Hydrothermal synthesis of Co-rich CoAPO-5 molecular sieves

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A series of CoAPO-5 materials have been hydrothermally synthesized to maximize the degree of isomorphous substitution of Co^{2+} ions in the AFI framework. The as-synthesized as well as the calcined CoAPO-5 materials have been characterized with XRD, SEM, ICP, DRS (diffuse reflectance spectroscopy) and FT-IR techniques. Optimum conditions for the synthesis of Co-rich CoAPO-5 molecular sieves have been obtained by evaluating the influence of the amount and type of cobalt source, the type of aluminium source, the type of template molecule, the [template] : $[P_2O_5]$ ratio and the amount of different monovalent cations on the isomorphous substitution of Co^{2+} in the lattice. It will be shown that highly-crystalline hexagonal CoAPO-5 crystals with a substitution degree of 12% can be obtained from a $CsCl \cdot Co(CH_3COO)_2 \cdot 4H_2O \cdot$ pseudo-γ-$AlO(OH) \cdot H_3PO_4 \cdot (C_2H_5)_3N \cdot H_2O$ gel (with $[(C_2H_5)_3N]$: $[P_2O_5]$ and [CsCl] : $[Co(CH_3COO)_2]$ ratios of respectively 1.0 and 0.5) autoclaved for 41 h at 190 °C. In addition, the effect of monovalent cations on the redox properties of Co^{2+} in CoAPO-5 molecular sieves will be discussed. The degree of oxidation of framework Co^{2+} to Co^{3+} is always relatively low and increases in the order $Li^+ < K^+ \approx Rb^+ \approx Cs^+ < NH_4^+ \approx Na^+$. Thus, the addition of Li^+ results in a stabilization of Co^{2+} in the framework of CoAPO-5 molecular sieves upon calcination.

Introduction

Microporous crystalline aluminophosphates (AlPO$_4$-n) consist of tetrahedra of Al^{3+} and P^{5+}, which corner-share an oxygen atom and build up a three-dimensional framework with channels and/or pores of molecular dimensions.[1] An example is AlPO$_4$-5, which has one-dimensional channels with a twelve-membered ring aperture of 7.3 Å.[1–3] The framework of these molecular sieves are neutral and defect-free and, as a consequence, do not possess any redox or acidic properties. Therefore, much attention has been focused on the isomorphous substitution of P^{5+} and/or Al^{3+} by transition metal ions, such as Mn^{2+},[4] Cr^{3+},[5] Zn^{2+},[6] Ti^{4+},[7] Ni^{2+},[8] Cu^{2+}[9] and Co^{2+}.[10–17]

Unambiguous evidence for the isomorphous substitution of Al^{3+} in AlPO$_4$-n molecular sieves has been presented for Co^{2+}, but the amount of framework Co^{2+} is rather low. For example, highly crystalline CoAPO-5 materials with framework Co^{2+} can only be prepared from a synthesis gel with a [Co] : [Al] ratio lower than 0.06[12] and attempts to synthesize CoAPO-5 with higher cobalt contents usually lead to low-crystalline products contaminated with impurities.[2,12,13] This is mainly because other competing crystalline phases, such as CoAPO-34, are formed when more Co^{2+} is present in the synthesis gel. In addition, some of the Co^{2+} exists in extra-framework positions (isolated octahedral Co^{2+}, clustered CoO, *etc.*) or in a dense Co-containing aluminophosphate.[2,12,13]

The goal of this paper is to study the influence of the synthesis conditions and gel composition to maximize the degree of isomorphous substitution of Co^{2+} in the AlPO$_4$-5 framework. It will be shown that highly-crystalline and single-phase hexagonal CoAPO-5 crystals with a substitution degree of 12% can be obtained from a $CsCl \cdot Co(CH_3COO)_2 \cdot 4H_2O \cdot$ pseudo-γ-$AlO(OH) \cdot H_3PO_4 \cdot (C_2H_5)_3N \cdot H_2O$ gel. In addition, the effect of the presence of monovalent cations, such as Li^+ and Na^+, on the redox properties of Co^{2+} in CoAPO-5 molecular sieves will be discussed.

