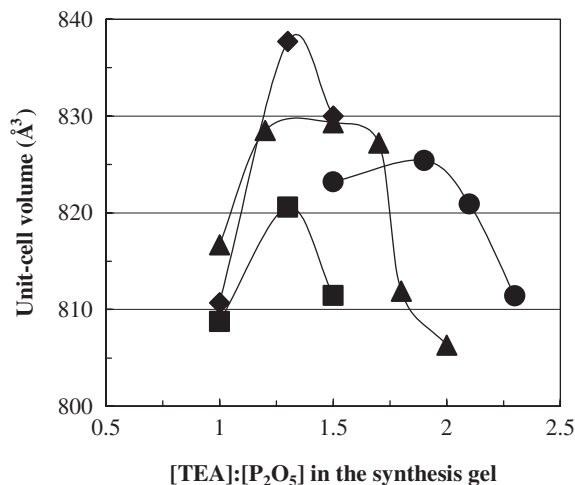


Fig. 3. Unit cell volume of as-synthesized CoAPO-34 molecular sieves vs. the molar [TEA]:[P₂O₅] ratio for a synthesis gel having a molar [Co]:[Al] ratio of 0.43: (◆) 0.67 (■), 1.00 (▲) and 1.50 (●).

formation of pink materials, the amount of which, moreover, increased with increasing Co content in the gel. The sample synthesized with the synthesis gel having a molar [Co]:[Al] ratio of 4.0 had a pink color contaminated with blue spots, implying that most of Co²⁺ ions were in extra framework positions or in the form of an amorphous material. The optimum composition of the gel for the synthesis of Co-rich CoAPO-34 with glycerol as solvent is 2.1TEA:1.4CoO:0.3Al₂O₃:P₂O₅:40HO-CH₂CHOHCH₂OH. The unit cell volume of the formed CoAPO-34 material reached a value of 824.0 Å³. A higher or lower tri-ethylamine content led to a decrease of the unit cell volume. Nevertheless, this value is obviously smaller than that achieved with ethanol as solvent.

In case ethylene glycol was used as solvent, CoAPO-5 was always found as by-product. Attempts to further increase the cobalt amount in the gel led to the formation of large amounts of pink materials. All these studies show again that the solvent molecule has a remarkable effect on the crystallization of CoAPO-34 molecular sieves. Among the studied solvents, ethanol is the most favorable for the synthesis of single-phase and highly crystalline Co-rich CoAPO-34 molecular sieves. Therefore, in the following part, we have focused on the physicochemical characterization of the as-synthesized CoAPO-CHA-*m-n*(E) samples.

As an example, the DR UV–Vis–NIR spectra of as-synthesized CoAPO-CHA-1.3–0.67(E) and CoAPO-CHA-1.9–0.51(E) are shown in Fig. 4. A strong triplet band between 500–650 nm with a shoulder at about 480 nm was present in both spectra, showing that most of Co²⁺ possesses a tetrahedral coordination. Regardless of this observation, the triplet band in the DR UV–Vis–NIR spectrum of CHA-1.3–0.67(E) is much more intense and well defined than that of CHA-1.9–1.5(E). It was observed that the integrated intensity of the triplet

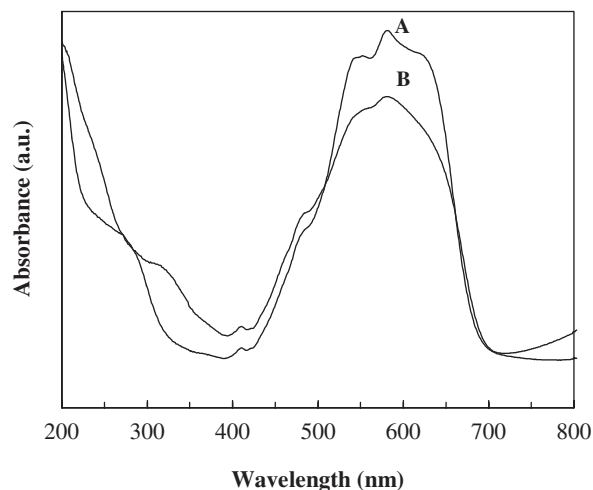


Fig. 4. Diffuse reflectance UV–Vis–NIR spectra of as-synthesized CoAPO-CHA-1.3–0.67(E) (A) and CoAPO-CHA-1.9–1.50(E) (B).

