Novel Type of Hydroprocessing Catalysts derived from the Precipitation from Homogeneous Solution (PFHS) Method

Vemulapalli Prasad,[b] Komandur Chary,[a] Kaza Somasekhara Rao,[b] and Panja Kanta Rao*[a]

[a] *Catalysis Section, Indian Institute of Chemical Technology, Hyderabad 500 007, India*
[b] *P.G. Centre, Andhra University, Nuzvid 521 201, India*

Oxygen chemisorption studies were carried out on alumina supported molybdenum sulphide catalysts, prepared by the precipitation from homogeneous solution (PFHS) method in a single step; it is found that oxygen chemisorption of these catalysts correlates with the hydrodesulphurization activity of thiophene.

Hydrotreating of petroleum crudes and coal derived liquids is an important catalytic process in the petroleum and fertilizer industries. The most commonly used hydrotreating catalysts consist of molybdenum promoted with cobalt or nickel supported on a high surface area γ-alumina.[1] The activity of these catalysts mainly depends on the dispersion of the active component which in turn depends on the method of preparation and nature of the support. These catalysts are generally prepared by impregnation of the alumina support using aqueous solutions, which contain ammonium molybdate and nitrates of cobalt or nickel, followed by calcination in air at higher temperature (~500 °C). The calcined oxide precursors are then converted into the active sulphide state. However, this interconversion of the oxidic phase into the sulphide phase is not complete. The precipitation from homogeneous solution (PFHS) method has been identified as a good means of making better controlled catalysts with respect to crystallite size, surface area, pore structure, uniform composition, and high dispersion of metals on supported catalysts.[2—6] With this background, a study has been undertaken to prepare better hydrotreating catalysts *via* the PFHS method.

Over the last decade low temperature oxygen chemisorption (LTOC) has provided quantitative information about the dispersion of molybdenum sulphide/oxide in supported catalysts.[7—12] This method has proved to be a promising surface specific probe for the characterization of Mo-containing hydroprocessing catalysts. Attempts have been made to correlate oxygen chemisorption capacities of supported molybdena catalysts with hydrodesulphurization activities of sulphur containing aromatics. In this communication we report for the first time the results of oxygen chemisorption and hydrodesulphurization activities towards thiophene by a series of MoS_2 catalysts prepared by the PFHS method.

The MoS_2/γ-Al_2O_3 catalysts with various molybdenum loadings were prepared by the PFHS method using thioacetamide as the precipitating agent. In a typical experiment γ-Al_2O_3 (Harshaw Al-111-61E; S.A., 234 m^2 g^{-1}; P.V. 0.65 ml g^{-1}) was suspended in a solution containing the required amounts of ammonium molybdate, thioacetamide, and nitric acid. The resulting mixture was heated to 90—95 °C with constant stirring to precipitate MoS_2 onto the γ-Al_2O_3 support. After the preparation was completed (pH 2—3), the resulting solids were filtered, washed, and dried at 110 °C.

Oxygen chemisorption (at −78 °C) experiments were performed on these catalysts using a static high vacuum adsorption unit following the method of Parekh and Weller.[8] Prior to the oxygen chemisorption, the samples were evacuated at 400 °C for several hours at 10^{-6} torr (1 Torr = 133.322 Pa) in order to clean the catalyst surface. The details of experimental procedure are described elsewhere.[13] Activity measurements for hydrodesulphurization (HDS) of thiophene were carried out at 400 °C in a continuous flow-micro reactor operating at atmospheric pressure and under differential conditions. The reaction products *i.e.*, butene and butane were analysed by an on-line gas chromatograph sensed by a flame ionization detector.

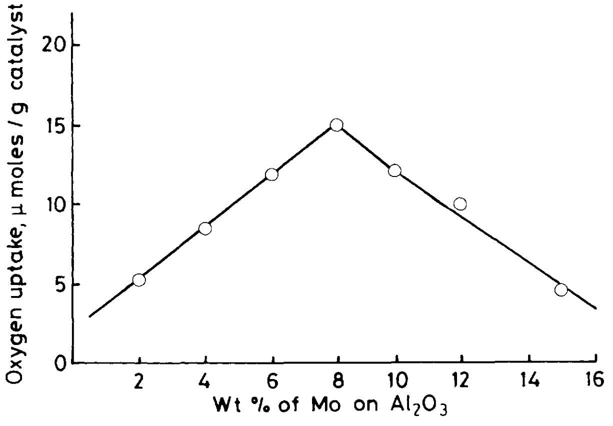

Figure 1. Oxygen uptake at −78 °C as a function of Mo loading on γ-Al_2O_3.