Experimental section

1. Hydrothermal synthesis

The synthesis gels of the CoAPO-5 molecular sieves were prepared in an ice bath under continuous stirring from H_3PO_4 (85 wt.% in H_2O, Acros), a template molecule, $(C_2H_5)_4NOH$ (40 wt.% in H_2O, Fluka), $(CH_3)_4NOH$ (25 wt.% in H_2O, Fluka), $(CH_3)_3N$ (45 wt.% in H_2O, Acros), $(C_2H_5)_3N$ (99%, Janssen Chimica), $(C_3H_7)_3N$ (98%, Fluka), $(C_2H_5)_2NCH_3$ (98%, Acros), $OHCH_2CH_2N(C_2H_5)_2$ (99%, Janssen Chimica) or $H_2NC_2H_4NH_2$ (99%, Janssen Chimica); a cobalt source, $(Co(CH_3COO)_2 \cdot 4H_2O$ (97%, Acros), CoF_2 (*p.a.*, Riedel-de Haen Ag.), CoI_2 (*p.a.*, Alfa), $CoCl_2 \cdot 6H_2O$ (97%, Acros) or $CoSO_4 \cdot 7H_2O$ (99%, Merck); an aluminium source, (pseudo-γ-$AlO(OH)$ (70 wt.% Al_2O_3, Catapal Vista), $Al(OCH(CH_3)_2)_3$ (98%, Acros), $Al_2(SO_4)_3 \cdot 18H_2O$ (99%, UCB), $AlCl_3 \cdot 9H_2O$ (99%, UCB) and $NaAlO_2$ (54%, Carlo Erba Reagents) and bidistilled water. Unless further specified, the [P] : ([Co] + [Al]) and $[H_2O]$: ([Co] + [Al]) ratios were always kept at 1 and 40, respectively. In particular cases, alkali metal chlorides (LiCl (99.0%, Analar), NaCl (99.9%, Analar), KCl (99.5%, Analar), RbCl (99.5%, Merck), CsCl (99%, Acros) or NH_4Cl (99.5%, Acros) were added to the synthesis gel to study the influence of these cations on the morphology of the CoAPO-5 crystals and the degree of

isomorphous substitution of Co^{2+}. The as-synthesized product is designated as MCoAPO-5.

The gel of the CoAPO-5 materials was prepared in a beaker placed in an ice bath. First, H_3PO_4 and the cobalt salt were mixed in bidistilled water. The aluminium source was then added to the solution under continuous stirring. Finally, the template molecule was slowly introduced into the synthesis mixture and the obtained gel was continuously stirred for 1 h. The gel was then transferred into a Teflon-lined autoclave and crystallization was carried out under autogenous pressure without stirring at 190 °C for 41 h. After crystallization, the obtained solids were washed with bidistilled water, followed by drying at 60 °C and eventually calcination at 550 °C in air in a muffle furnace.

2. Characterization techniques

The phase purity of the CoAPO-5 molecular sieves was evaluated with a Siemens D5000 X-ray diffractometer with Cu Kα radiation. An estimation of the CoAPO-5 phase fraction in each sample was obtained by comparing the area of selected diffraction lines (2θ at 7.5, 19.8, 21.0 and 22.5°) in the X-ray diffraction (XRD) patterns of the as-synthesized CoAPO-5 materials with that of zeolite Y (TSZ, Si : Al ratio of 2.71) as reference material. About 0.5 g of the CoAPO-5 material was mixed with 0.25 g of zeolite Y and the mixture was placed in a desiccator. After equilibration the sample was immediately measured by XRD. The reproducibility of this procedure was verified by measuring several mixtures of a crystalline CoAPO-5 material and zeolite Y followed by plotting the crystallinity degree of the CoAPO-5 material as a function of its content in the mixture. A straight line was obtained, confirming the reproducibility of the method. The crystal morphology of the materials was determined with scanning electron microscopy (SEM) by using a JEOL superprobe 733 instrument, while the chemical composition of the CoAPO-5 materials was determined by inductively coupled plasma (ICP) and electron microprobe micro-analysis (EMMA). Diffuse reflectance spectroscopy (DRS) was performed to evaluate the presence of tetrahedral and octahedral $Co^{2+/3+}$ in as-synthesized and calcined CoAPO-5 materials. DRS spectra were measured at room temperature on a Varian Cary 5 spectrometer equipped with an integration sphere. The spectra were recorded against a halon white reference standard in the region 200–2500 nm. The intensity of the triplet bands between 500 and 650 nm was calculated in terms of the sum of their absorbance.

Results and discussion

1. Synthesis of Co-rich CoAPO-5 molecular sieves

In what follows we will discuss the influence of the type of cobalt source, the aluminium source, the template molecule and the amount of the template molecule on the phase purity of the as-synthesized materials and on the degree of isomorphous substitution of Co^{2+} in the AFI framework.

A series of materials were synthesized at 190 °C for 41 h from a $1.0(C_2H_5)_3N \cdot 0.4CoO \cdot 0.8Al_2O_3 \cdot 1.0P_2O_5 \cdot 40H_2O$ gel prepared with $Co(CH_3COO)_2 \cdot 4H_2O$, CoF_2, CoI_2, $CoCl_2 \cdot 6H_2O$ or $CoSO_4 \cdot 7H_2O$ as cobalt source and pseudo-γ-AlO(OH) as aluminium source. As an example, the XRD pattern of a CoAPO-5 material (denoted as TEACoAPO-5) made from a synthesis gel containing $Co(CH_3COO)_2 \cdot 4H_2O$ is shown in Fig. 1. The phase purity and phase fraction of CoAPO-5 present in the as-synthesized sample was determined by comparison with a reference material. Based on this analysis it was concluded that single-phase CoAPO-5 molecular sieves with good crystallinity can be obtained by using $Co(CH_3COO)_2 \cdot 4H_2O$ and CoF_2, while the use of $CoCl_2 \cdot 6H_2O$ and $CoSO_4 \cdot 7H_2O$ results in the formation of a
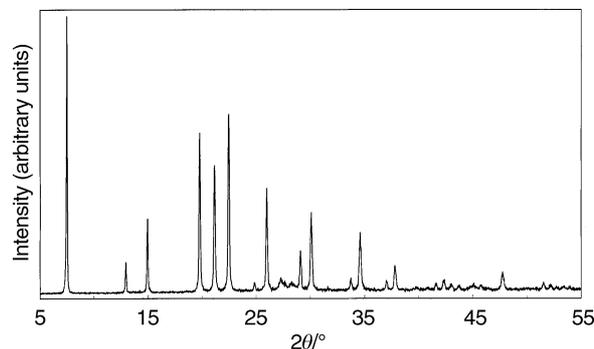