band increased with increasing molar [Co]:[Al] ratio in the gel up to a value of 0.67. This shows that the optimum molar [Co]:[Al] ratio in the gel for the synthesis of Co-rich CoAPO-34 in ethanol is about 0.67. This is further proven by the chemical analysis results, summarized in Table 5. It was found that the molar [Co]:[Al] ratio in the framework of the as-synthesized CHA-*m-n*(E) samples reached a value of 0.572, as roughly estimated from the molar [P–Al]:[Al] ratios of these samples. The relationship between the molar [P–Al]:[Al] ratio of the as-synthesized samples and the molar [Co]:[Al] ratio in the synthesis gel is consistent with the dependence of the integrated intensity of the triplet band on the molar [Co]:[Al] ratio in the gel. This indicates that about 36% of framework Al has been replaced by Co²⁺. This value is clearly higher than that achieved when using the classical hydrothermal synthesis methods [27,35].

The quality of the as-synthesized CoAPO-CHA(E) samples was also verified by determining the molar [Co²⁺]_{tetra}: [Co²⁺]_{octa} ratio from the DR UV–Vis–NIR spectra making the same assumptions as outlined above. It was observed that the molar [Co²⁺]_{tetra}: [Co²⁺]_{octa} ratio was larger than 10 for the samples synthesized with the synthesis gel having a [Co]:[Al] ratio less than 1.0. This

Table 5
Chemical composition of a selection of the as-synthesized CoAPO-34 molecular sieves

Sample	Molar [Co]:[Al] ratio in the solid	Molar [P–Al]:[Al] ratio in the solid
CHA-1.3–0.43	0.487	0.364
CHA-1.3–0.67	0.869	0.572
CHA-1.5–1.00	0.734	0.503
CHA-1.9–1.50	0.579	0.439

suggests that a substantial fraction of the Co^{2+} present in the samples is tetrahedrally coordinated.

3.3. Synthesis of CoAPO-11 molecular sieves

It is known that the Co concentration in the framework of CoAPO-11 is very limited as a substitution degree of only 0.5% was achieved for this material [36]. Since alcohols as solvents has shown for CoAPO-5 and CoAPO-34 molecular sieves to significantly promote the incorporation of Co in the framework, we have used ethanol, ethylene glycol and glycerol as solvents in an attempt to synthesize Co-rich CoAPO-11 molecular sieves. Table 6 summarizes the crystallization results for the synthesis of CoAPO-11 in different solvents. The sample notations are similar to those of CoAPO-5. It was shown that single-phase well-crystalline CoAPO-11 could be synthesized by using ethylene glycol and glycerol as solvents when the synthesis gel contained the appropriate amounts of cobalt and di-propylamine. The optimum amount of di-propylamine in the gel increased with the molar $[\text{Co}]:[\text{Al}]$ ratio in the gel for both solvents, as evident from the relationship between the relative crystallinity of the as-synthesized samples and the molar $[\text{Co}]:[\text{Al}]$ ratio in the gel. When ethylene glycol was used as solvent, the appropriate molar $[\text{Pr}_2\text{NH}]:[\text{P}_2\text{O}_5]$ ratios in the gel were 1.3, 1.4, and 1.4–1.6, while the molar $[\text{Co}]:[\text{Al}]$ ratios in the gel were 0.43–0.67, 1.0 and 1.5, respectively. In contrast, in the case of glycerol as solvent, the optimum molar $[\text{Pr}_2\text{NH}]:[\text{P}_2\text{O}_5]$ ratios were 0.9, 1.1 and 1.2–1.4 for the synthesis gel having a molar $[\text{Co}]:[\text{Al}]$ ratio of 0.25, 0.33 and 0.43, respectively. Irrespective of this, ethanol as solvent led to the formation of pink dense phases, such as α -quartz and α -cristobalite. In case water was used as solvent, some CoAPO-31 or an unknown impure crystalline phase was always formed as by-product. A progressive increase of the amount of cobalt in the gel resulted in the formation of CoAPO-H₂, α -cristobalite and α -quartz. This shows that the choice of solvent also has a great effect on the crystallization of CoAPO-11.