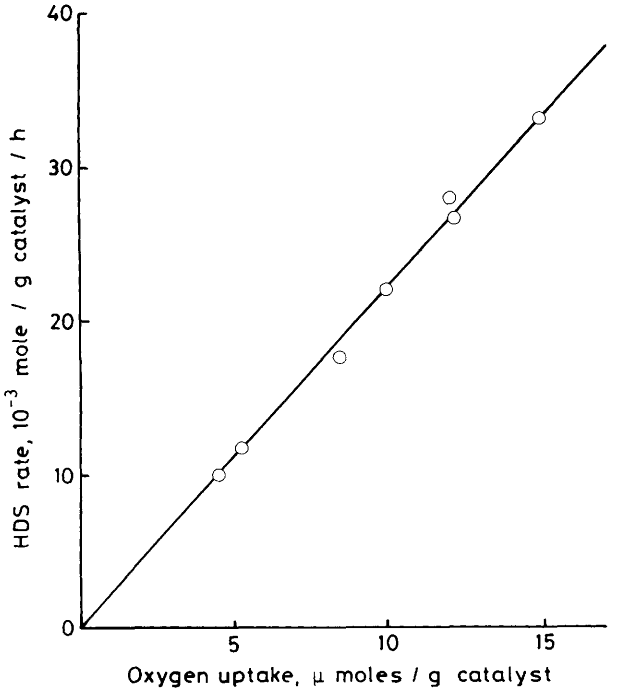

Figure 2. HDS activity of thiophene with various catalysts at 400 °C plotted as a function of oxygen uptake.

The oxygen chemisorption capacities of various MoS_2/γ-Al_2O_3 catalysts have been plotted as a function of Mo loading in Figure 1. It is observed that oxygen chemisorption increases linearly as a function of Mo loading up to 8% (w/w) and then decreases with higher Mo content. This 8% (w/w) level corresponds to the attainment of a monolayer of MoS_2 on the alumina surface. The dispersion of MoS_2 (O/Mo × 100) derived from oxygen chemisorption results for monolayer catalyst is found to be 0.036. The monolayer formation of MoS_2 catalysts, prepared from impregnation of the γ-Al_2O_3 support using an aqueous solution of ammonium heptamolybdate, is also observed at 8% of Mo (w/w).[10] The monotonic decrease of oxygen chemisorption capacities of the catalysts beyond the monolayer composition might be due to the presence of MoS_2 crystallites of larger size on the alumina surface. However, *X*-ray diffraction (XRD) results indicated that MoS_2 is present in a highly dispersed or an amorphous state on the alumina surface. In this study no XRD peaks corresponding to MoS_2 were observed even at the highest concentration of molybdenum. It is generally accepted that co-ordinatively unsaturated sites (CUS) on partially reduced/sulphided Mo/Al_2O_3 catalysts are the active sites responsible for hydrogenolysis and hydrogenation reactions. Oxygen selectively chemisorbs dissociatively on these sites at −78 °C and offers quantitative information about them. These CUS are located on the MoS_2 phase as a patchy-monolayer on the surface of the γ-Al_2O_3 support.[7]

HDS activity of thiophene at 400 °C for various catalysts has been plotted as a function of oxygen uptake in Figure 2. There is a direct correlation between oxygen chemisorption capacities of the catalysts and HDS activity of thiophene. The activity of monolayer catalyst [8% (w/w) of Mo] is found to be higher than the other catalysts. The linear correlation between oxygen chemisorption and HDS activity suggests that the MoS_2 phase contains CUS on the patchy-monolayer phase and these are the sites responsible for HDS of thiophene which were measured by oxygen chemisorption. The HDS activity of thiophene by MoS_2 catalysts prepared by the PFHS method is found to be higher than on those prepared by conventional routes.[10,11]

Thus PFHS is found to be a novel method for preparing highly active hydroprocessing catalysts containing MoS_2 supported on γ-Al_2O_3.

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