

## The Effect of Molybdenum Precursor on the Dispersion and Hydrodeoxygenation Activity of Mo/Al<sub>2</sub>O<sub>3</sub> Catalysts

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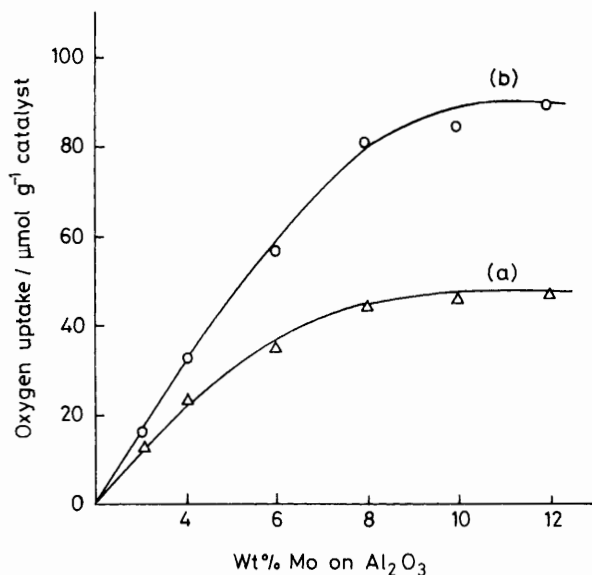
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Oxygen chemisorption at  $-78^{\circ}\text{C}$  has been measured on the reduced surface of Mo/Al<sub>2</sub>O<sub>3</sub> catalysts prepared from two different precursors of molybdena and it is found that Mo-oxide shows better dispersion and activity when the precursor used is an organometallic compound.

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Among the hydroprocessing reactions, catalytic hydrodeoxygenation (HDO) is receiving<sup>1-3</sup> increased attention owing to the presence of organo-oxygen compounds in coal derived liquids, shale oil, and petroleum feed stocks. Removal of reactive oxygen containing species is essential in order to

stabilize the commercial fuels obtained from synthetic crudes. Sulphided catalysts of molybdenum/tungsten promoted with cobalt/nickel are found to be generally employed for this process and in many cases these catalysts are prepared from conventional inorganic salts. Yermakov<sup>4</sup> has shown that

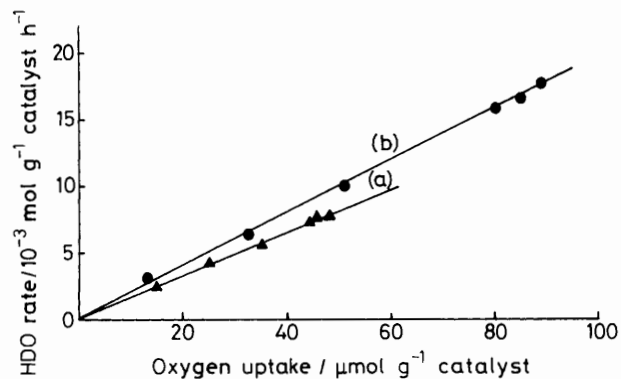


**Figure 1.** Oxygen uptake as a function of Mo loading. (a)  $\Delta$  catalysts prepared from ammonium heptamolybdate; (b)  $\circ$  catalysts prepared from molybdenum acetylacetonate.

organometallic compounds can be adsorbed in a well dispersed fashion on oxide supports. Metal acetylacetonates exhibit some of the properties of organometallic compounds. During the past decade, low temperature oxygen chemisorption (L.T.O.C.) has been applied successfully<sup>5-9</sup> to provide quantitative information about the dispersion of molybdena in supported catalysts. This technique 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 these catalysts with hydrodesulphurization (HDS) activities of sulphur containing aromatics. However, as yet there is no report relating the oxygen chemisorption sites with catalytic activity for hydrodeoxygenation using  $\text{MoO}_3/\text{Al}_2\text{O}_3$  catalysts. Although it is not proven that HDO takes place on the same sites as HDS, it is generally believed that HDO takes place on similar sites.<sup>1,11</sup> In the present Communication a correlation is shown between oxygen chemisorption capacities of the catalysts and the activities towards HDO of furan. A comparison is also made with the catalysts prepared from two different precursors of molybdena (molybdenum acetylacetonate and ammonium heptamolybdate) with respect to their activity and dispersion. The HDS activities of thiophene by these catalysts correlates linearly with oxygen chemisorption up to a certain level of Mo loading (corresponds to 8% Mo w/w) and levels off at higher Mo-loadings.