The unit cell volume of the as-synthesized CoAPO-11 materials as a function of the molar $[\text{Co}]:[\text{Al}]$ ratio in the synthesis gel is given in Fig. 5. The maximum value of 2106.9 \AA^3 in the hydrothermally synthesized samples was achieved for sample AEL-0.9–0.05(W), while a decrease or an increase of the Co amount in the gel both led to a contraction of the unit cell. In contrast, when glycerol and ethylene glycol were used as solvent molecules, the unit cell expanded with increasing molar $[\text{Co}]:[\text{Al}]$ ratio in the synthesis gel. In spite of this, glycerol as solvent is much more beneficial than ethylene glycol for the incorporation of Co^{2+} ions in the framework of CoAPO-11. This observation was further confirmed by DR UV–Vis–NIR spectroscopy. It was found that the integrated intensity of the triplet band between 500

and 650 nm in the DR UV–Vis–NIR spectra of the samples synthesized with these two solvents both increased with increasing molar $[\text{Co}]:[\text{Al}]$ ratio in the gel, showing a gradual increase of the amount of tetrahedrally coordinated Co^{2+} . As for the samples synthesized with a synthesis gel having the same molar $[\text{Co}]:[\text{Al}]$ ratio, the triplet band of the sample made with glycerol as solvent was more intense than with ethylene glycol as solvent. However, the former had a very low crystallinity (Table 6), which, moreover, markedly decreased with increasing Co content in the gel. When the molar $[\text{Co}]:[\text{Al}]$ ratio in the synthesis gel was larger than 0.43, most of the solid in the as-synthesized sample was amorphous since the crystallinity of CoAPO-11 only reached a value of 10–20%. Attempts to increase the crystallinity by prolonging the crystallization time from 28 to 60 days failed. Occasionally, a sample with a relative crystallinity of about 40% might be obtained, but the unit cell severely contracted. In contrast, the samples synthesized with ethylene glycol as solvent all gave a relative crystallinity of more than 60%, although the relative crystallinity decreased with increasing Co content in the gel.

