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Coexistence of framework Co^{2+} and non framework Co^0 in CoAPO-5

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ABSTRACT

We report about the synthesis and characterization of a microporous CoAPO-5 catalyst. Diffuse Reflectance UV–Vis spectroscopy was employed to follow the changes upon oxidation and reduction treatments, showing that a small fraction of Co^{2+} ions can be reversibly oxidized to Co^{3+}, responsible for the change of colour from blue to green. A large fraction of Co^{2+} ions are not oxidized in the employed conditions, in agreement with literature reports. FTIR spectroscopy of adsorbed probe molecules was employed to monitor the surface properties of Co ions. NO adsorption resulted in the formation of two stable $Co^{2+}(NO)_2$ complexes (bands at 1890/1812 cm^{-1} and at 1880/1798 cm^{-1}), assigned to two unoxidized framework Co^{2+} with an adjacent oxygen vacancy. A labile $Co^{2+}(NO)$ adduct adsorbing at 1845 cm^{-1} could be assigned to Co^{2+} ions on small extraframework clusters. CO adsorption confirmed the presence of defective Co^{2+} ions with strong Lewis character that could not be oxidized in the present conditions. Upon reduction, highly dispersed Co^0 clusters were formed within the microporous channels. In the presence of CO, surface Co^0 atoms were extracted from the clusters to form volatile $Co^0(CO)_n$ ($n = 2$ or 4) complexes and bridged $(Co^0)_n(CO)$ species (bands at 2047 and 2008/1990 cm^{-1}, respectively). These results show that the insertion of heteroatoms in large pore AFI structure is strongly sensitive upon the synthetic conditions and metal loading, that have to be carefully tuned to get the desired catalytically active sites.

1. Introduction

The discovery of microporous aluminophosphates (AlPOs), the first family of framework oxide molecular sieves synthesized without silica [1], improves the current application areas of microporous system in catalysis [2] and material science [3]. The AlPOs framework is neutral, being composed of alternating AlO_4 and PO_4 tetrahedral units, but can be functionalized with redox (and Brønsted) sites by isomorphous substitution of transition metal ions. The resulting Me-APOs materials showed promising applications in selective oxidation of hydrocarbons by molecular oxygen [4]. CoAPOs are definitely the most studied systems, as testified by the large number of different AlPO structures where the insertion of cobalt in framework positions has been claimed [5].

The one-dimensional AlPO-5 framework (AFI structure) in CoAPO-5 catalyst, consists of a unique structure with no zeolite analogue, mainly composed of 4-, 6- and 12-ring straight channels which are interconnected by 6-ring windows. The main channels are nearly circular with a free diameter of 7.3 Å. CoAPO-5 catalysts were found to be active in many reactions involving large molecules, like the selective oxidation of cyclohexane [6–9], the oxidative dehydrogenation of ethane under oxygen [6] and the autoxidation of p-cresol to p-hydroxybenzaldehyde [10]. The structure of Co ions in CoAPO-5 has been the subject of a lively debate about the structure of Co ions inserted during the synthesis, as summarized in a concise paper by Thomson et al. [11].

Briefly, it has been proposed that Co^{2+} ions, as observed in other structures (CoAPO-18, 36, etc.), could be incorporated in tetrahedral framework positions forming Co(OH)P Brønsted groups, where they can be involved in reversible redox cycles (Scheme 1) [12–14]. This redox behavior, at the basis of the catalytic activity of CoAPO-5, was evidenced by changes in the EXAFS/XANES spectra [14]. The Co^{3+}/Co^{2+} redox cycles summarized in Scheme 1 was also employed to explain the changes in the colour of the samples and in their UV–Vis spectra upon oxidation/reduction cycles and molecules adsorption [5,15]. However, the EPR work by Krushev et al. [16], could not provide any evidence for the oxidation of framework Co^{2+} during calcination. The authors suggested that the changes in colour (and in the UV–Vis spectra) had to be interpreted with the distortion of the tetrahedral local symmetry of the cobalt ions to dihedral, caused by the adsorption of two oxygen molecules (Scheme 2) [16]. Similar results were then reported by other authors with different techniques [11,17,18]. These authors mainly agreed that the a large fraction of framework Co^{2+} ions in CoAPO-5 cannot be oxidized to Co^{3+}, and that some extra-framework cobalt species could be responsible for the reaction with hydrogen, oxygen and alcohols.

