

## Dispersion and Hydrodesulphurization Studies of RuS<sub>2</sub> and MoS<sub>2</sub> Catalysts supported on $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

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Thiophene hydrodesulphurization activity and oxygen chemisorption have been measured for RuS<sub>2</sub> and MoS<sub>2</sub> supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>; RuS<sub>2</sub> shows better dispersion and activity than MoS<sub>2</sub>.

Hydrodesulphurization (HDS) of sulphur-containing aromatics is a well known process in petroleum refining. The typical catalysts employed were molybdenum oxide or tungsten oxide promoted with cobalt or nickel supported on high-surface-area alumina. The activities of these catalysts depend mainly on the dispersion of the active component and the nature of the support material. Considerable efforts have been made to develop methods for the determination of molybdena dispersion in supported catalysts. These include use of ESCA<sup>1-4</sup> and low temperature oxygen chemisorption (LTOC).<sup>5-10</sup> The latter method offers the advantages of being simple, inexpensive, and providing quantitative data for determining the dispersion of molybdena phase. This method has been applied quite successfully to the determination of dispersion of active phase of partially reduced metal sulphides and oxides. There have been many recent reports on the use of LTOC for the

determination of the active phase dispersion of supported molybdena catalysts. Good correlations have also been reported between oxygen chemisorption and activity of the unpromoted catalysts for hydrodesulphurization (HDS) reactions.

RuS<sub>2</sub> is an example of a well behaved catalyst system, unlike MoS<sub>2</sub> where the effect of anisotropy plays a major role in HDS catalysts; only a few recently reported studies have used these catalysts for hydrodesulphurization reactions.<sup>11-13</sup> In the present investigation, a comparison is made between RuS<sub>2</sub> and MoS<sub>2</sub> supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with respect to their dispersion and activity towards HDS of thiophene.

A series of Ru/Al<sub>2</sub>O<sub>3</sub> catalysts with 'Ru' loadings ranging from 1.25 to 5% were prepared by incipient wetting of alumina support with solutions of appropriate concentrations of RuCl<sub>3</sub>·3H<sub>2</sub>O. The samples were dried at 120 °C for 16 h. In

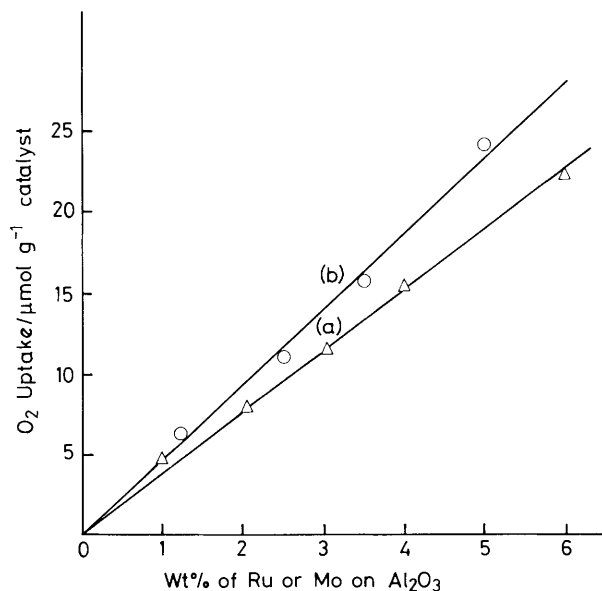


Figure 1. Oxygen uptake as a function of metal loading: (a)  $\Delta$   $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ , (b)  $\circ$   $\text{RuS}_2/\gamma\text{-Al}_2\text{O}_3$ .

another series  $\text{Mo}/\text{Al}_2\text{O}_3$  catalysts with 'Mo' loadings ranging from 1–6% were prepared by incipient wetting of alumina with aqueous solutions containing ammonium heptamolybdate. The samples were subsequently dried and calcined in air at  $540^\circ\text{C}$  for 16 h.

Oxygen chemisorption experiments were performed using a static high vacuum apparatus, following the method of Parekh and Weller.<sup>5</sup> Before the oxygen adsorption experiment, the catalysts were presulphided with a mixture of  $\text{CS}_2/\text{H}_2$  at  $400^\circ\text{C}$  for 2 h. The details of the experimental procedure are described elsewhere.<sup>8</sup> Thiophene HDS was then carried out on the presulphided catalysts at  $400^\circ\text{C}$  in a continuous flow microreactor operating at atmospheric pressure under differential conditions. No chlorine was found after 2 h of sulphiding the  $\text{Ru}/\text{Al}_2\text{O}_3$  catalysts prepared from impregnating  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ , indicating that all the chlorine, including the adsorbed chlorine, had been eliminated from the catalyst. The reaction products of thiophene HDS were butene and butane, and these were analysed by g.c., using a 2 m stainless steel column packed with 10% OV-17. The rates were measured under steady-state conditions and in the absence of any diffusion effects.

