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G. Sankar, J. Thomas, G. Greaves, A. Dent. In Situ Studies of Zeotype Materials Under Operating Conditions. Journal de Physique IV Proceedings, 1997, 7 (C2), pp.C2-871-C2-873. 10.1051/jp4:1997262 . jpa-00255345

HAL Id: jpa-00255345

<https://hal.science/jpa-00255345>

Submitted on 1 Jan 1997

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In Situ Studies of Zeotype Materials Under Operating Conditions

G. Sankar, J.M. Thomas, G.N. Greaves* and A.J. Dent*

Davy Faraday Research Laboratory, The Royal Institution of GB, 21 Albemarle Street, London W1X 4BS, UK

CCLRC, Daresbury Laboratory, Daresbury, Warrington Cheshire WA4 4AD, UK

Abstract. The power of *in situ* combined XRD/XAS technique in tracking the formation of microporous solid acid catalyst and the generation of active sites particularly by taking examples of cobalt substituted aluminophosphates is demonstrated.

1. INTRODUCTION

Heterovalent ions substituted aluminophosphates (divalent in place of Al^{3+} or tetravalent for P^{5+}) or trivalent (for eg. Al^{3+} or Fe^{3+} or Ga^{3+} in place of Si^{4+}) ions in substituted zeolites[1] have been shown to be efficient catalysts for Brønsted acid catalysed reactions. Furthermore, some of the framework-incorporated divalent ions such as Co^{2+} or Mn^{2+} are known to exhibit oxidation-reduction properties thereby introducing a new dimension to the catalytic performance. Although only relatively small amounts of these heterovalent substituents have been achieved (of the order of 2 wt%), they nevertheless produce highly active catalytic centres. Understanding the overall framework structure of these microporous solid acid catalysts on the one hand, and the local structure around the hetero atoms on the other, allows the precise description of these shape selective catalysts. It was demonstrated earlier that the combined use of the XRD/XAS techniques enhances our understanding of the structure of various active catalysts[2-5]. In addition, insights into their stability (retention of microporous structure) and oxidation-reduction properties[6,7] are also gained. Here we show how the combined XRD/XAS permits us to characterise zeotype materials under operating conditions either during hydrothermal synthesis or during the activation of the solid acid catalysts.

1.1 EXPERIMENTAL

In situ combined XRD/XAS measurements were carried out at station 9.3 of Daresbury Laboratory employing a specially designed cell that permits the measurement of fluorescence and transmission EXAFS as well as XRD data. Details of the *in situ* cell and the conditions employed are described elsewhere[6,8]

1.2 RESULTS AND DISCUSSION

Here we show results of the combined XRD/QuEXAFS measurements demonstrating the power of this technique in characterising materials under operating (non-ambient) conditions. For this purpose, we have chosen two examples. First, the crystallisation of microporous CoAlPO-5 catalyst from its nutrient gel—mother liquor[8] and second, the generation of active sites during activation process of a solid acid catalyst, CoAlPO-18[6].

Synthesis of CoAlPO-5: The XRD pattern (figure 1(a)) shows initially a broad hump typical of amorphous nature of the nutrient gel comprised of aluminium hydroxide, phosphoric acid, cobalt acetate and triethylamine (organic template). As the temperature was increased above 170°C reflections associated with the AlPO-5 structure starts to appear indicating the onset of crystallisation. It is rather interesting to see that both the pre-edge and main absorption edge intensities of the cobalt K-edge XANES (shown in figure 1(b)) change just prior to crystallisation. This increase in pre-edge intensity and decrease in main absorption (a well known phenomena in many other systems[9]) reflects the change from octahedral (in the cobalt acetate) to tetrahedral (cobalt after incorporation into the framework) coordination. This is corroborated not only by the colour change from pink to blue, but also from the detailed analysis of the EXAFS data which clearly shows a decrease in both coordination number (6 to 4) and Co-O distance (2.06 Å to 1.93 Å).

Active site generation in CoAlPO-18: In our earlier study, it was pointed out that CoAlPO-18 retains its porous structure (from XRD) as well as undergoes $\text{Co(II)} \rightarrow \text{Co(III)}$ during the calcination (in oxygen) process to remove occluded organic template molecules[6]. In addition, a closer look at the change in average Co-O distance at different temperatures (see figure 2a), in particular around 350°C reveals that there is an initial decrease from 1.93 Å to 1.90 Å and subsequently above 500°C it

Figure 1. (a) XRD and (b) Co K-edge XANES patterns recorded sequentially employing the experimental arrangement shown in ref 9.

attains a value of $\text{ca } 1.83\text{\AA}$. However, the edge position (scale on the right hand side of the figure) was unchanged (like that of the starting material) until 500°C , above which there is a distinct positive shift, reflecting an increase in oxidation state of cobalt. Thus the intermediate regime where a slight decrease in Co-O distance around the Co(II) ions is due to the collapse of

Figure 2. Variation of the average Co-O distance (filled circles) and Co K-edge position (open squares) Vs the calcination (in oxygen to remove occluded template) temperature are shown on the left. On the right, schematic representation of the local structure around cobalt (derived from the analysis of the EXAFS data and IR studies, measured during the calcination process) corresponding to the three regions denoted (a), (b) and (c) on the left of this figure.

charge compensating template leading to protonation (to compensate the negative framework charge which is well supported by the appearance of OH stretching band associated with Bronsted acid site in the IR spectrum) of the bridging oxygen (Co-O-P) prior to the complete removal the organic template and subsequent conversion of Co(II) to Co(III) above 500°C . This protonated Bronsted acid sites are shown to possess a distorted tetrahedra with the dominant Co-O distance at $\text{ca } 1.90\text{\AA}$ [10] and the derived structural parameters are found to be identical to that of the one obtained after reduction in hydrogen[6].

Acknowledgements

We thank EPSRC for financial support and CCLRC for the provision of facilities at Daresbury Laboratory

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