Synthesis and Characterization of a New Cobalt Aluminophosphate with an Open-Framework Structure

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A new cobalt aluminophosphate, $Co_xAl_{1-x}PO_4[(NH_4)_x(NH_3)_{0.5-x}]$, with relatively high cobalt content ($x \leq 0.4$) has been hydrothermally synthesized and characterized by single-crystal X-ray diffraction, thermogravimetric analysis, and infrared and visible light spectroscopies. The structure of the compound is a new zeolite-like open framework (monoclinic, $C2/c$, $Z = 4$, $a = 13.312(3)$, $b = 13.160(3)$, $c = 8.914(2)$ Å, $\beta = 100.94(3)°$ for $x = 0.38$). It contains channels of eight-membered rings of alternating tetrahedra of $(Co,Al)O_4$ and PO_4. The templates of NH_4^+ and NH_3 reside in the channels and are surrounded by oxygen atoms with N−O distances of 3.0 Å and above.

Introduction

Cobalt-substituted aluminophosphates, the CoAPO family, are extensively studied mainly due to their potential use as solid-acid catalysts, and the possibility for redox reactions. A Brønsted acid site is generated by each substitution of Al^{III} by Co^{II}, and the corresponding need of a proton to balance the charges. It has been shown that such CoAPO molecular sieves catalyze the autooxidation of cyclohexane in the liquid phase.[1−4] Redox properties, on the other hand, may be expected from possible reversible oxidation of Co^{II} to Co^{III}.[5−11] All of the known to date CoAPOs are isostructural with the corresponding AlPO (aluminophosphate) parents.[4,12−17] In contrast, there are several examples of Co-substituted gallophosphates, CoGaPOs, that are not structurally related to any of the known GaPOs, AlPOs, or zeolites.[18,19] The atomic ratio Co:Al in the known CoAPOs varies between 0.06 in CoAPO-5 to about 0.33 in CoAPO-44.[9,17] Here we report the synthesis and characterization of a new cobalt aluminophosphate, $Co_xAl_{1-x}PO_4[(NH_4)_x(NH_3)_{0.5-x}]$ (CoAPO−NH hereafter), with relatively high molar fraction of cobalt, up to 0.4, and with a novel zeolite-like structure that is different from any of the known AlPOs.

Experimental Section

Synthesis. Initially the compound was made accidentally in a reaction designed to produce the microporous cobalt borophosphate, $CoB_2P_3O_{12}(OH)\cdot C_2H_{10}N_2$.[20] The apparent source of aluminum was a piece of wool-like aluminosilicate used for insulation in our furnaces (placed nearby the reaction-loading bench). After the structure and the stoichiometry of the compound were determined it was synthesized in a more rational way. A typical reaction is run with approximately 3-fold excess of aluminum and phosphate. Mixed in such a reaction are 0.046 g of Al_2O_3 (Catapal B alumina boehmite from Vista), 0.036 g of $Co_3(PO_4)_2\cdot 8H_2O$ (Alfa), 0.130 g of H_3PO_4 (Aldrich), and 10 mL of H_2O. The mixture is continuously stirred while aqueous solution of ammonia (Aldrich, 35%) is added until the pH reaches 8.5−8.8. The mixture is heated in an autoclave for 3−5 days at 200−205 °C. Despite the excess mentioned above, the product usually contains the purplish $Co_7P_6O_{20}(OH)_4$ and $Co_2(PO_4)(OH)$ in addition to the major phase of deep-blue CoAPO−NH.[21] Stoichiometric reactions with different pH produce either amorphous material or cobalt hydroxyphosphates only. Small variations of the reaction time and temperature as well as excess of NH_3 and/or Al_2O_3 did not seem to affect the outcome.

Since the known CoAPOs are isostructural with the corresponding "parent" AlPOs, we also tried to synthesize a pure AlPO with the CoAPO−NH structure, i.e., reactions without cobalt were loaded and carried out at the above-described conditions. The resulting products of all of them were amor-

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Table 1. Data Collection and Refinement Details for CoAPO−NH

formula	$Co_{0.379(8)}Al_{0.621}PO_4[(NH_4)_{0.379}(NH_3)_{0.121}]$
space group, Z	$C2/c$, 4
unit-cell parameters[a]	$a = 13.312(3)$ Å
	$b = 13.160(3)$ Å
	$c = 8.914(2)$ Å
	$\beta = 100.94(3)°$
	$V = 1533.2(6)$ Å^3
crystal size	0.1 × 0.1 × 0.1 mm
density (calculated)	2.478 g cm^{-3}
$2\theta_{max}$, radiation	50°, Mo Kα, graphite monochromated
absorption coefficient	23.1 cm^{-1}
octants measured	$-hk\pm l$
scan method	$\omega-2\theta$
reflections collected	2153
independent reflections with I > $2\sigma_I$	1058
no. of variables	137
R indexes ($I > 2\sigma$)[b]	$R1 = 4.32\%$, $wR2 = 8.80\%$
R indexes (all data)[b]	$R1 = 6.02\%$, $wR2 = 9.79\%$

