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Letter

The effect of molybdenum precursor on the dispersion and hydrodesulfurization activity of carbon-supported sulfide catalysts*

K. V. R. Chary, H. Ramakrishna and G. Murali Dhar**
Catalysis Section, Indian Institute of Chemical Technology, Hyderabad 500 007 (India)

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Introduction

Hydrodesulfurization (HDS) of sulfur-containing compounds is of considerable importance in petroleum refining and upgrading of coal-derived liquids [1–4]. The typical catalysts employed are molybdenum disulfide and tungsten disulfide promoted with cobalt or nickel, supported on high surface area alumina. One area of research which has received much attention in recent years is carbon-supported hydrodesulfurization catalysts [5–10]. They are found to show better catalytic activity towards hydrodesulfurization than the conventional alumina-supported hydrotreating catalysts in laboratory tests. However, on employing actual feed stocks at high pressures, carbon-supported catalysts show rapid deactivation. The advantages of using carbon as a support have been emphasized by de Beer's group [5–9] and Abotsi and Scaroni [10]. Carbon has several attractive characteristics as catalyst support, which include high surface area, low cost and the possibility of recovering metals from the spent catalysts. Another advantage is that carbon has weak adsorption affinity for aromatics and nitrogen-containing compounds, therefore these catalysts must be less susceptible to poisoning and fouling than the alumina-supported catalysts that are presently employed.

Of late, metal acetylacetonate complexes supported on inorganic materials have been employed as catalysts for various reactions [11–14]. In the present communication, we report the effect of molybdenum acetylacetonate precursor on dispersion and activity for HDS on molybdenum sulfide supported on carbon. For comparison purposes, results on ammonium molybdate-derived Mo/C are also included.

Experimental

Two series of Mo catalysts with molybdenum loading ranging from 2–12% Mo (w/w) are prepared using different precursors of molybdenum. In the

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**Author to whom correspondence should be addressed.

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first series, the catalysts were prepared by incipient wetness impregnation of the carbon support (Lurgi 1160 $m^2 g^{-1}$, P.V. 1.2 ml g^{-1}) with aqueous solutions containing ammonium molybdate (pH 9). In the second series, Mo/C catalysts were prepared by impregnating an ethanolic solution containing molybdenum acetylacetonate. The solvent was evaporated on a water bath. In both series the catalyst samples were dried at 110 °C for 16 h. The catalysts from both series were sulfided using CS_2/H_2 mixture (30 ml min^{-1}) at 400 °C for 2 h before thiophene hydrogenolysis reaction and oxygen chemisorption.

Oxygen chemisorption experiments were performed on presulfided catalysts using a static high vacuum volumetric adsorption unit, following the method of Parekh and Weller [15]. The details of experimental procedures have been described elsewhere [16]. The activity measurements for HDS of thiophene were carried out at 400 °C on presulfided catalysts in a continuous flow microreactor operating at atmospheric pressure under differential conditions. The reaction products were analysed by on-line gas chromatography using a flame ionisation detector.

Results and discussion

The oxygen chemisorption capacities of the catalysts prepared from two different precursors of molybdena have been plotted as a function of loading in Fig. 1. The oxygen uptake increases linearly up to the highest loading (12 wt.%) used in this investigation. The oxygen uptakes of acetylacetonate