Fig. 1 XRD pattern of as-synthesized TEACoAPO-5.

mixture of tridymite and α-quartz and α-cristobalite, respectively. Small amounts of tridymite were also detected for the CoI_2 samples, whereas the most crystalline CoAPO-5 materials were obtained from gels prepared with $Co(CH_3COO)_2 \cdot 4H_2O$. The morphologies of these materials were investigated with SEM and crystals of, e.g., the $Co(CH_3COO)_2 \cdot 4H_2O$ sample have the classical hexagonal shape, whereas the CoI_2 sample possess flower-shaped crystals (Fig. 2).

The as-synthesized products prepared with $Co(CH_3COO)_2 \cdot 4H_2O$, CoF_2 and CoI_2 are deep blue. This observation is confirmed by the DRS spectra of Fig. 3, which shows the presence of an intense triplet band between 500 and 650 nm due to the $^4A_2 \rightarrow {}^4T_1(P)$ transition of high-spin tetrahedral $Co^{2+}(d^7)$.[2,18,19] The DRS spectrum of the CoF_2 sample, however, also reveals the presence of a significant amount of high-spin octahedral Co^{2+} as evidenced by the shoulder at 480 nm. In contrast, the $CoCl_2 \cdot 6H_2O$ and $CoSO_4 \cdot 7H_2O$ samples appear as white–pink materials, indicative of the presence of octahedrally coordinated non-framework Co^{2+}. It is also clear from Fig. 3 that the CoAPO-5 material prepared with $Co(CH_3COO)_2 \cdot 4H_2O$ has the most intense triplet band, indicating that this sample contains the most framework Co^{2+}. This observation suggests

Fig. 2 Scanning electron micrograph of as-synthesized CoAPO-5 molecular sieves prepared with CoI_2.
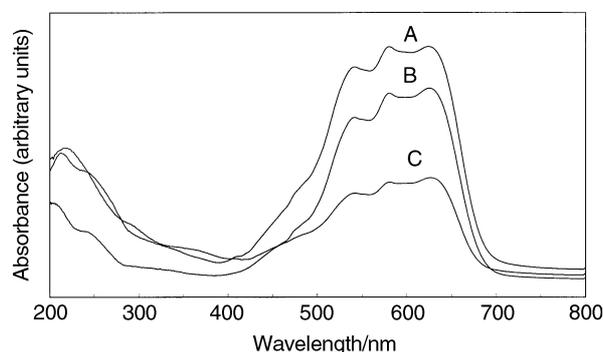
Fig. 3 Diffuse reflectance spectra of as-synthesized CoAPO-5 molecular sieves prepared with different cobalt sources: (A) $Co(CH_3COO)_2 \cdot 4H_2O$; (B) CoF_2 and (C) CoI_2.

that cobalt acetate is the most suitable cobalt source for the hydrothermal synthesis of Co-rich CoAPO-5. Table 1 shows that the $([Co] + [Al]) : [P]$ ratio of this as-synthesized solid is close to unity, strongly supporting the isomorphous substitution of Al^{3+} by Co^{2+}, and the substitution degree is about 8.4%, roughly estimated in terms of the $([P] - [Al]) : [P]$ ratio. This value is slightly higher than the highest isomorphous substitution degree reported up to now in the literature, namely 6%.[12] Nevertheless, the analytical data suggest that part of the Co^{2+}, probably as cobalt oxide and/or dense-phase cobalt phosphate, is occluded in the as-synthesized material or present at the ion-exchange sites.[13] In addition, the data also indicate that the $[Co] : [Al]$ ratio in the as-synthesized material is less than that in the synthesis gel, suggesting that about 35% of Co^{2+} initially present in the synthesis gel is removed by washing the solid after synthesis. An additional experiment was conducted in which the initial synthesis gel had a $[Co] : [Al]$ ratio of 0.33 instead of 0.25. The obtained solid is pink–blue and the fraction of pink materials increases with increasing Co content in the gel. This is consistent with that found by Clearfield et al.,[13] confirming the presence of a lot of extraframework octahedral Co^{2+}, and showing that the maximum $[Co] : [Al]$ ratio in the gel must be around 0.25.