The relationship between the molar $[\text{Co}^{2+}]_{\text{tetra}}: [\text{Co}^{2+}]_{\text{octa}}$ ratio of the CoAPO-11 molecular sieves synthesized in different solvents and the molar $[\text{Co}]:[\text{Al}]$ ratio in the synthesis gel is given in Fig. 6. The molar $[\text{Co}^{2+}]_{\text{tetra}}: [\text{Co}^{2+}]_{\text{octa}}$ ratio of the hydrothermally synthesized samples significantly decreased with the cobalt amount in the synthesis gel. When the molar $[\text{Co}]:[\text{Al}]$ ratio in the gel reached a value of 0.43, the molar $[\text{Co}^{2+}]_{\text{tetra}}: [\text{Co}^{2+}]_{\text{octa}}$ ratio reduced to a value of 1.65. In contrast, the molar $[\text{Co}^{2+}]_{\text{tetra}}: [\text{Co}^{2+}]_{\text{octa}}$ ratio of the samples synthesized with ethylene glycol as solvent was larger than 13 up to a molar $[\text{Co}]:[\text{Al}]$ ratio in the gel of 1.5, showing that almost all Co^{2+} in the AEL-*m-n*(EG) samples have a tetrahedral coordination. This was also true for the materials synthesized with glycerol as solvent. Table 7 lists the chemical compositions of the as-synthesized AEL-*m-n*(EG) samples. As expected, the cobalt content in the samples increased with increasing Co amount in the gel. However, the molar $[\text{Al}]:[\text{Co}+\text{P}]$ ratios were much larger than 1, indicating that some Al_xO_y clusters were present in the samples. This was also supported by the fact that white spots could be observed. Thus, the Co content in the framework can be roughly estimated in terms of the molar $[\text{Co}]:[\text{P}]$ ratio in the as-synthesized materials. Table 7 shows that the molar $[\text{Co}]:[\text{P}]$ ratio for the AEL-1.4–1.50 sample reached a value of 0.102, which is double of that achieved for the hydrothermal synthesis [37]. EMMA revealed that the $[\text{Co}]:[\text{Al}]:[\text{P}]$ ratio is in good agreement with the ICP-AES analysis results, showing that around 10% of the Al sites in the framework were replaced by Co^{2+} . This is also substantiated by the TGA-DTA measurements, which showed that there were two di-propylamine molecules per unit cell in the AEL-1.4–1.5(EG)

Table 6

A selection of the crystallization results for the synthesis of CoAPO-11 molecular sieves with different solvents from a $x\text{Pr}_2\text{NH}:2y\text{CoO}:(1-y):\text{Al}_2\text{O}_3:\text{P}_2\text{O}_5:40\text{solvent}$ gel, and in water from a $x\text{Pr}_2\text{NH}:2y\text{CoO}:(1-y):\text{Al}_2\text{O}_3:\text{P}_2\text{O}_5:75\text{H}_2\text{O}$ gel (U: unknown; C: α -cristobalite and Q: α -quartz)

x	y	Water as solvent		Ethanol as solvent		Ethylene glycol as solvent			Glycerol as solvent		
		Sample	Crystal phase	Sample	Crystal phase	Sample	Crystal phase	Crystal degree (%)	Sample	Crystal phase	Crystal degree (%)
0.9	0.03	AEL-0.9–0.03(W)	AEL + U								
0.9	0.05	AEL-0.9–0.05(W)	AEL + ATO								
1.0	0.10	AEL-1.0–0.11(W)	AEL + ATO								
1.0	0.15	AEL-1.0–0.18(W)	AEL + ATO + AHT								
0.9	0.20								AEL-0.9–0.25(G)	AEL	54
1.0	0.20	AEL-1.0–0.25(W)	AEL + AHT + C			AEL-1.0–0.25(EG)	AEL	79	AEL-1.0–0.25(G)	AEL	45
1.0	0.25								AEL-1.0–0.33(G)	AEL + C + Q	
1.1	0.25								AEL-1.1–0.33(G)	AEL	36
0.7	0.30			AEL-0.7–0.43(E)	AEL + Q						
1.0	0.30	AEL-1.0–0.43(W)	AEL + AHT + C	AEL-1.0–0.43(E)	AEL + C	AEL-1.0–0.43(EG)	AEL	89	AEL-1.0–0.43(G)	AEL + C	
1.1	0.30	AEL-1.1–0.43(W)	AEL + AHT + C	AEL-1.1–0.43(E)	AEL + C						
1.2	0.30	AEL-1.2–0.43(W)	C + Q	AEL-1.2–0.43(E)	C	AEL-1.2–0.43(EG)	AEL	93	AEL-1.2–0.43(G)	AEL	26
1.3	0.30					AEL-1.3–0.43(EG)	AEL	100			
1.4	0.30					AEL-1.4–0.43(EG)	AEL + AFI	–	AEL-1.4–0.43(G)	AEL	27
1.5	0.30					AEL-1.5–0.43(EG)	AEL + AFI	–	AEL-1.5–0.43(G)	AEL	27
1.2	0.40					AEL-1.2–0.67(EG)	AEL	74			
1.3	0.40			AEL-1.3–0.67(E)	AEL + C	AEL-1.3–0.67(EG)	AEL	81			
1.4	0.40			AEL-1.4–0.67(E)	AEL + C	AEL-1.4–0.67(EG)	AEL + AFI	–			
1.5	0.40			AEL-1.5–0.67(E)	AEL + C	AEL-1.5–0.67(EG)	AEL + AFI	–			
1.1	0.50					AEL-1.1–1.00(EG)	AEL	40			
1.4	0.50					AEL-1.4–1.00(EG)	AEL	85			
1.1	0.60					AEL-1.1–1.50(EG)	AEL	12			
1.3	0.60					AEL-1.3–1.50(EG)	AEL	37	AEL-1.3–0.67(G)	AEL	20
1.4	0.60					AEL-1.4–1.50(EG)	AEL	58	AEL-1.4–0.67(G)	AEL	14
1.6	0.60					AEL-1.6–1.50(EG)	AEL	61	AEL-1.6–0.67(G)	AEL	17
1.8	0.60					AEL-1.8–1.50(EG)	AEL	45			