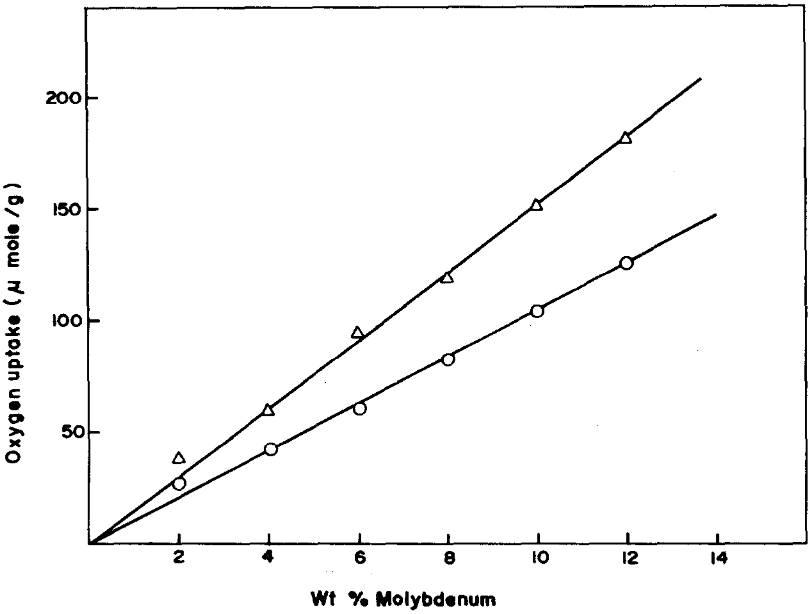

Fig. 1. Oxygen uptake as a function of molybdenum loading; (△) acetylacetonate, (○) ammonium molybdate.

precursor-derived catalysts are consistantly higher than those of catalysts prepared using ammonium molybdate solution. The oxygen uptake capacities are reported by Zmierczak *et al.* [17] to be related to the general state of dispersion of the molybdenum phase. De Beer's group [7] from their studies on Mo/C concluded that the oxygen uptake measures a property related to the active surface area of the molybdena. Therefore, the increase in oxygen uptakes reported in this investigation on acetylacetonate-derived catalysts indicate an increase in surface area of molybdena. Based on this consideration, it can be concluded that the dispersion of acetylacetonate-derived catalysts is higher than the ammonium molybdate-derived catalysts.

The thiophene HDS rate is presented in Fig. 2 as a function of molybdenum loading. It can be observed that in both cases the thiophene HDS rate increases linearly up to the highest loading studied. In the case of acetylacetonates, however, the point corresponding to 12 wt.% deviates from the trend. The thiophene HDS rates are consistently higher for the acetylacetonate-derived catalysts compared to those prepared using ammonium molybdate. To clarify further, we have calculated quasi-turnover frequencies (QTOF) (*i.e.* the thiophene converted per mol molybdenum per hour) which are plotted in Fig. 3 as a function of loading. It can be noted that the QTOF are higher for the acetylacetonate-derived catalysts. The QTOF are found to decrease with loading in both series. It is significant to note that the shapes of the QTOF curves are similar to O/Mo curves against loading. De Beer and coworkers [7] have reported similar results on Mo/C.

HDS rate as a function of oxygen uptake is shown in Fig. 4. A linear correlation passing through the origin is obtained between HDS activity and oxygen uptake in both cases. Vissers *et al.* [7] reported that such a correlation

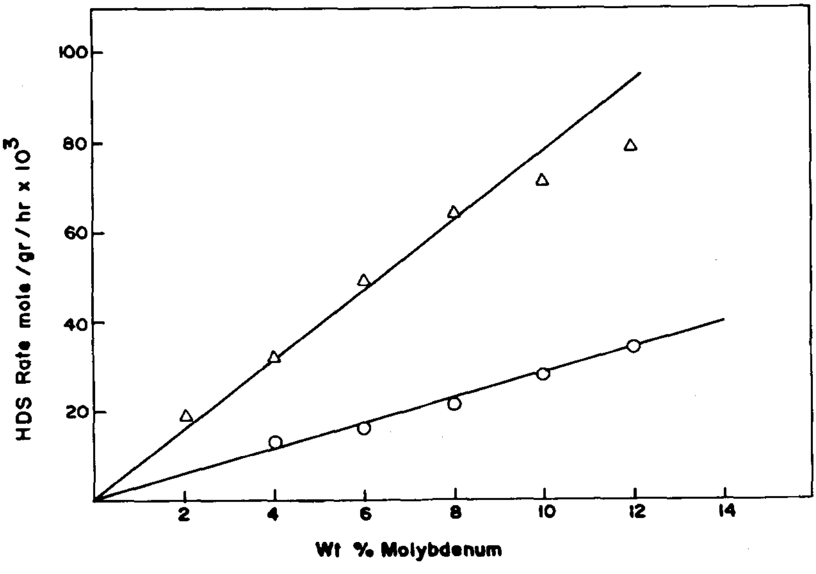

Fig. 2. Thiophene HDS rate as a function of molybdenum loading. Symbols as in Fig. 1.