In a second series of experiments, we have studied the influence of the type of aluminium source on the phase purity and crystal morphology of as-synthesized CoAPO-5 materials by taking $Co(CH_3COO)_2 \cdot 4H_2O$ as the cobalt source and $(C_2H_5)_3N$ as the template molecule. Comparison of the phase purity and crystallinity degree of the obtained solids indicate that well-crystalline CoAPO-5 materials can be obtained when pseudo-γ-AlO(OH), $Al(OCH(CH_3)_2)_3$ and $NaAlO_2$ were used, whereas the use of $AlCl_3 \cdot 9H_2O$ and $Al_2(SO_4)_3 \cdot 18H_2O$, however, leads to the formation of α-quartz. In addition, the crystallinity of the $NaAlO_2$ sample is rather low. In this respect, it is striking that the CoAPO-5 crystals of the $NaAlO_2$ sample grow predominantly along the 001 plane as evidenced by the SEM picture and XRD pattern of Fig. 4(A) and 4(B), respectively. Fig. 4(B) shows a very intense diffraction line at $2\theta = 7.5°$, while the other diffraction lines of CoAPO-5 are almost absent. It can also be estimated from the SEM picture of Fig. 4(A) that the crystal length : width ratio is more than 200. The above information reveals that the use
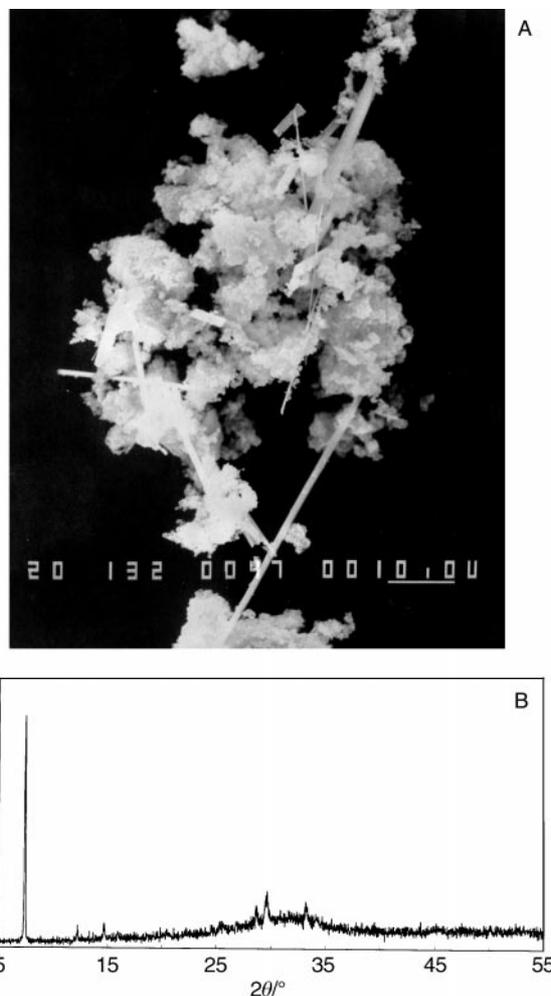

Fig. 4 Scanning electron micrograph (A) and X-ray diffraction pattern (B) of as-synthesized CoAPO-5 molecular sieves prepared with sodium aluminate.

of a different aluminium source significantly influences the gel-formation and crystallization processes of CoAPO-5, and consequently results in the formation of different crystalline phases and/or various crystal morphologies. The aluminium source also has an influence on the degree of isomorphous substitution of Co^{2+} in the framework. The triplet bands located at about 540, 580 and 625 nm in the DRS spectra of the sample synthesized with pseudo-γ-AlO(OH) are more intense than those of the materials synthesized with $Al(OCH(CH_3)_2)_3$ and $NaAlO_2$. This suggests that pseudo-γ-AlO(OH) is the most appropriate aluminium source for the isomorphous substitution of Al^{3+} by Co^{2+}.

In the hydrothermal synthesis of CoAPO-5 molecular sieves, template molecules not only play a pH-adjusting role but also balance the negative charges due to the isomorphous substitution of Al^{3+} by Co^{2+}.[11,12,20,21] This suggests that $(C_2H_5)_3N$ as well as other template molecules, such as $(C_2H_5)_4NOH$, $(CH_3)_4NOH$, $(C_2H_5)_3N$, $(C_3H_7)_3N$, $(C_2H_5)_2NCH_3$, $OHCH_2CH_2N(C_2H_5)_2$ and $H_2NC_2H_4NH_2$,

Table 1 Chemical compositions of the as-synthesized TEACoAPO-5 and CsCoAPO-5 and corresponding gels (F: framework, EF: extraframework)

