Synthesis of Co-rich CoAPO-CHA molecular sieves in the presence of ethanol and caesium

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CoAPO-CHA molecular sieves with Co(II) occupying 75% of the framework Al sites can be synthesized in the presence of ethanol and caesium.

Microporous crystalline aluminophosphate ($AlPO_4$-*n*) molecular sieves have a strict alternation of aluminium– and phosphorus–oxygen tetrahedra and their frameworks are neutral and, as a consequence, do not possess ion-exchange or acidic properties.[1] Acidic and redox sites can be generated in these materials by incorporating transition metal ions in the framework positions of these molecular sieves. This incorporation process gives rise to materials with interesting catalytic properties.[1–3] In this respect, the isomorphous substitution of Co(II) in $AlPO_4$-*n* materials has been studied in great detail, although the amounts of framework Co(II) remain still relatively low.[4–8] To the best of our knowledge, the framework Co : Al ratio reported is always < 1 with the exception of some $AlPO_4$-*n* molecular sieves with extremely small pores.[5,6,8] In fact, up to now not more than 38% of the Al(III) sites have been replaced by Co(II) in $AlPO_4$-*n* molecular sieves with pore openings > 3.5 Å. An example is CoAPO-50 with a framework substitution of 37.5%,[9] while for CoAPO-46 *ca.* 26% of the Al(III) sites can be replaced by Co(II).[10] It has also been reported that CoAPO materials with a chabazite structure can be prepared containing *ca.* 30% framework Co(II) by using $[NEt_4]_2CoCl_4$ and tetraethylamine hydroxide as the Co(II) source and template, respectively.[4] In this work, we report on the synthesis of crystalline CoAPO molecular sieves with the CHA structure having a Co : Al ratio substantially > 1. This high substitution degree has been made possible by using ethanol as solvent and by adding appropriate amounts of caesium to the synthesis gel.

CoAPO-CHA materials were prepared with H_3PO_4 (85 wt.%, Acros), $Co(MeCO_2)_2·4H_2O$ (97 wt.%, Acros), pseudoboehmite (70 wt.% Al_2O_3, Catapal), caesium chloride (p.a., Acros), triethylamine (TEA, 99%, Acros) and ethanol (99.7–100%, BDH Laboratory) starting from the following gel composition: $(1.0–2.3)TEA·(0-0.8)Cs_2O·(0.6–1.6)CoO·(0.2–0.7)Al_2O_3·P_2O_5·(30–60)EtOH$. A typical synthesis procedure is as follows: 2.93 g H_3PO_4 was dissolved into a mixture of 30 ml ethanol and 3.00 g CsCl. Then, 5.22 g $Co(MeCO_2)_2·4H_2O$ was added to the solution, followed by the addition of 0.37 g pseudoboehmite and 2.73 g TEA under constant stirring. This mixture was then further stirred for *ca.* 1 h in an ice bath. Finally, the resultant mixture was transferred into a Teflon-lined autoclave and crystallization was carried out at 190 °C for 14 days. The obtained solid was filtered off, washed and dried at 60 °C. ICP was used to analyze the chemical composition of the initial gels and the as-synthesized samples, while XRD was used to identify the crystalline phase of the materials synthesized.

Table 1 gives an overview of the prepared CoAPO-CHA materials, the sample notations and the chemical compositions of the gel materials and final solids. Fig. 1 shows, as examples, the powder X-ray diffraction patterns of CsCoAPO-1.50 and CoAPO-1.50 and indicates that the as-synthesized solids are well crystalline and possess a CHA structure.[4,11] It is also clear that the addition of Cs(I) to the synthesis gel results in a decrease of the intensity of the peaks at lower 2θ values, particularly those at *ca.* 9.4 and 20.5°. It was observed that these peaks further decrease in intensity with increasing Cs(I) content in the synthesis gel, while at the same time the peaks at 2θ *ca.* 24.6,

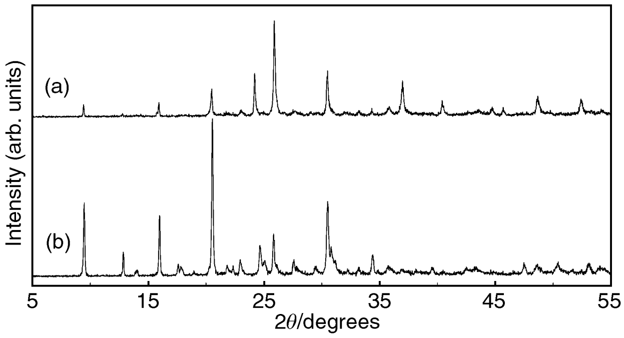

Fig. 1 XRD patterns of the as-synthesized CsCoAPO-1.5 (a) and CoAPO-1.5 (b) molecular sieves.