^a Crystallinity degree (%) determined by comparing the area of the selected diffraction of hkl of 110, 020, 310, 002 and 240 in the X-ray diffraction patterns of the as-synthesized materials with that of a reference sample.

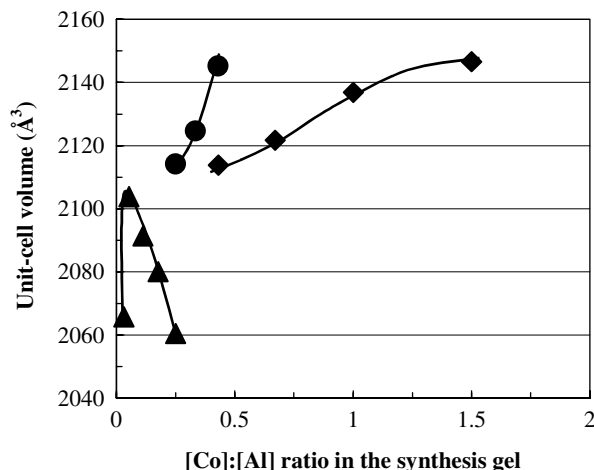


Fig. 5. Unit cell volume vs. the molar [Co]:[Al] ratio in the synthesis gel for as-synthesized CoAPO-11 molecular sieves prepared in ethylene glycol (◆), water (▲) and glycerol (●).

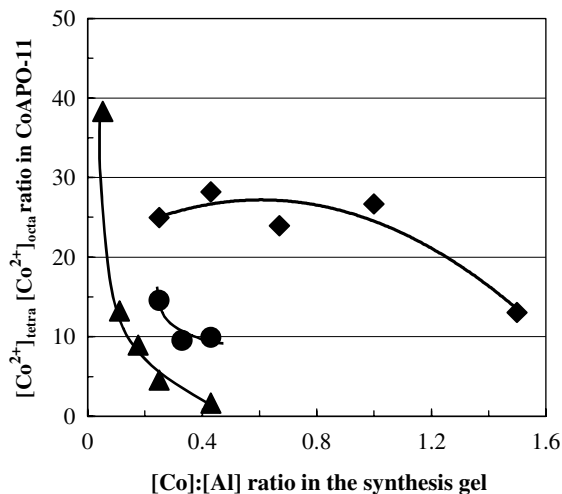


Fig. 6. Molar [Co²⁺]_{tetra}: [Co²⁺]_{octa} ratio vs. the molar [Co]:[Al] ratio in the synthesis gel for as-synthesized CoAPO-11 molecular sieves prepared in ethylene glycol (◆), water (▲) and glycerol (●).

sample, while the AEL-0.9–0.05(W) sample contained only 0.72 di-propylamine molecules per unit cell. Nevertheless, it is very difficult to incorporate more Co²⁺ in the lattice of AlPO-11 since a significant increase of the Co content in the synthesis gel only slightly increases the amount of framework Co²⁺.