[a] Room-temperature Guinier data with Si as an internal standard ($\lambda = 1.540\ 562$ Å). [b] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]]^{1/2}$. $w = 1/[s^2F_o^2 + (0.0353P)^2 + 41.9798P]$ where $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Positional and Isotropic Equivalent Displacement Parameters for CoAPO−NH

atom	x	y	z	U_{eq}[a] [Å^2]
Co/Al1	0.0785(1)	0.3761(1)	0.0584(1)	0.019(1)
Co/Al2	0.1319(1)	−0.0560(1)	−0.1122(1)	0.018(1)
P1	0.1459(1)	0.5605(1)	−0.0901(1)	0.020(1)
P2	0.0756(1)	0.1359(1)	0.0421(1)	0.019(1)
O1	−0.0390(3)	0.1343(2)	0.0335(4)	0.031(1)
O2	0.2453(3)	0.5982(3)	0.0064(4)	0.035(1)
O3	0.0596(3)	0.6117(3)	−0.0285(4)	0.041(1)
O4	0.1104(3)	0.2444(3)	0.0253(5)	0.049(1)
O5	0.1347(3)	0.4463(2)	−0.0795(4)	0.037(1)
O6	0.1052(3)	0.0773(3)	−0.0903(4)	0.035(1)
O7	0.1300(3)	0.0906(3)	0.1914(4)	0.045(1)
O8	0.1462(4)	0.5913(4)	−0.2523(4)	0.056(1)
N	0.1761(4)	0.2518(4)	−0.2771(5)	0.039(1)

[a] U_{eq} is defined as one-third of the trace of the ortogonalized U_{ij} tensor. [b] The atomic fractions of cobalt in Co/Al1 and Co/Al2 are 37.8(6) and 38.0(6)%, respectively.

phous gels, indicating that apparently cobalt is needed in order to stabilize the CoAPO−NH structure.

Characterization. A few crystals with hexagonal prismatic shape were chosen from the first (accidental) reaction, mounted on glass fibers, and checked for singularity on a CAD4 diffractometer. One of them, 0.1 × 0.1 × 0.1 mm, was chosen, and the 25 reflections from a random search were indexed with C-centered monoclinic cell. Two octants of data ($2\theta \leqslant 50°$) were collected at room temperature with monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). After corrections for Lorentz and polarization effects, the data were consistent with two space groups, *Cc* and *C*2/*c*. The Wilson plot statistics strongly suggested a centrosymmetric space group, and therefore the latter was selected. The structure was solved by direct methods and refined on F^2 with the aid of the SHELXTL-V5.0 software package. There are two positions with mixed Al/Co occupancies in addition to two phosphorus, eight oxygen, and one nitrogen positions. The final refinement of the structure with all non-hydrogen atoms with anisotropic thermal parameters, and refinement of the fractions of Al and Co with their sum constrained to full occupancy converged at $R1/wR2 = 4.32/8.8\%$ for 1058 reflections with $I > 2\sigma_I$ and 137 variables. Further details of the data collection and refinement are listed in Table 1. Positional and isotropic thermal parameters and essential distances are listed in Tables 2 and 3, respectively.

The phase identification of the products of the different reactions was done by powder X-ray diffraction on an Enraf-Nonius Guinier camera with Cu Kα_1 radiation ($\lambda = 1.540\ 562$ Å) and NBS (NIST) silicon as an internal standard. The lattice parameters of the CoAPO−NH were determined from such a photograph by least-squares refinement of the measured 2θ values of the lines of the sample and those of the standard. Qualitative energy-dispersive X-ray analysis was used to confirm the presence of Co, Al, and P in the compound. Quantitative elemental analyses were carried out on an ICP spectrometer. Standards of Al and Co with three concentrations of each were used for that purpose. Thermogravimetric measurements were done in helium atmosphere with a heating rate of 5 °C/min. The compound was also characterized by IR and vis spectra.

