

Following the Formation of Active Co(III) Sites in Cobalt Substituted Aluminophosphates Catalysts by *In-Situ* Combined UV-VIS/XAFS/XRD Technique

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Abstract. Cobalt substituted aluminophosphates, CoAlPO-34 (Chabazite structure) and DAF-8 (Phillipsite structure) were investigated by *in situ* combined XRD/EXAFS/UV-VIS technique. *In-situ* combined XRD, Co K-edge EXAFS and UV-Vis measurements carried out during the calcination process reveal that CoAlPO-34 containing 10 wt percent cobalt is stable and the cobalt ions are converted from Co(II) in the as synthesised form to Co(III); DAF-8 containing about 25 percent cobalt is not stable and does not show change in oxidation state.

Keywords: EXAFS, XANES, XRD, Combined XRD/EXAFS/UV-VIS, Catalyst, microporous, CoAlPO.

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INTRODUCTION

Transition metal ions substituted aluminophosphates have attracted considerable attention over the years due to their unique catalytic properties of oxidising organic molecules in the presence of molecular oxygen under moderate temperatures and pressures [1]. Among them, cobalt substituted aluminophosphate (CoAlPO) materials were the most extensively studied by X-ray absorption, UV-VIS and IR spectroscopies; iron, manganese and vanadium substituted materials were also investigated by X-ray absorption spectroscopy [1-8]. Although these microporous materials are highly crystalline solids, only small amounts of Co(II) ions (less than 10 percent) are substituted in place Al(III) to maintain stability of the microporous system, since high cobalt containing materials lose its crystallinity and become dense materials during the calcinations process to remove the organic template, which is used to produce these solids[9]. Because of the low concentration of hetero-atom (cobalt in this case) and random substitution of these metal ions, X-ray diffraction studies are not able to provide adequate information to ascertain the local structure of cobalt which is critical for the determination of structure - catalytic function relationships[10-12]. However, X-ray absorption spectroscopy (both near edge and

extended fine structure) has been found to be the appropriate technique to determine the local structure around cobalt ions. Similarly, UV-VIS spectroscopy has been used extensively to determine the oxidation state of cobalt ions in both as-synthesised and activated (calcined) state [2,4,6,7,13]. Despite these independent efforts there are some controversies about the oxidation state of cobalt ions in the activated state. We developed an *in situ* cell that has the facility to measure X-ray absorption spectrum (XAS) in both fluorescence and transmission mode, X-ray diffraction (XRD) data using a position sensitive detector[14] and UV-VIS spectrum; XAS and diffraction are measured sequentially while the UV-VIS measurements are carried out continuously during the X-ray measurements. Here we show the power of this combined technique by investigating the changes that takes place during the activation of two cobalt containing aluminophosphates materials, CoAlPO-34 and DAF-8.

EXPERIMENTAL

CoAlPO-34 and DAF-8 were prepared by hydrothermal synthesis and the details are given elsewhere[9,15].

In-situ time-resolved XRD/EXAFS/UV-VIS data were collected at station 9.3 of the Daresbury

Laboratory, which operates at 2 GeV with a typical current of 120 to 200 mA[10-12]. In a typical experiment, 100 mg of the sample was pressed into a disc and loaded into the *in situ* cell. XRD and XAS (transmission mode) data were collected sequentially during the entire calcination process. 180 seconds and 372 seconds were used for measuring XRD and Co K-edge XAS data, respectively. UV-VIS spectra were recorded during the course of this calcinations procedure using a portable spectrometer connected through a fiber optic probe. The sample was heated, in flow of air, at a rate of 5°C/minute. XRD data were collected at a wavelength of 1.6393Å. XAS data were processed using the programs available at the Daresbury Laboratory, namely EXCALIB, EXBROOK and EXCURV98.