Table 1 The chemical compositions of the gels and the as-synthesized CoAPO-CHA materials

	Gels					Products					
Sample	(Co	Al	P)O_2	Co : Al	Cs : Co	(Co	Al	P)O_2	(Co+Al) : P	Co : Al	(P−Al) : Al
CoAPO-0.43	0.15	0.35	0.50	0.43	0.00	0.178	0.366	0.500	1.090	0.487	0.364
CoAPO-0.67	0.20	0.30	0.50	0.67	0.00	0.277	0.318	0.500	1.189	0.869	0.572
CoAPO-1.00	0.25	0.25	0.50	1.00	0.00	0.244	0.333	0.500	1.154	0.734	0.503
CoAPO-1.50	0.30	0.20	0.50	1.50	0.00	0.201	0.348	0.500	1.097	0.579	0.439
CsCoAPO-1.00	0.25	0.25	0.50	1.00	0.80	0.256	0.263	0.500	1.038	0.974	0.910
CsCoAPO-1.50	0.30	0.20	0.50	1.50	0.83	0.348	0.220	0.500	1.136	1.582	1.276
CsCoAPO-2.33	0.35	0.15	0.50	2.33	0.86	0.439	0.176	0.500	1.230	2.494	1.846
CsCoAPO-4.00	0.40	0.10	0.50	4.00	0.88	0.483	0.121	0.500	1.208	3.992	3.123

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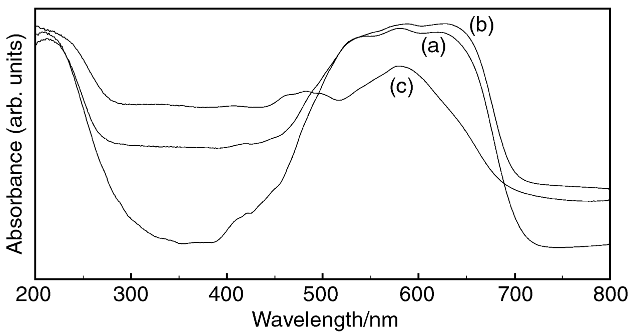

Fig. 2 DRS spectra of as-synthesized (a) and calcined (b) CsCoAPO-4.0, and calcined CoAPO-1.5 (c).

25.8, 30.5 and 37.0° increase in intensity. Such intensity changes are typical for isomorphous substitution processes.

Besides the key factors of the charge and geometry of the structure-directing amine molecules,[5] the solvent also plays a very important role in increasing the concentration of transition metals in the framework. It was reported that the Co : Al ratio of the reaction mixture can be maximized to 0.5 if TEA was used as a template in the hydrothermal synthesis of CoAPO-CHA.[5] We found that attempts to synthesize the samples with reaction mixtures containing higher cobalt contents led to the formation of a pale blue crystalline mixture of CoAPO-5 and an unknown phase. In contrast, when ethanol is used as solvent, pure CoAPO-CHA molecular sieves with an intense blue colour can be synthesized with the synthesis gel having a Co : Al ratio up to 0.67. The framework Co : Al ratio of the as-synthesized material is *ca.* 0.57, as estimated from the (P − Al) : Al ratio (Table 1). The blue colour and the absence of pink materials is indicative of tetrahedral Co(II) in the framework. The amount of framework Co(II) is much higher than that reported previously in the literature. However, further increase of the Co(II) content in the reaction mixture not only results in the formation of pink materials, but also decreases the relative amount of framework Co(II) of the as-synthesized samples. Thus, the more Co(II) in the synthesis gel, the less Co(II) in the framework. In particular, when the Co : Al ratio of the reaction mixture is >1.5, the pink colour of the material cannot be removed by washing.