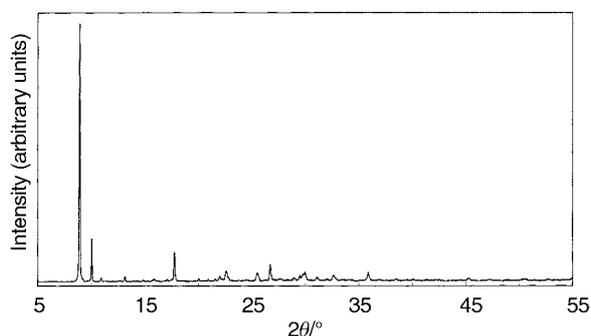| Samples | Gels | | | | Products | | | | | | Co^F (%) | Co^{EF} (%) |
	(Co	Al	P)O$_2$	Co/Al	(Co	Al	P)O$_2$	(Co + Al)/P	Co/Al	(P − Al)/P		
TEACoAPO-5	0.1	0.4	0.5	0.25	0.074	0.458	0.5	1.064	0.162	0.084	56.8	43.2
CsCoAPO-5	0.1	0.4	0.5	0.25	0.079	0.439	0.5	1.036	0.180	0.122	77.2	22.8

Fig. 5 X-Ray diffraction pattern of as-synthesized CoAPO-*n* material prepared with ethylenediamine as template molecule.

should have a strong effect on the crystallinity degree, the phase purity and the degree of isomorphous substitution of Co^{2+}. This was investigated by using a $1.0R \cdot 0.4CoO \cdot 0.8Al_2O_3 \cdot P_2O_5 \cdot 40H_2O$ gel made with pseudo-γ-AlO(OH) as aluminium source, $Co(CH_3COO)_2 \cdot 4H_2O$ as cobalt source and R, one of the above-mentioned template molecules.

Detailed comparison between the XRD patterns of the as-synthesized solids indicates that only $(C_2H_5)_3N$ and $OHCH_2CH_2N(C_2H_5)_2$ template molecules result in the formation of single-phase and well-crystalline CoAPO-5 molecular sieves. Instead, $(C_2H_5)_4NOH$ and $(CH_3)_4NOH$ lead to the formation of CoAPO-34 and CoAPO-SOD, respectively. However, both template molecules can result in the formation of CoAPO-5 when a little amount of cobalt, *e.g.*, a molar ratio of Co to Al of about 0.011, was present in the synthesis gel. When $(CH_3)_3N$ and $(C_2H_5)_2NCH_3$ were used as templates, CoAPO-43 and a mixture of CoAPO-5 and CoAPO-11 were obtained, respectively. In contrast, when $(C_3H_7)_3N$ was used as template the dense phases of tridymite and α-cristobalite were formed, whereas a $H_2NC_2H_4NH_2$ template leads to the crystallization of an unknown crystalline material. The XRD pattern of this material is shown in Fig. 5.

DRS spectroscopy shows that, compared with *N,N*-diethylethanolamine, TEA is more favorable for the incorporation of cobalt into the framework. Our results effectively prove Stucky's hypothesis which states that the synthesis of a
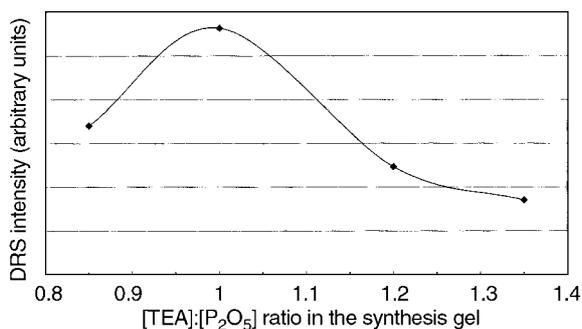

Fig. 6 Dependence of the overall intensity of the triplet bands between 500 and 650 nm of the as-synthesized TEACoAPO-5 samples as a function of the [TEA] : [P_2O_5] ratio in the synthesis gel.
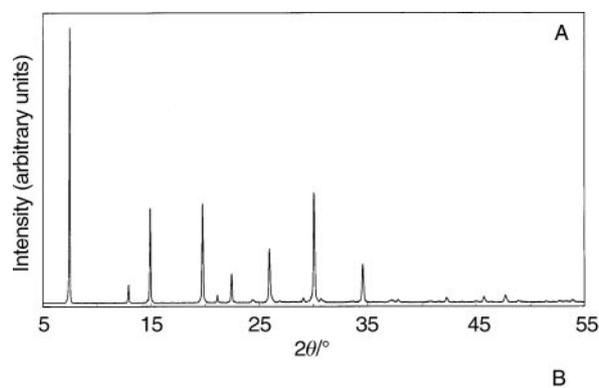

Fig. 7 X-ray diffraction pattern (A) and scanning electron micrograph (B) of as-synthesized CsCoAPO-5.

divalent-metal-rich framework requires amines with a high charge : volume ratio (usually a low [C] : [N] ratio).[20] It can be seen from Table 2 that the TEA content in the reaction mixture also has a strong effect on the as-synthesized products. When less TEA was added to the reaction mixture ([TEA] : [P_2O_5] $\leqslant$ 0.7), α-cristobalite was crystallized as an impurity, whereas CoAPO-34 was formed when more TEA was added. Our experiments show that although pure CoAPO-5 can be obtained when the molar ratio of [TEA] : [P_2O_5] is more than 1.2, the reproducibility is not high due to the formation of the competing crystalline phase of CoAPO-34. Fig. 6 shows the intensity of the triplet bands between 500 and 650 nm in the DRS spectra of the samples synthesized with different amounts of TEA. It is clear that the overall intensity of the triplet bands increases with increasing [TEA] : [P_2O_5] ratio when this ratio is less than one. A ratio higher than one results in a decrease of the overall intensity of the triplet bands. This indicates that the optimum molar ratio for the incorporation of Co^{2+} into the framework is around one.