Two series of  $\text{Mo}/\text{Al}_2\text{O}_3$  catalysts with Mo loadings ranging from 2 to 12% of Mo (w/w) were prepared by different precursors of molybdena. In the first series, the catalysts were prepared by incipient wetting of an  $\gamma\text{-Al}_2\text{O}_3$  support using an aqueous solution containing ammonium heptamolybdate. In the second series, the  $\text{Mo}/\text{Al}_2\text{O}_3$  catalysts were prepared by impregnation of an  $\text{Al}_2\text{O}_3$  support with an ethanolic solution containing molybdenum acetylacetonate. The solvent was slowly evaporated off. In both series, the catalysts were subsequently dried and calcined at 540 °C for 16 h.

Oxygen chemisorption experiments were performed on pre-reduced catalysts using a static high vacuum adsorption unit following the method of Parekh and Weller.<sup>6</sup> The details



**Figure 2.** HDO activity at 400 °C of various catalysts plotted as a function of oxygen uptake. (a)  $\blacktriangle$  catalysts prepared from ammonium heptamolybdate; (b)  $\bullet$  catalysts prepared from molybdenum acetylacetonate.

of the experimental procedure are described elsewhere.<sup>10</sup> Activity measurements for HDO of furan were carried out at 400 °C on presulphided catalysts in a continuous flow micro-reactor operating at atmospheric pressure under differential conditions. The reaction products were analysed by an on-line gas chromatograph with a flame ionization detector.

The oxygen chemisorption capacities of the catalysts prepared from two different precursors of molybdena have been plotted as a function of Mo loading in Figure 1. The uptake of oxygen increases as a function of Mo-loading up to 8% w/w and then tends to level off. This levelling corresponds to the attainment of a monolayer of Mo-oxide on the alumina surface. The oxygen chemisorption capacities of the catalysts derived from the organometallic compounds (acetylacetonates) are much higher than those derived from conventional inorganic salts. This indicates that molybdenum oxide disperses better on an alumina surface when the catalysts were synthesized from an organometallic precursor. However, the monolayer composition (8% w/w) is not affected by the Mo-precursor. The dispersion of molybdena ( $\text{O}/\text{Mo} \times 100$ ) calculated from oxygen chemisorption for monolayer catalysts (corresponds to 8% w/w), prepared from the two precursors, *i.e.* ammonium heptamolybdate and molybdenum acetylacetonates was 0.106 and 0.192 respectively. The X-ray diffraction results of these catalysts indicate that Mo-oxide is present in a highly dispersed amorphous state on the alumina surface. It is generally accepted that co-ordinatively unsaturated sites (C.U.S.) on partially reduced  $\text{Mo}/\text{Al}_2\text{O}_3$  catalysts are the active sites responsible for hydrogenation and hydrogenolysis reactions. Oxygen selectively chemisorbs dissociatively on these sites at -78 °C and offers quantitative information about them. The C.U.S. are located on the  $\text{MoO}_2$  phase as a 'patchy-monolayer' on the surface of alumina.<sup>7,12</sup>

HDO activity of furan for various catalysts has been plotted as a function of oxygen uptake in Figure 2. There is a good correlation between oxygen chemisorption capacities of the catalysts and HDO activity. The activities of the catalysts increase with oxygen chemisorption and do not change much at higher Mo contents. The HDO activities of the catalysts derived from organometallic precursors were found to be twice that of those derived from inorganic salts. The linear correlation in Figure 2 suggests that  $\text{MoO}_2$  contains C.U.S. on the 'patchy-monolayer' phase and these are the sites responsible for HDO of furan and are titratable by L.T.O.C.

Thus the catalysts derived from organometallic compounds were found to show better dispersion and activity than those derived from conventional inorganic salts.

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