RESULTS AND DISCUSSION

In-situ combined XRD/XAS study were carried out on CoAlPO-34 and DAF-8 materials to investigate the stability of the microporous framework structure and the redox chemistry associated with the cobalt ions when heated in oxygen. Stacked XRD and Co K-edge XAS data and UV-VIS spectra obtained from the combined experiment of CoAlPO-34 are shown in Figure 2. Although there are changes in intensity of the reflections in the XRD data, which is probably due to the removal the organic present in side the pores, the presence of all the reflections suggest the microporous structure is stable upon removal of the organic template. Co K-edge XANES also shows changes during the calcination, in particular a small shift in the edge position to a higher value, suggesting a change in oxidation state. UV-VIS spectra of the starting material shows three characteristic bands at 565, 590 and 630 nm which are typical for Co(II) ions present in tetrahedral coordination. Upon heating, the spectral features undergo number of changes and consistent with the formation of Co(III) ions .

Although the interpretation of the X-ray diffraction data, in particular, following the structural stability and phase identification is relatively straight forward, interpretation of EXAFS data, recorded at various temperatures during the heat treatment process, requires accurate determination of the structural parameters such as coordination number, bond distance and Debye-Waller (DW) factors at different temperatures. To do so, it was essential to study a model system which has similar local structural characteristics to that of the materials under investigation. We employed CoAl₂O₄ as the standard, since in this material Co(II) ions are present in a tetrahedral environment[9] and the spinel phase remains unaltered at temperatures *ca* 600°C. Here, we have focused our attention on the Co-O distances,

since this is the most accurate parameter that can be determined from EXAFS and furthermore the bond distances are sensitive to both coordination geometry and oxidation state and thus will allow us to determine the nature of cobalt species present in the catalyst.

In Figure 2 we show the variation in Co-O distance (top) and Debye-Waller factor (bottom) as a function

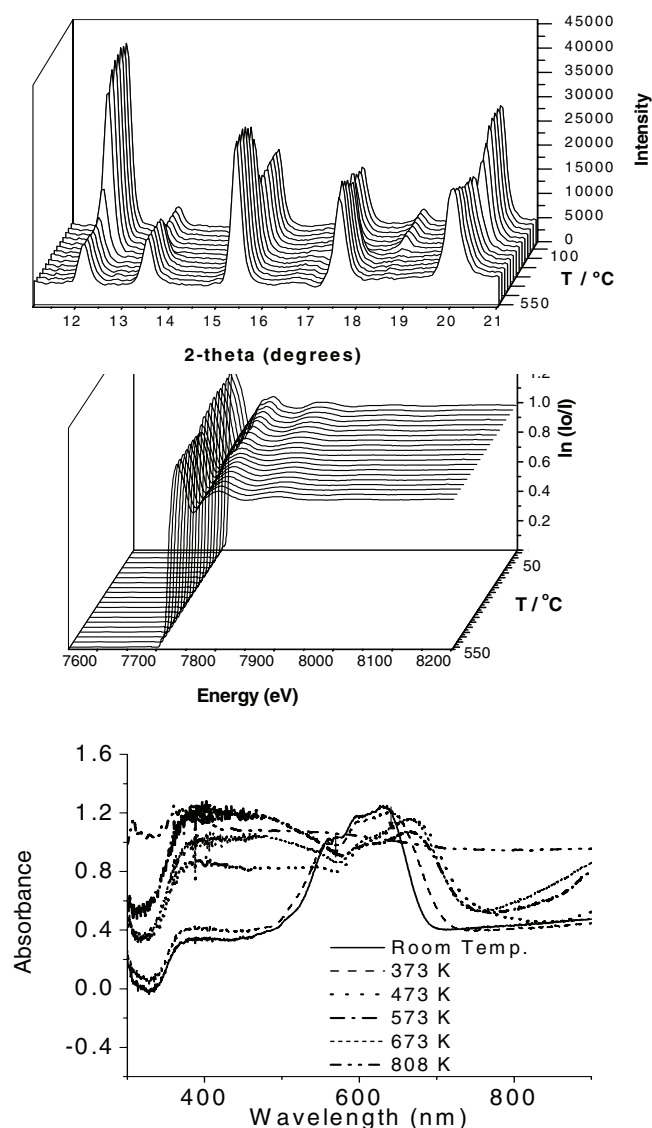


FIGURE 1. XRD (top), Co K-edge XAS (middle) and selected UV-VIS (bottom) spectra recorded during the calcination of CoAlPO-34 catalyst.