Table 2 Influence of the amount of triethylamine on the phase purity and crystallinity of the as-synthesized products prepared from a synthesis gel with the following composition (autoclaved at 190 °C for 41 h)

[Triethylamine] : [P_2O_5]	Crystalline phase	Relative phase fraction of CoAPO-5 in the sample (%)
1.35	CoAPO-5 + CoAPO-34	53
1.2	CoAPO-5 + CoAPO-34	90
1.0	CoAPO-5	100
0.85	CoAPO-5	87
0.7	CoAPO-5 + α-cristobalite	12

2. Influence of the presence of monovalent cations on the isomorphous substitution of Co^{2+} and the degree of oxidation of framework Co^{2+} to Co^{3+} upon calcination

It is known that cations, in particular alkali metal ions, strongly influence the nucleation and crystal growth of molecular sieves and, as a consequence, determine the structural and physicochemical properties of molecular sieves by their "structure-forming" and "structure-breaking" properties.[22] They also have an influence on the isomorphous substitution reaction. For example, Na^+-ions inhibit the isomorphous substitution of Si^{4+} by Ti^{4+} in zeolites,[23] whereas NH_4^+- and K^+-ions have a positive influence on the incorporation of Ga^{3+} into the MFI framework.[24] To the best of our knowledge, no systematic study is available in the literature reporting the influence of alkali metal ions on the synthesis of microporous aluminophosphates.

Therefore, it is one of the goals of this work to investigate the influence of different monovalent co-cations (NH_4^+; Li^+; Na^+; K^+; Rb^+ and Cs^+) on the crystallization of CoAPO-5 molecular sieves and the degree of isomorphous substitution of Co^{2+} for Al^{3+} in the lattice. A series of samples were prepared from a $1.0(C_2H_5)_3N \cdot 0.1M_2O \cdot 0.4CoO \cdot 0.8Al_2O_3 \cdot P_2O_5 \cdot 40H_2O$ gel with cobalt acetate as cobalt source and pseudo-boehmite as aluminium source autoclaved for 41 h at 190 °C. Detailed comparison between the XRD patterns of the as-synthesized solids indicates that all the gels resulted in the formation of CoAPO-5, although minor amounts of α-cristobalite were also formed in the presence of Li^+ and Na^+. EMMA analysis confirmed the presence of alkali metal ions in the final solids. XRD and SEM further show that the as-synthesized MCoAPO-5 materials all have a high crystallinity and in most cases also a uniform crystal morphology. As an example, the XRD pattern and SEM micrograph of the as-synthesized CsCoAPO-5 are given in Fig. 7. The XRD pattern of Fig. 7(A) is typical for CoAPO-5 materials, while Fig. 7(B) shows the formation of classical hexagonal CoAPO-5 crystals with an eroded surface. Although the introduction of different monovalent cations in the synthesis gel does not affect the final topology of the as-synthesized material, it has an influence on the morphology of the crystals. It is clear that the addition of monovalent cations, particularly Rb^+ and Cs^+, to the reaction mixture favors the growth of crystals along the 100 plane as evidenced by a much larger $[P_{100}] : [P_{210} + P_{002} + P_{211}]$ ratio (with P taken as the intensity of the corresponding diffraction line). Indeed, ratios of 279 and 216 were obtained for RbCoAPO-5 and CsCoAPO-5 materials, while a ratio of 51 was measured for a CoAPO-5 material without any alkali metal ion. This observation was also confirmed by SEM. The crystallite morphology of the as-synthesized MCoAPO-5 molecular sieves is given in Table 3. This table shows that all the samples are composed of hexagonal crystals. The crystallite dimension of TEACoAPO-5 is, however, very different, and the NH_4CoAPO-5 crystallites are also not uniform, but it is very interesting to realize that some of the crystallites are very big, reaching 400 μm in length. In contrast, the crystallites of the samples prepared with different alkali metal cations, particularly Cs^+, are more uniform, and the ratio of the length to the diameter of crystallites increases with increasing atomic weight of alkali metal cations. The ratio $L : D$ of LiCoAPO-5 and NaCoAPO-5 is about one, while that of CsCoAPO-5 is about 2.5.