The oxygen chemisorption capacities of various  $\text{RuS}_2$  and  $\text{MoS}_2$  catalysts supported on  $\text{Al}_2\text{O}_3$  are plotted as a function of metal loading, in Figure 1. Oxygen chemisorption per gram of catalyst is found to increase linearly as a function of Ru or Mo loading. However,  $\text{RuS}_2/\gamma\text{-Al}_2\text{O}_3$  catalysts show higher oxygen chemisorption capacities than  $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ . The dispersions of  $\text{RuS}_2$  or  $\text{MoS}_2$  calculated from the results of oxygen chemisorption are plotted as a function of metal loading in Figure 2. The dispersion is found to be higher at low concentrations of the active component, decreasing monotonically, and finally levelling off at higher metal loadings. This indicates that ruthenium ions are intrinsically more active than molybdenum ions. It is generally accepted that co-ordinatively unsaturated Mo ions (CUS) on reduced or sulphided catalysts are the active sites for hydrodesulphurization reaction and that oxygen chemisorbs dissociatively on these sites at  $-78^\circ\text{C}$ . During sulphidation of the oxide catalysts these sites were generated and were quantitatively determined by LTOC. The

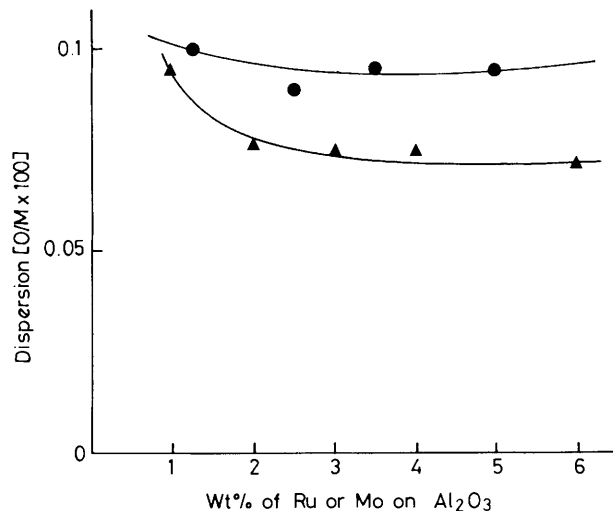


Figure 2. Percentage dispersion as a function of metal loading:  $\bullet$  = Ru,  $\blacktriangle$  = Mo.

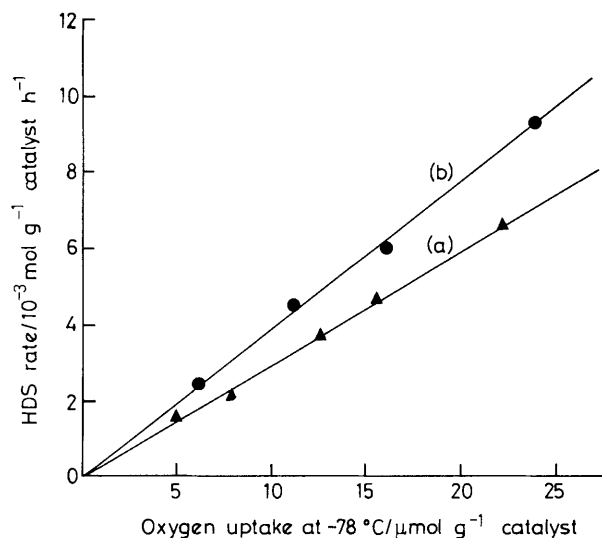


Figure 3. HDS activity at  $400^\circ\text{C}$  of various catalysts plotted as a function of oxygen uptake: (a)  $\blacktriangle$   $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ , (b)  $\bullet$   $\text{RuS}_2/\gamma\text{-Al}_2\text{O}_3$ .

CUS are located by  $\text{MoS}_2$  or  $\text{RuS}_2$  phases as a 'patchy-monolayer' on the surface of the alumina support.<sup>7</sup>

HDS activities of thiophene for various catalysts are plotted as a function of oxygen uptake in Figure 3. The results suggest that there is a linear correlation between oxygen uptake and HDS activity. However, the HDS activities of  $\text{RuS}_2/\gamma\text{-Al}_2\text{O}_3$  catalysts are found to be higher than those of the  $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$  catalysts, which further supports the results in Figure 2. This higher HDS activity can be attributed to the fact that ruthenium ions are intrinsically more active than molybdenum ions. The linear correlation in Figure 3 suggests that the functionality of the dispersed  $\text{MoS}_2$  or  $\text{RuS}_2$  phase is responsible for HDS of thiophene and this phase is located as a 'patchy-monolayer' on the surface of alumina.

Thus RuS<sub>2</sub> is found to be a better catalyst for hydrodesulphurization (HDS) of thiophene than the conventional MoS<sub>2</sub>.

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