

Highly active alumina-supported molybdenum sulphide and related hydroprocessing catalysts derived from precipitation from homogeneous solution*



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Introduction

Hydrodesulphurization (HDS) of petroleum feedstocks is one of the most important industrial catalytic processes [1–4]. The commonly employed catalysts during HDS are MoS_2 or WS_2 promoted with cobalt or nickel supported on high surface area alumina. Usually, these catalysts are prepared by the impregnation of alumina support using aqueous solutions containing ammonium molybdate and nitrates of cobalt or nickel, followed by calcination at higher temperatures (500 °C). The calcined precursors are pre-sulphided during the HDS process. However, the extent of sulphidation, *viz.* the formation of metal sulphides or metal oxosulphides, has long been a moot point [1, 4]. The sulphidation of an oxide catalyst always leads to partial conversion into sulphide form. A direct single-step sulphide catalyst preparation method has not been reported so far. Recently, the precipitation from homogeneous solution (PFHS) method has been identified as a good means of improving catalysts with respect to their crystallite size, high dispersion and uniform composition of the active component in supported catalysts [5–9]. Very recently we applied the PFHS method for preparation of a novel type of unpromoted $\text{MoS}_2/\gamma\text{-Al}_2\text{O}_3$ catalysts [10]. In this communication we report the hydrodesulphurization of thiophene by various γ -alumina-supported MoS_2 , Co–Mo and Ni–Mo catalysts prepared by PFHS method. A comparison of HDS activity is also made with those of commercial hydrotreating catalysts and with those derived from the conventional impregnation method.

Experimental

It has been reported [11, 12] that Mo oxide forms a monolayer at 8 wt.% of Mo on $\gamma\text{-Al}_2\text{O}_3$ support. Therefore, in this study the catalysts were prepared using 8% Mo by two different methods, *i.e.* conventional impregnation

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of the support by ammonium heptamolybdate and PFHS method. In the first series, the catalysts were prepared by the conventional impregnation method. Mo (8% w/w), Co–Mo and Ni–Mo catalysts were prepared by incipient wetting of γ -Al₂O₃ support (Harshaw, S. A. 234 m² g⁻¹, P.V., 0.65 ml g⁻¹) using an aqueous solution containing the requisite quantities of ammonium heptamolybdate alone or in combination with cobalt or nickel nitrates respectively. The samples were subsequently dried at 110 °C and then calcined in air at 540 °C for 16 h. BET surface areas of the catalysts have been measured by nitrogen adsorption at -196 °C.

In the second series, MoS₂/ γ -Al₂O₃ (8% Mo) catalyst was prepared by the PFHS method using thioacetamide as the precipitating agent. In a typical experiment γ -Al₂O₃ was suspended in a solution containing the required amount of ammonium molybdate, thioacetamide and nitric acid. The resulting mixture was heated to 90–95 °C with constant stirring until the MoS₂ was deposited on γ -Al₂O₃ support. After the precipitation was complete (pH 2–3), the resulting solids were filtered, washed and dried at 110 °C. The promoted catalysts were prepared by precipitation of cobalt sulphide and nickel sulphide on oven-dried MoS₂/ γ -Al₂O₃ (8% Mo) catalyst. This was accomplished by suspending MoS₂/ γ -Al₂O₃ in a solution containing the requisite amounts of urea, thioacetamide, nitric acid and cobalt or nickel nitrate and then heating the mixture on a water bath until completion of the precipitation at pH 7–9. The resulting solids were filtered, washed and dried at 110 °C.

Activity measurements for HDS of thiophene and hydrogenation of cyclohexene were carried out at 400 °C in a continuous flow microreactor operating at atmospheric pressure and under differential conditions. The reaction products, *i.e.* butene and butane during HDS and cyclohexane during hydrogenation, were analysed by an on-line gas chromatograph. The catalysts prepared by the impregnation method, and the commercial hydrotreating catalysts, were pre-sulphided with CS₂/H₂ mixture at 400 °C for 2 h before the HDS reaction. However, the catalysts prepared by the PFHS method are subjected directly to thiophene HDS and hydrogenation of cyclohexene. The details of the experimental procedure are described elsewhere [11].