Fig. 8 shows that the introduction of Cs^+ greatly increases the cobalt content in framework lattice, while the addition of NH_4^+ and, in particular, Li^+ strongly decreases the amount of lattice cobalt. The introduction of Na^+, K^+ and Rb^+ does not have a substantial effect on the isomorphous substitution of Co^{2+} for Al^{3+}. This can also be concluded from Table 4, which summarizes the XRD data of the as-synthesized samples. The d_{100} values increase in the order: LiCoAPO-5 < NH_4CoAPO-5 < TEACoAPO-5 < KCoAPO-5 ~ RbCoAPO-5 < CsAPO-5, indicating an increase in the unit cell volume of MCoAPO-5 molecular sieves in the same order, and, consequently, the cobalt concentration in the framework gradually increases. FT-IR measurements of the calcined samples show that the frequencies attributed to the internal asymmetric stretching vibrations shift to lower wavenumbers in the order Li ($1318 cm^{-1}$), NH_4 ($1291 cm^{-1}$), K ($1267 cm^{-1}$), TEA ($1257 cm^{-1}$) and CsCoAPO-5 ($1234 cm^{-1}$). This also indicates the incorporation of Co^{2+} species in the framework of aluminophosphates.[25]
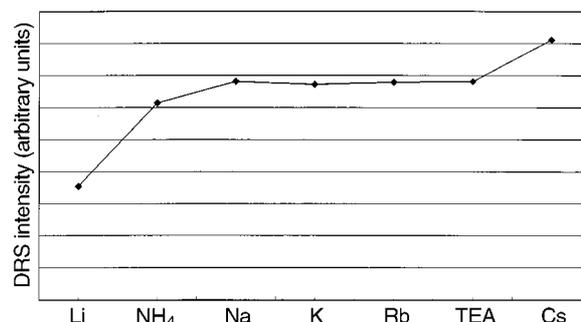

Fig. 8 Overall intensity of the triplet bands between 500 and 650 nm of the as-synthesized MCoAPO-5 molecular sieves as a function of the type of co-cation.

Table 3 Crystal shape and size (D = diameter and L = length of the particles in μm) of the as-synthesized MCoAPO-5 molecular sieves

M	NH_4	Li	Na	K	Rb	Cs	TEA
Shape	Hexagonal rod	Hexagonal rod	Hexagonal rod	Hexagonal rod	Hexagonal rod	Hexagonal rod	Hexagonal rod
Size (μm)	D: 30–65	D: 20–25	D: 35–45	D: 20–40	D: 25–35	D: 15–35	D: 6–40
	L: 30–400	L: 20–25	L: 35–50	L: 40–50	L: 40–65	L: 55–65	L: 25–55

Table 4 XRD data of the MCoAPO-5 samples synthesized in the presence of different monovalent cations

d_{hkl}	LiCoAPO-5	NH_4CoAPO-5	KCoAPO-5	RbCoAPO-5	CsCoAPO-5	TEACoAPO-5
d_{100}	11.63	11.78	11.80	11.80	11.81	11.79
d_{110}	6.78	6.83	6.85	6.84	6.85	6.83
d_{200}	5.88	5.92	5.92	5.93	5.93	5.93
d_{210}	4.46	4.48	4.49	4.49	4.49	4.48
d_{002}	4.18	4.20	4.20	4.21	4.21	4.20
d_{211}	3.94	3.95	3.96	3.96	3.96	3.96

There is still a lot of debate in the literature about the amount of Co^{2+} and Co^{3+} present in calcined CoAPO molecular sieves. Some authors reported that Co^{2+} ions in the framework of microporous aluminophosphates cannot be oxidized to Co^{3+}.[10,16,17] For example, it has been concluded by Howe and coworkers that CoAPO-5 molecular sieves have no redox properties in the absence of extraframework cobalt.[16] In contrast, other researchers believe that at least (a small) part of the framework Co^{2+} ions can be oxidized to Co^{3+} during a calcination treatment. This is evidenced by (a) changes in sample colour from blue to green–yellow or blue–green upon calcination; (b) the significant decrease in the intensity of the triplet bands between 500 and 650 nm of tetrahedral Co^{2+} accompanied by an appearance of two new absorption bands around 320 and 390 nm in the DRS spectra;[2,11,15,18,19,26,27] (c) a shortening of the Co–O bond length as determined by EXAFS upon calcination;[27] (d) an intensity decrease of the Co^{2+} EPR signal upon calcination;[28] (e) the presence of oxidizing sites capable of forming cation radicals from adsorbed hydrocarbons[29] and (f) a strong increase in the number of acidic sites and in the cation exchange capacity upon reduction of Co^{3+} to Co^{2+}.[14]