Table 3. Selected Distances in CoAPO−NH

Co/Al1	O3	1.814(4)	P1	O2	1.518(3)
	O4	1.821(4)		O3	1.521(4)
	O5	1.810(4)		O5	1.514(3)
	O8	1.807(4)		O8	1.502(4)
Co/Al2	O1	1.847(4)	P2	O1	1.514(4)
	O2	1.813(4)		O4	1.517(4)
	O6	1.807(4)		O6	1.523(3)
	O7	1.805(4)		O7	1.511(4)

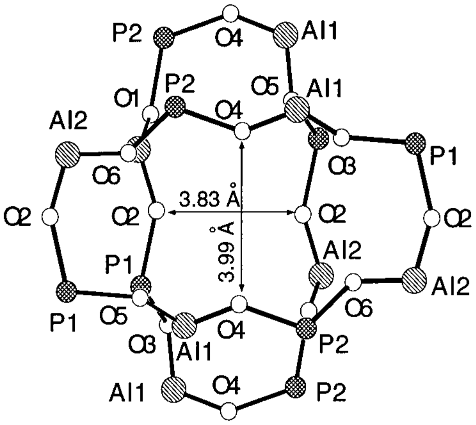

Figure 1. View of the channels running along (001) in CoAPO−NH with the shortest distances in the two types of 8-member rings shown. Al1 and Al2 label the two different Co/Al mixed positions.

Results and Discussion

The structure of the compound is a new three-dimensional framework of alternating corner-shared tetrahedra of $(Co,Al)O_4$ and PO_4, as in most of the pure and substituted AlPOs. The tetrahedra form two types of eight-membered elliptical rings with planes perpendicular to the *c* axis (Figure 1). The rings are very similar in shape but differ in sizes, i.e., the closest oxygen−oxygen contacts across the ring. For the two rings these distances are 3.83 Å (between two O4 atoms) and 3.99 Å (between two O2 atoms), respectively. Alternating the rings are stacked along the *c* direction with their long axes perpendicular to each other. Thus they form channels where the ammonia molecules and ammonium cations are positioned (Figure 2a).

The two Co/Al positions (labeled Al1 and Al2 in Figure 1) refined with virtually equal atomic fractions of cobalt, 37.8(6) and 38.0(6) at. %. As a result of this, the average (Co/Al)−O distances around the two sites are also practically equal, 1.813(4) and 1.818(4) Å. As expected, due to the presence of cobalt they are longer than a typical Al−O distance, 1.74 Å in $AlPO_4$-12, for example.[4] They are also longer than the corresponding distances in cobalt-substituted AlPOs with smaller fractions of cobalt, 1.77 Å in CoAPO-21 with 2 at % Co, for example.[12] The P−O distances around the two inde-

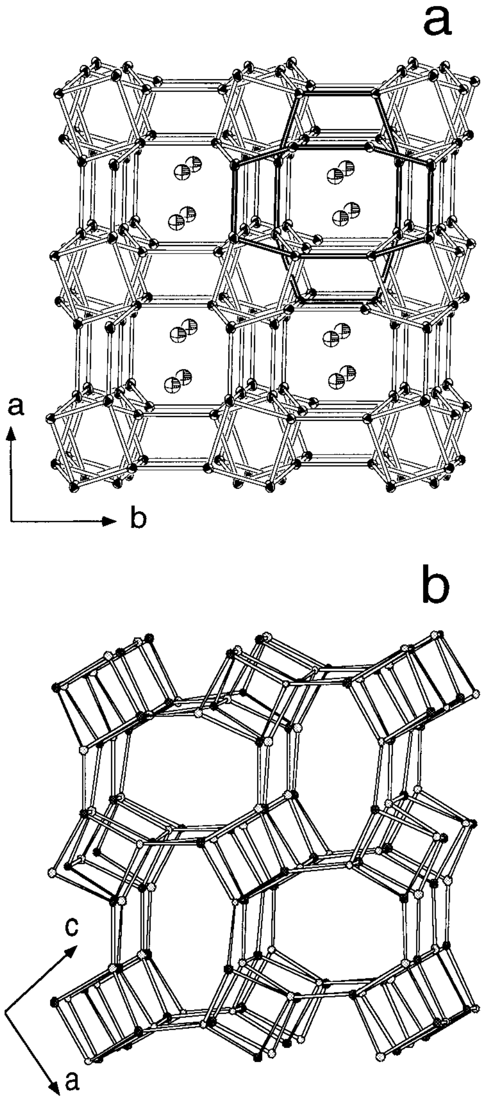

Figure 2. (a) ORTEP plot of the structure of CoAPO−NH with 50% probability thermal ellipsoids. The isolated ellipsoids are the nitrogen atoms of the NH_3 and NH_4^+ groups. (b) Structure of APD (or AlPO4-D) is shown for comparison.

pendent P-sites, $d_{ave} = 1.515(4)$ Å, on the other hand, are within the normal range. All oxygen atoms are shared by Co/Al and P tetrahedra.

