A new Co-substituted aluminophosphate (AlPO) with MO_5 units: high-temperature framework modifications by *in situ* single crystal X-ray diffraction

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Open-framework aluminophosphate ($AlPO_4$) are a class of microporous crystalline materials belonging to the zeolite family. The tetrahedral framework can be modified by the incorporation of metal cations (Me), which lead to the formation of different polyhedral units, pores and channels type. In particular, the presence of Me^{2+} ions creates a net-negative charged framework, which is of interest because of the formation of acid sites. Moreover, $AlPO_4$ containing divalent heteroatoms (e.g. Co, Mg, Fe) have shown enhanced redox, acidic, and magnetic properties, making them promising materials in a wide range of applications [1-3]. In this contribution, we report on the synthesis and characterization of a Co-aluminophosphate (CoAPO-1), where Co partially substitutes Al at the tetrahedral and octahedral sites. This substitution leads to the formation of MO_5 units, mostly occupied by Co, which makes the obtained structure unique among the known heteroatoms-containing aluminophosphates [4].

The compound was obtained by hydrothermal synthesis using 1,2-Diaminopropane ($R^{+2} = C_3H_{12}N_2$) as a template. The chemical composition is $Al_{2.78}Co_{1.22}(PO_4)_4(OH)(C_3H_{12}N_2)H_2O$. The structure was determined by single-crystal X-ray diffraction in the triclinic space group P-1, with the following unit-cell parameters: a = 9.7751(2), b = 9.8044(2), c = 10.9649(3) Å, α = 72.905(2), β = 73.398(2), γ = 88.326(2)°, V = 960.84(4) $Å^3$. The framework is built by PO_4, AlO_4, AlO_6, and CoO_5 polyhedra, where Al is partially replaced by Co (Fig. 1). The H_2O and the R^{+2} template are disorderly distributed within the channels.

Thermal gravimetric analysis (TGA) indicated the presence of three main dehydration steps at 110, 220, and 310°C. To get an insight into the temperature-induced structural modifications, we performed *in situ* SC-XRD measurements from 25 to 300°C, in steps of 25°C. These experiments allowed monitoring stepwise the release of H_2O and OH and the corresponding transformations of the porous framework. The loss of OH groups is followed by a change in the coordination number of the CoO_5 and AlO_6 polyhedra, which at 200°C reorganize into tetrahedra. This rearrangement leads to a pure tetrahedral framework and modifies the channels connectivity. In contrast to what usually reported for zeolite-type materials upon heating, after a first drop of the unit-cell volume up to 100°C, as a consequence of the H_2O release, an expansion is observed starting form 150°C, when the structure rearranges because of the OH loss. This dehydrated structure is stable up 300°C. These results demonstrate that this kind of material maintains its crystallinity at high temperature and most important the channels porosity is not significantly affected by the thermal treatment.

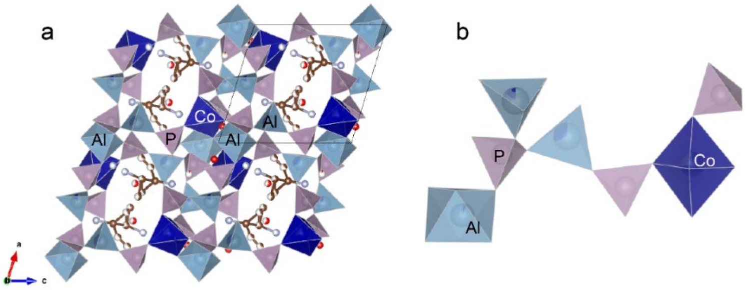

Figure 1. (a) Crystal structure of CoAPO-1. Red, brown, and violet spheres represent, H_2O, C, and N, respectively. Polyhedra labels of Al and Co sites are assigned based on the most abundant cation. Partial occupancies correspond to partial coloured spheres. (b) Fragment of the crystal structure highlighting the different polyhedral units.

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