One of the intriguing questions is then what the effect is of the presence of alkali metal ions on the redox behavior of CoAPO-5 materials? It was observed that the LiCoAPO-5 sample after calcination at 550 °C for 6 h in air still resulted in a blue-coloured material very similar to that obtained after synthesis. In contrast, the colour of the TEACoAPO-5, NH_4CoAPO-5 and NaCoAPO-5 materials after an identical heat treatment turns into yellow–green. The other calcined samples had different colour grades between blue–green and yellow–green, indicating that the introduction of monovalent alkali metal ions in the CoAPO-5 materials have an influence on the redox behavior of framework Co. This was further confirmed by DRS spectroscopy. As an example, the DRS spectra of calcined LiCoAPO-5 and CsCoAPO-5 molecular sieves are shown in Fig. 9. The DRS spectra of the other samples are comparable to that of the CsCoAPO-5 material. It is clear that two very intense absorption bands around 322 and 410 nm, attributed to $O \rightarrow Co^{3+}$ charge transfer transitions[2,5,10,14,18,19,26] are present in the DRS spectra of all samples with the exception of the LiCoAPO-5 sample. The latter observation indicates that Co^{2+}-cations in the framework of LiCoAPO-5 cannot be oxidized to Co^{3+} during calcination. It was also found that the oxidation degree of Co^{2+} to Co^{3+} depends on the type of monovalent co-cations present in the molecular sieves. Compared with framework Co^{2+}-species in TEACoAPO-5, NH_4CoAPO-5 and NaCoAPO-5 molecular sieves, Co^{2+} in KCoAPO-5, RbCoAPO-5 and CsCoAPO-5 is much more difficult to oxidize.

Finally, Fig. 10 shows that the overall intensity of the triplet bands between 500 and 650 nm increases with increasing [Cs] : [Co] ratio up to a value of 0.5. In contrast, the triplet
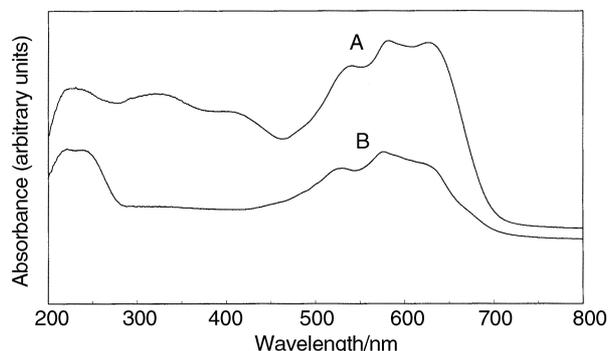
Fig. 9 Diffuse reflectance spectra of the calcined (A) CsCoAPO-5 and (B) LiCoAPO-5 molecular sieves.
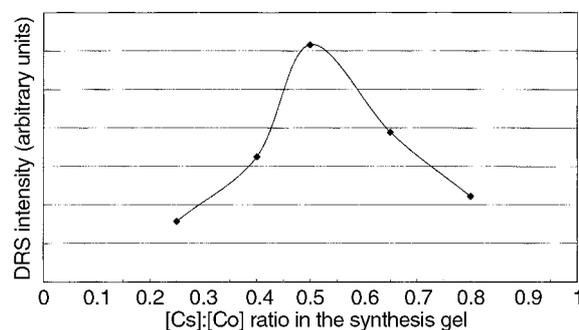
Fig. 10 Dependence of the overall intensity of the triplet bands between 500 and 650 nm of the as-synthesized CsCoAPO-5 samples on the [Cs] : [Co] ratio of the corresponding reaction mixture.

band intensity decreases above a [Cs] : [Co] ratio of 0.5. This implies that the optimum Cs content is about half of the Co content of the sample. It was also found that addition of more H_3PO_4, e.g., [P] : ([Co] + [Al]) = 1.1, is not beneficial for the incorporation of Co^{2+} into the framework, suggesting that the most appropriate [P] : ([Co] + [Al]) ratio is about one. The chemical composition of the corresponding product is listed in Table 1. The ([Co] + [Al]) : [P] ratio close to 1 indicates that Co^{2+} indeed substitutes for Al^{3+}, and the substitution degree is about 12%, which is substantially higher than for the TEACoAPO-5 sample synthesized in the absence of Cs^+. It was also observed that about 28% of the Co^{2+} in the synthesis gel is lost after washing the solid, but this is less than in the absence of Cs^+. In particular, the amount of extra-framework Co^{2+} present in the CsCoAPO-5 sample is much less than that present in the TEACoAPO-5 molecular sieve. In any case, the optimized synthesis procedure for CoAPO-5 materials and the addition of the optimal amount of Cs^+ cations to the synthesis mixture results in a CoAPO-5 material containing about 100% more framework Co^{2+} than what has been reported up to now in the literature.[12]

Conclusions

This work shows that cobalt acetate, pseudo-boehmite and triethylamine are the best synthesis materials for the preparation of Co-rich CoAPO-5 molecular sieves. The optimum [TEA] : [P_2O_5] ratio is 1.0, while the [Co] : [Al] and [P] : ([Co] + [Al]) ratios should not be higher than 0.25 and 1.0, respectively. The Co and Al source have also a significant effect on the morphology and structure of the molecular sieves. When $NaAlO_2$ is used, the crystallites grow predominantly along the 001 plane. Addition of different monovalent co-cations to the synthesis mixture not only influences the morphologies of the molecular sieves, but also the degree of isomorphous substitution of Co^{2+}. In this respect, Cs^+ strongly promotes the incorporation of Co^{2+} in the framework, and the optimum [Cs] : [Co] ratio is 0.5. In contrast, Li^+ strongly inhibits the isomorphous substitution of Co^{2+}; however, this cation prevents the oxidation of Co^{2+} to Co^{3+} upon calcination.

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