A study of Co/Mo/Al₂O₃ hydrodesulphurization catalysts and related model compounds by XPS and x-ray absorption spectroscopy (XANES and EXAFS)

G SANKAR, P R SARODE, A SRINIVASAN, C N R RAO*, S VASUDEVAN† and J M THOMAS‡*

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India
† Department of Physical Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EP, U.K.

Abstract. A detailed investigation of sulphided Co/Mo/Al₂O₃ catalysts, their oxide precursors and several model oxides and sulphides of cobalt and molybdenum has been carried out using x-ray photoelectron spectroscopy and x-ray absorption spectroscopy (XANES and EXAFS). Octahedrally coordinated Co(II) and Mo(IV) are shown to be present in a sulphidic environment on the surfaces of these catalysts. The surface species contain an excess of sulphur, probably involving disulphide linkages. The surface compositions of the catalysts examined conform to the general formula CoₓMoᵧ₂ (2n + 3) S₂²⁻ (2n - 2)S³⁻.

Keywords. Hydrodesulphurization; cobalt-molybdenum catalysts; EXAFS; XANES.

1. Introduction

Cobalt-molybdenum catalysts, widely used commercially for the hydrodesulphurization of petroleum feedstocks, are nominally composed of cobalt oxide (CoO) in the concentration range of 3–5% and molybdenum oxide (MoO₃) in the range of 12–15% and are usually supported on alumina. The concentration ranges of Co and Mo in these catalysts make it possible to examine them under non-reactor conditions by x-ray photoelectron spectroscopy (XPS), x-ray absorption spectroscopy and a variety of other techniques (Thomas and Lambert 1980). Structural chemistry of these catalysts has been investigated by a number of workers (Ratnaswamy and Sivasankar 1980). Despite several investigations, it has not yet been possible to establish the nature of the active sites in these catalysts. At least four distinct models have been proposed hitherto, but none of these is capable of accommodating all the known facts. We therefore embarked on a systematic investigation of the oxide precursors and sulphided catalysts with a range of Co:Mo ratios as well as with several model compounds of cobalt and molybdenum. In order to examine the nature of the Co and Mo species present on the surfaces, we have utilised core-level binding energies of Co and Mo in x-ray photoelectron spectra, chemical shifts of K-absorption edges, spectroscopic transition energies and site-symmetries deduced from x-ray-absorption-near-edge-structure (XANES), as well as bond distances and coordination numbers evaluated from extended-x-ray-absorption-fine-structure (EXAFS).

* To whom all correspondence should be addressed.
2. Experimental

MoO$_3$ was prepared by heating pure ammonium para-molybdate to 723 K for 12 hr. Al$_2$(MoO$_4$)$_3$ was obtained by heating a mixture containing the requisite amount of Al(NO$_3$)$_3$ and ammonium paramolybdate solutions to dryness, grinding them together and then heating the solid mixture to 900 K for 24 hr. CoMoO$_4$ was prepared similarly starting from an aqueous solution mixture of Co(NO$_3$)$_2$ and ammonium para-molybdate. CoAl$_2$O$_4$ was prepared starting from a solution mixture of Co(NO$_3$)$_2$ and Al(NO$_3$)$_3$. Co$_3$O$_4$ was obtained by heating Co(NO$_3$)$_2$ to 1000 K for 24 hr. CoO was prepared by heating Co$_3$O$_4$ at 1200 K in a CO$_2$ atmosphere for 48 hr. CoS and Co$_3$S$_4$ were prepared by heating stoichiometric mixtures of the pure elements inside a sealed tube at high temperatures. Co:MoS$_2$ samples were prepared by the so-called 'co-maceration method' in which MoO$_3$ and Co$_3$O$_4$ were co-digested in an aqueous ammonium sulphide solution for 6 hr at 350 K. The compounds obtained were subsequently heated in a H$_2$S-Ar atmosphere for 6 hr at 650 K. Co/Mo/Al$_2$O$_3$ catalyst precursors were obtained first by impregnating $\gamma$-alumina to pore-volume saturation with ammonium paramolybdate, drying at 400 K, and calcining at 900 K. This binary mixture, with the required proportion of Mo on alumina served as a support for introducing cobalt to different extents by a second pore-volume saturation impregnation step. These Co-Mo catalyst precursors were then dried at 400 K and calcined at 900 K. Sulphidation was carried out by heating the mixed oxide precursors in a stream of nitrogen at 650 K, followed by passing a mixture of H$_2$S and H$_2$ (10:90) over them at a flow rate of 30 ml/min for nearly 12 hr. The resulting sulphided catalysts were cooled to room temperature while the H$_2$S:H$_2$ mixture continued to flow. MoS$_2$ was made from (NH$_4$)$_2$MoS$_4$ by the method of Wildervanck and Jellinek (1964).

X-ray photoelectron spectra were recorded using an ESCA-3 Mark II spectrometer of V.G. Scientific Limited, U.K., fitted with a sample preparation chamber. The operating vacuum was 10$^{-10}$ torr. This chamber was fitted with an argon ion gun and a quadrupole mass spectrometer. The radiation employed was AlK$_{\alpha}$ (1486.6 eV). The spectrometer was calibrated with reference to the binding energy of Au (4f$_{7/2}$) at 83.7 eV. The spectra were analysed in terms of relative intensities (peak areas) and relative changes in binding energies of Mo(3d), Co(2p), S(2p) and Al(2p) lines. Peak separations and satellite structure have also been used in the case of the Co(2p) band. Decomposition of Mo(3d) and Co(2p) bands were attempted assuming the peaks to be gaussian. A bent-crystal spectrograph of diameter 1000 mm with a mica crystal (the 201 planes of which serve as the analyzer) was employed to record x-ray absorption spectra. Sealed x-ray tubes with Cu and Mo targets were used as sources of continuous radiation. Uniform absorbing screens of the compounds were prepared by sandwiching them as fine powders between two thin cellophane adhesive tapes. The energy analysis of the spectra was carried out with the aid of a Carl-Zeiss MD 100 microdensitometer. In order to obtain finer details of the spectra, 200 x magnification scans were taken on the densitometer for each compound. The densitometer plots which represent the transmitted intensity as a function of the energy of the x-ray photon were converted into absorption coefficient vs the energy of the x-ray photon after determining the photodensities. The absorption edge was taken as the inflection point (mid-point of the steeply rising linear part of the plot) on the microdensitometer plots. The uncertainties in the measurements of absorption edge positions were found to be within ±0.5 eV. In order to determine spectroscopic transition energies corresponding to the various