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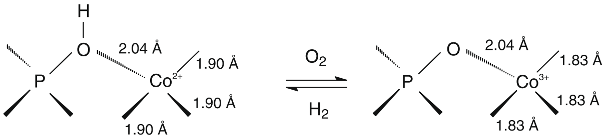
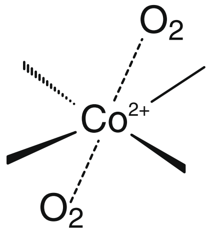
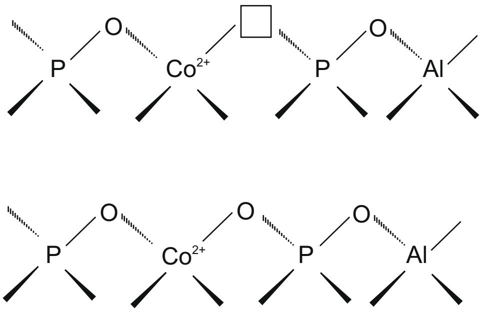


Scheme 1. Reversible redox cycle of (distorted) tetrahedral Co ions. Bond distances estimated by EXAFS in CoAlPO-18 [14].



Scheme 2. Dihedral symmetry of framework Co^{2+} ions in interaction with two oxygen molecules, as proposed by Kurshev et al. [16].



Scheme 3. Structure of unoxidized framework Co^{2+} ions, with an adjacent oxygen vacancy for every two Co^{2+} sites [14].

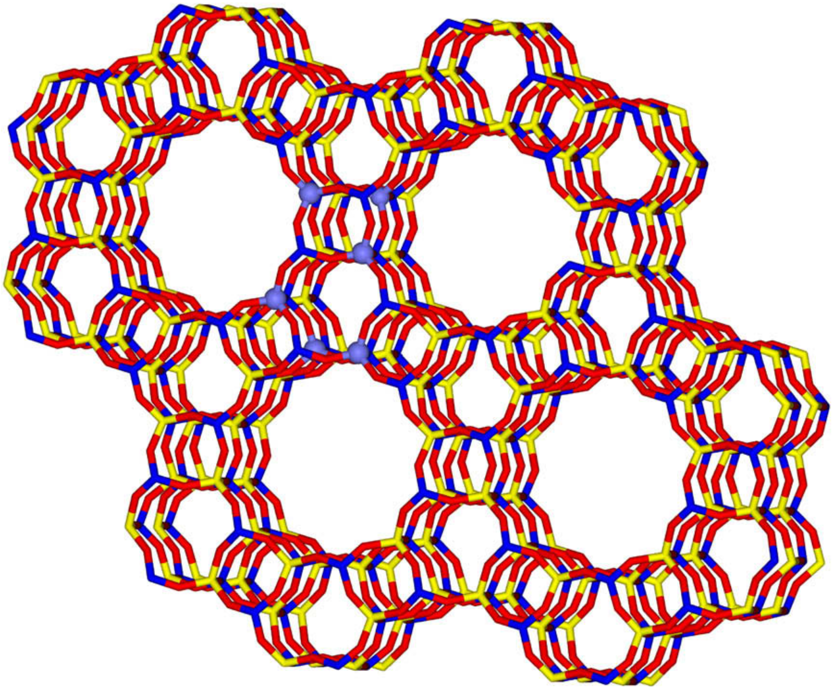
More insight about the nature of Co ions in CoAPO-5 came from the work of Barrett et al. [14]. On the basis of their EXAFS data the authors suggested that, together with a fraction of framework Co ions as in Scheme 1, unoxidized framework sites with an adjacent oxygen anion vacancy (Scheme 3) could be present. One oxygen vacancy occupying a site adjacent to a cobalt ion was supposed to be formed for every two Co^{2+} species, giving the structures reported in Scheme 3. Among the many papers on the subject, we recall the interesting work of Breukelen et al. [19], based on ^{31}P MAS NMR measurements. These authors showed that in their CoAPO-5 sample, Co ions in framework positions are not randomly distributed, but form Co–O–P–O–Co clusters consisting of five or six cobalt atoms. A schematic representation of one of these framework Co clusters is reported in Scheme 4, where the one-dimensional channels of CoAPO-5 can be appreciated.

In this work, a CoAPO-5 sample was synthesized and characterized by structural (XRD, BET, TEM) and spectroscopic techniques (Diffuse Reflectance UV–Vis and FTIR). Our results support the general picture that a large fraction of framework Co^{2+} ions in CoAlPO-5 cannot be oxidized to Co^{3+}. The use of CO and NO as probe molecules allowed us to monitor the presence of framework Co^{2+} in defective tetrahedral coordination in both the oxidized and reduced samples. Upon reduction in hydrogen, small Co^0 clusters were also observed, that could be reversibly oxidized to some Co-oxo particles. The nature of these particles was investigated by following their evolution with the treatment temperature and by the use of $^{13}CO/^{12}CO$ isotopic mixtures. To our knowledge this is the first report about the formation of metallic Co particles of controlled dimension inside the AlPO structure.

2. Experimental section

2.1. Catalyst preparation

CoAPO-5 was prepared following the procedure described in the literature [1,20], slightly modified according to Elangovan



Scheme 4. Schematic representation of CoAPO-5 structure with a framework cluster of Co cations as proposed in Ref. [19]. Blue, yellow and red sticks are for P, Al and O atoms, respectively; light blue spheres represent Co cations.