The negative charge of the network due to the presence of Co^{2+} is compensated for by ammonium countercations positioned in the channels of the structure, and therefore the number of ammonium cations per unit cell must equal that of the cobalt atoms. This also defines the fraction of the NH_3 molecules since the nitrogen position is fully occupied. Considering that there are two Co/Al atoms per a nitrogen atom (Table 2) the formula can be written as $Co_{0.379(8)}Al_{0.621}PO_4$-[$(NH_4)_{0.379}(NH_3)_{0.121}$]. Also, it is clear that the upper limit for the cobalt in the structure is 0.5, if all of the template species were NH_4^+. In our study, however, the cobalt fraction was always between 0.25 and 0.4. Certain limitations for the observed lower maximum (0.4) than the theoretically possible one (0.5) could be attributed to intolerable elongations of the average Co/Al−O distances and to the distortions caused by the longer Co−O bonds. It is not clear, on the other hand, why the synthesis of the corresponding “pure” AlPO failed. Apparently the role of the cobalt and most likely the need of accompanying ammonium cations are quite important for the formation and the stability of the structure.

The structure of CoAPO−NH can be compared with that of a known AlPO, the so-called $AlPO_4$-D (APD).[16] The structure of the latter is built of similar elliptical 8-membered rings. The difference is that the rings are of one type and are stacked with their long axes parallel to each other (Figure 2b). Similarities with the structures of some zeolites can be found as well. Gismondine, $CaAl_2Si_2O_8{\cdot}4H_2O$, and merlinoite, $K_5Ca_2Al_9Si_{23}O_{64}{\cdot}24H_2O$, also have 8-membered rings that are stacked somewhat similarly to the APD.[16] Unlike CoAPO−NH though none of these compounds has NH_3 or NH_4^+ in its channels.

The elemental analyses by ICP gave Co:Al ratios of 0.31(8) and 0.34(8) from two runs. This clearly contradicts the results from the structure refinement, Co:Al = 0.60 in average, and is apparently due to a range of Co concentrations in the different crystallites. To clarify these discrepancies, single-crystal X-ray data were collected from a second crystal from the same reaction. The refinement converged at different Co:Al ratio of 0.43, which clearly suggests that the degree of substitution varies in the crystallites.

The TGA curve showed a desorption step (with an uneven slope) starting at 380 and ending at 480 °C with a weight loss of 5.9(3) wt %. This number compares well with the calculated 5.7 wt % for desorption of all of the ammonia in the compound (0.5 NH_3 molecule/formula). The rather long step of 100 °C is quite typical for temperature-programmed desorption (TPD) of ammonia from zeolite-like phases.[13,15] The sample remains crystalline up to 500 °C, but above that it becomes amorphous and changes color from deep blue to light blue-gray. The relatively high desorption temperature and the lack of two separate steps in the curve (expected for the desorption of ammonia from the charged and neutral templates) are most likely results of the environment of the template and the shape of the channels. There are five framework oxygen atoms around the template at N−O distances of 2.99−3.09 Å, and another five at distances of 3.15−3.29 Å. This indicates that some multiple or multicenter hydrogen bonding may exist for the NH_3 and NH_4^+ molecules. This will result in practically identical and relatively high desorption temperatures for the two species. In addition, despite of the relatively large size of the rings forming the channels, their positioning in a crisscross fashion leads to relatively small effective channel cross section. This may hinder the escape of the ammonia and cause also higher desorption temperatures and a longer step of desorption.

IR spectra from a few samples clearly showed the characteristic phosphate and ammonia bands. The VIS-measurements showed broad bands with maxima at 542, 552, 585, and 636 nm. Bands with similar positions are reported for CoAPO-5, -34 and -44 and have been interpreted as an evidence for the presence of tetrahedrally coordinated Co^{2+} in the structure.[9,11]

It is well-known that the catalytic activity of the metal aluminophosphates is due to their acidity which in turn is the result of the substitution of Al^{III} by M^{II} and the need of a proton to balance the charge.[17] Since CoAPO−NH is with relatively high fraction of M^{II} (one of the highest among the CoAPOs) it will have very high acidity (based on the deammoniation results), and therefore high catalytic activity can be expected.

Note added in proof: Two recent publications report on new CoAPOs with even higher Co:Al atomic ratios.[22]

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Supporting Information Available: Tables of anisotropic thermal parameters of the non-hydrogen atoms and positional and isotropic equivalent displacement parameters for the hydrogen atoms (1 page); structure factor tables (6 pages). Ordering information is given on any current masthead page.

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