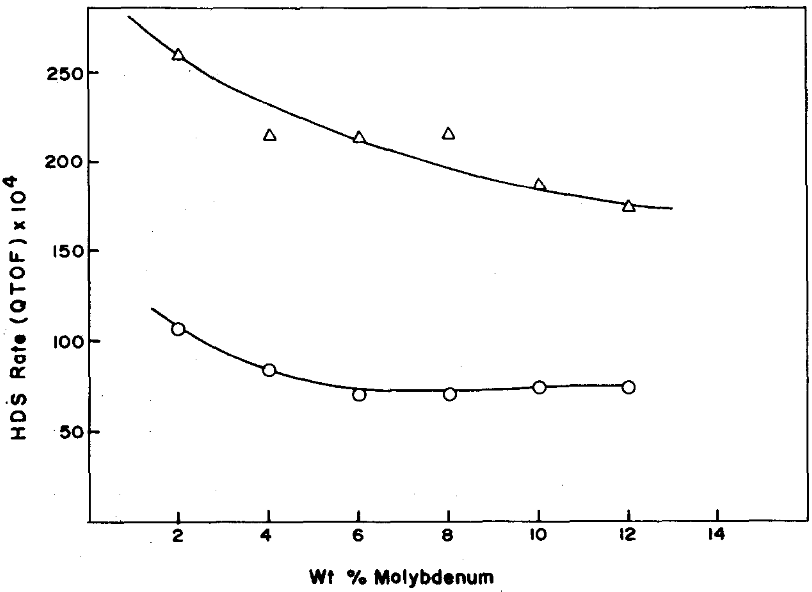

Fig. 3. QTOF as a function of molybdenum loading. Symbols as in Fig. 1.

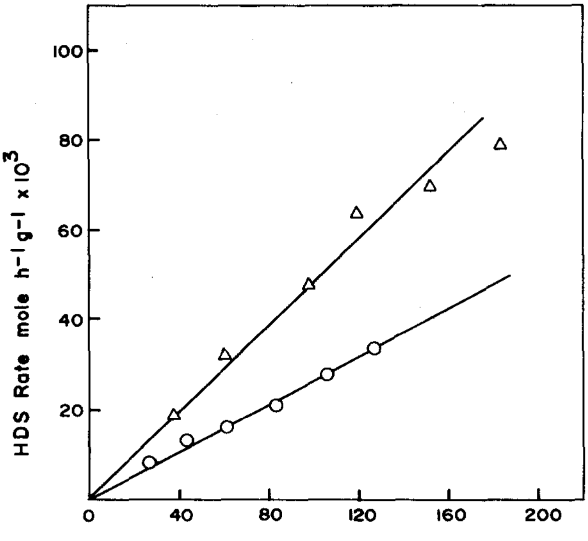

Fig. 4. Thiophene HDS rate as a function of oxygen uptake. Symbols as in Fig. 1.

demonstrates that the same kind of site exists irrespective of Mo loading. The fact that similar behaviour is observed in both cases suggests that the use of both precursors leads to the same kind of active site.

Oxygen chemisorption and its relation to HDS activity have been addressed by several authors [16–21]. Some have concluded that oxygen chemisorption is related to active edge sites of molybdenum sulfide, while others have attributed the same to molybdenum sulfide dispersion. In a more recent study, de Beer's group established a relationship between the XPS intensity ratio (Mo/C) and Mo/O, indicating that oxygen chemisorption is related to active crystallite size and hence to dispersion. Based on their observation, O/Mo ratios can be taken as a measure of dispersion. Now, considering the reasons for the improved catalytic activity of acetylacetonate-based Mo/C catalysts, three possibilities exist. The improved activity may be related to (i) dispersion of the active phase or (ii) better morphology of the acetylacetonate-derived catalysts or (iii) enhancement of activity per site. In considering the last possibility, the turnover frequency (TOF) or activity per site is useful. The slopes of the O_2 uptake *vs.* activity (Fig. 4) are proportional to the turnover frequency. A glance at Fig. 4 indicates that the TOF values are higher in the case of acetylacetonate-derived catalysts. The improved activity of the acetylacetonate-derived ones appears to be due to increased dispersion. From these investigations, however, no conclusions can be made on the role of improved morphology in the increased activity of the acetylacetonate-derived catalysts.

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