Results and discussion

The results of hydrodesulphurization of thiophene and hydrogenation of cyclohexene by various catalysts are given in Table 1. It was found that the catalysts prepared from PFHS method not needing pre-sulphidation prior to HDS reaction exhibited higher activity than the presulphided conventional and commercial catalysts. The HDS activities of cobalt- and nickel-promoted catalysts appear to be more than twice that of the unpromoted catalysts. A similar observation has been made by Zmierczak *et al.* [12] and Reddy *et al.* [11], who found that the cobalt-promoted catalysts have shown about 4 times higher activities than the unpromoted catalysts towards hydrodesulphurization (HDS) of thiophene. Therefore it appears from the results that the role of promoter is mainly to increase the intrinsic activity of the HDS sites, and not to increase the number of active sites responsible for HDS

TABLE 1
Results of thiophene hydrodesulphurization and cyclohexene hydrogenation activities of various catalysts

Catalyst	Composition (wt.%)			BET surface area ($\text{m}^2 \text{g}^{-1}$)	HDS rate ($10^{-3} \text{ mol h}^{-1} \text{ g}^{-1} \text{ catalyst}$)	HYD rate ($10^{-3} \text{ mol h}^{-1} \text{ g}^{-1} \text{ catalyst}$)
	Mo	Co	Ni			
Mo/Al ₂ O ₃ ^a	8	—	—	178	10.9	26.3
Co-Mo/Al ₂ O ₃ ^a	8	3	—	164	26.4	29.4
Co-Mo/Al ₂ O ₃ ^a	8	5	—	161	28.6	23.0
Ni-Mo/Al ₂ O ₃ ^a	8	—	3	169	22.7	33.4
Ni-Mo/Al ₂ O ₃ ^a	8	—	5	158	24.2	38.5
Mo/Al ₂ O ₃ ^b	8	—	—	200	27.9	23.8
Co-Mo/Al ₂ O ₃ ^b	8	3	—	184	37.3	20.0
Co-Mo/Al ₂ O ₃ ^b	8	5	—	182	46.5	28.0
Ni-Mo/Al ₂ O ₃ ^b	8	—	3	187	34.1	17.8
Ni-Mo/Al ₂ O ₃ ^b	8	—	5	187	43.4	23.6
Harshaw (HT-400)	9.86	2.52	—	200	25.7	43.5
Keijfne-124	7.73	3.26	—	267	24.7	44.1
Harshaw (HT-500)	9.93	—	2.51	210	21.3	47.0
Keijfne-802	7.67	—	4.09	273	22.3	35.3

^aPrepared by impregnation method.

^bPrepared by precipitation from homogeneous solution method.

of thiophene. It is generally accepted that coordinatively unsaturated Mo ions (CUS) on sulphided catalysts are the active sites for hydrodesulphurization and hydrogenolysis reactions, and that these are located on MoS₂ as a 'patchy monolayer' on the surface of the alumina support [13, 14]. The hydrogenation activities of all the catalysts are lower than the corresponding HDS activities. However, on promotion by Co or Ni, hydrogenation activity differs marginally compared to the unpromoted catalysts.

The higher HDS activities of the catalysts prepared by the PFHS method might be due to better dispersion of molybdenum sulphide on γ -Al₂O₃. This observation has been evidenced from the X-ray diffraction results of these catalysts, wherein no peaks due to MoS₂ were observed, indicating that the molybdenum sulphide is present in highly dispersed or amorphous form on the surface of γ -Al₂O₃.

Thus the unpromoted and Co- or Ni-promoted molybdenum sulphide catalysts prepared by the PFHS method are found to show better HDS activities of thiophene than those prepared by conventional routes.

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