of temperature, obtained from the detailed analysis of the Co K-edge EXAFS of CoAlPO-34 and DAF-8 samples. Comparison of the variation in Co-O inter-atomic distance of CoAlPO-34 with CoAl₂O₄ clearly suggest that the decrease in Co-O distance, at high temperatures, of CoAlPO-34 is due to change in oxidation state from Co(II) to Co(III). This change is

consistent with the changes observed in the UV-VIS spectra of microporous CoAlPO-34 that Co(II) ions present in the as-synthesised material are oxidised to Co(III) during the calcination processes. On the other hand DAF-8 which has large amounts of cobalt present in the material shows increase in Co-O distance during calcination process. The change in distance from 1.94Å to higher value for DAF-8 occurs at *ca* 350°C which coincides with the loss in crystallinity seen in the diffraction data [15]. Assuming that the variation in the Debye-Waller (DW) factor for CoAl₂O₄ represents the change in the dynamic disorder, we compare the results of CoAlPO-34 and

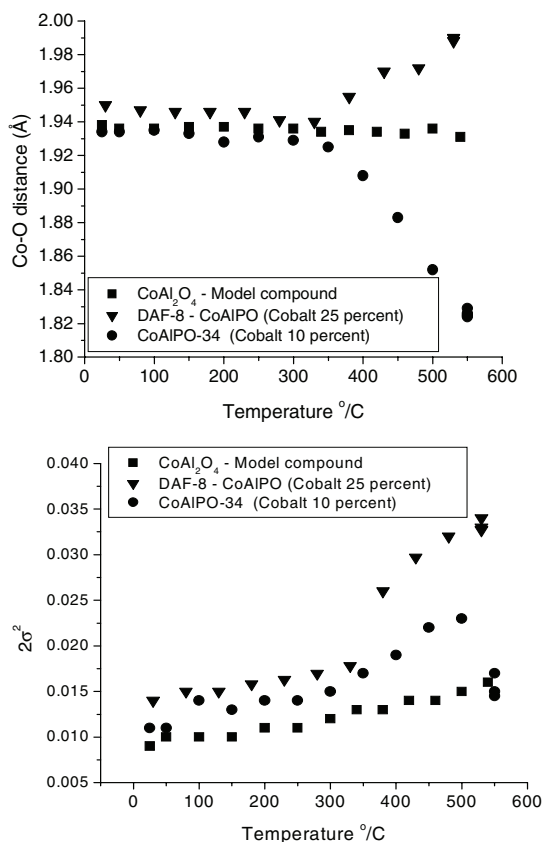


FIGURE 2. Variation in Co-O distance (top) and the corresponding Debye-Waller factor (bottom) with temperature obtained from the analysis of the Co K-edge EXAFS data

DAF-8 system. Above 350°C, there is a sudden change in the DW for both DAF8 and CoAlPO-34 samples indicating an increase in static disorder; changes in DW for DAF8 is much larger compared to the one observed for CoAlPO-34. This change for DAF-8 coincides with the loss in crystallinity[15]. The stable CoAlPO-34 material shows gradual change in DW with temperature and there is a sudden decrease

in its value which coincides with the decrease in Co-O bond distance (see Figure 2). This decrease in DW may be associated with the presence of shorter bond distance.

In summary we have been able to use the combined XRD/EXAFS/UV-VIS technique to follow the changes in both over all structure of microporous cobalt substituted aluminophosphates and oxidation state of cobalt ions. This technique will provide unique information on other transition metal ions containing materials.

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