It is known that alkali metal cations have a strong influence on the crystallization of molecular sieves. We found that by introduction of Cs(I) cations in the synthesis gel, the Co : Al ratio of the reaction mixture can be dramatically increased to 4.0 for the synthesis of CHA-type Co-containing aluminophosphate molecular sieves. These materials are not contaminated with pink crystalline impurities. These as-synthesized CsCoAPO-*x* (*x* represents the Co : Al ratio of the reaction mixture) samples all have a deep blue colour. This is evident from the diffuse reflectance (DRS) spectrum of CsCoAPO-4.0 shown in Fig. 2(a). The strong triplet bands between 500 and 650 nm confirm that most of the Co(II) ions have been incorporated into the framework lattice, while a broad and weak band around 480 nm indicates the presence of only a small amount of extraframework Co(II).

Table 1 clearly shows that the Co : Al ratio of the CsCoAPO-*x* samples is basically the same as that of the reaction mixture, which is expected if Co(II) isomorphously substitutes for Al(III) in the framework. This behavior is different from that observed for the synthesis conducted in the absence of Cs(I). When the Co : Al ratio of the reaction mixture <1, the (Co+Al) : P ratio of the as-synthesized solid, *e.g.* CsCoAPO-1.0, is very close to 1. This fact strongly supports the incorporation of most Co(II) in the framework lattice sites. With the addition of more cobalt into the reaction mixture, the (Co+Al) : P ratio is gradually >1, indicating that a small amount of extraframework Co(II) ions is present in the products. This is in accord with the chemical analysis results. Nevertheless, it can be seen that the (P − Al) : Al ratio of the CsCoAPO-*x* samples maximally reaches about 3.12 (CsCoAPO-4.0), which means that *ca.* 75% framework Al sites have been replaced with Co(II). Table 1 also indicates that the amount of caesium needed in the synthesis increases with increasing cobalt content. The amazing ability of Cs(I) to increase the Co(II) concentration in the framework can be related to its role as a counter cation, possibly resulting in a decrease of framework distortion owing to a stronger Cs–O bond than the TEA–O bond, and consequently an increase of the stability of the as-synthesized CsCoAPO-CHA. Thus, Cs(I) promotes the incorporation of Co(II) into the framework of the CoAPO-CHA material.

As expected, the hydrothermal stability of the as-synthesized products decreases upon increasing the Co : Al ratio. It was found that CsCoAPO-*x* synthesized with reaction mixtures having a Co : Al ratio >2.33 gradually becomes pale blue upon washing with water. This is further evidenced by the corresponding DRS spectra in which the triplet bands characteristic of tetrahedral Co(II) obviously decrease in intensity at the expense of the appearance of an absorption at 480 nm typical for extraframework octahedral Co(II). This may be due to the hydrolysis of framework Co(II) since this ion shows a strong interaction with water, and competes with Cs(I) for H_2O coordination.[5] Therefore, the products synthesized with high amounts of cobalt should be better washed with ethanol.

On the other hand, Cs(I) as a counter cation can effectively prevent oxidation of Co(II) to Co(III) during calcination. Upon calcination at 550 °C for 6 h, the sample CoAPO-*x* becomes yellow-greenish, and even pink materials are evident when the Co : Al ratio of the synthesis gel is >0.43. This is evidenced by DRS for the CoAPO-1.5 sample [Fig. 2(c)]. This spectrum is characterized by a band at *ca.* 450–500 nm and a band at *ca.* 320 nm, indicating the presence of octahedral Co(II) and Co(III), respectively. This shows that many framework Co(II) ions have been expelled from the framework, indicating the instability of CoAPO-*x* molecular sieves. In contrast, the calcined CsCoAPO-*x* is still deep-blue, as confirmed by the strong triplet bands at *ca.* 530, 580 and 630 nm in the DRS spectrum of the calcined CsCoAPO-4.0 sample [Fig. 2(b). This proves that the presence of Cs(I) can stabilize tetrahedral Co(II) in the framework of CoAPO-CHA materials.

In conclusion, Co-rich CoAPO molecular sieves with CHA structure have been prepared using ethanol and Cs(I) as solvent and counter cation, respectively. Co(II) can be maximized to occupy about 75% of the framework metal sites. The presence of Cs(I) significantly inhibits the oxidation of Co(II) to Co(III).

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