4. Concluding remarks

The following conclusions can be drawn on the basis of the above described studies on solvent effects in the synthesis of Co-containing crystalline microporous aluminophosphates:

- (1) The amount of Co²⁺ that can be incorporated in the framework of microporous aluminophosphates depends on the structure of the AlPO₄-*n*. The substitution degree of Co²⁺ for Al³⁺ decreases in the sequence: CoAPO-34 > CoAPO-5 > CoAPO-11.
- (2) The type of protonic solvent has a drastic influence on the crystallization and substitution degree of Co²⁺ for Al³⁺ in the framework. Alcohols are much more effective than water for the incorporation of Co²⁺ in the framework, but the choice of solvent is closely related to the structures of AlPO₄-*n* molecular sieves. In the case of Co-rich CoAPO-5, glycerol is the solvent of choice. In contrast, ethanol and ethylene glycol are the best solvents for the synthesis of Co-rich CoAPO-34 and CoAPO-11, respectively. In this manner, around 10, 25 and 36% of Al³⁺ could be replaced by Co²⁺ in the framework of CoAPO-11, CoAPO-5 and CoAPO-34, respectively. Unfortunately, we do not observe a simple relationship between the physicochemical properties of the protonic solvents under study (Table 1), the type of molecular sieve made and the amount of Co²⁺ incorporated in the lattice.
- (3) The amounts of Co²⁺ ion and template molecules in the synthesis gel also significantly affect the crystallization of CoAPO molecular sieves. Too large or too small amounts of Co²⁺ and template molecules not only lead to the formation of impure crystalline materials, but also result in a decrease of the final Co²⁺ content in the framework. The optimum template amount increases with the Co²⁺ content.
- (4) Attempts to prepare single-phase well-crystalline CoAPO-34 molecular sieves often lead to the formation of CoAPO-5 as a side-product and vice versa.

One may hypothesize why alcohols are better solvents for obtaining high substitution degrees of framework

Table 7
Chemical composition of a selection of the as-synthesized CoAPO-11 molecular sieves

Sample	Molar [Al]:[Co + P] ratio in the solid	Molar [Al]:[P] ratio in the solid	Molar [Co]:[Al] ratio in the solid
AEL-1.0–0.25	1.243	1.360	0.069
AEL-1.3–0.67	1.246	1.380	0.078
AEL-1.4–1.00	1.254	1.410	0.088
AEL-1.4–1.50	1.280	1.472	0.102

Co^{2+} in microporous aluminophosphates. First of all, it should be clear that there is no simple correlation between the physicochemical properties of the solvents (Table 1) and the observed effects on crystallization and Co^{2+} incorporation. This is certainly due to the nature and complexity of crystallization processes in general and unfortunately not much knowledge exists on the precise physicochemical processes taking place in a crystallization vessel. On the other hand, it should also be evident that the solvent effects are related to the different coordination behavior of Co^{2+} with e.g., glycerol and water. In fact, glycerol forms more stable complexes with Co^{2+} due to a chelate effect in the synthesis gel. This results in a more gradual release of the Co^{2+} ions in the crystallization mixture when synthesis proceeds. In addition, the use of alcohols as solvents prevents the formation of $\text{Co}(\text{OH})_2(\text{H}_2\text{O})_4$ or other hydroxylated Co compounds, which are easily made in aqueous solutions when the pH gradually increases during the synthesis of microporous aluminophosphates. Similar effects hold for ethylene glycol and to a lesser extent for ethanol, although at present we do not have any explanation why different CoAPO materials require different solvent molecules in order to increase the amount of framework Co^{2+} . Future studies will be focused on gathering mechanistic insight using in situ spectroscopy [38] to monitor the changes in the Co coordination using different protonic solvents under synthesis conditions.

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