

Hydrodeoxygenation of Furan by Carbon Supported Molybdenum Sulphide Catalysts

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The removal of sulphur-containing compounds in petroleum refining and hydrocarbons is of considerable importance. Alumina supported sulphided cobalt-molybdenum catalysts are currently used for hydrotreating applications. Recently, carbon supported molybdena catalysts promoted with cobalt or nickel were found to show better catalytic activity towards hydrodesulphurization (HDS) than the commercial hydrotreating catalysts [1-9]. A detailed account of using carbon as a support is reviewed by Abotsi and Scaroni [1]. The advantages of employing carbon as a support material have been emphasised by de Beer et al [2] and Duchet et al [5]. Due to the weak interaction of the active Mo-phase with the surface of the carbon, the oxidic catalyst precursor species can be converted completely into the sulphide form, while in the case of conventional Al_2O_3 supported catalysts MoO_3 interacts more strongly with the support resulting in partial conversion to the sulphide phase. The structure and dispersion of the active phase present in carbon supported Mo and Co-Mo sulphide catalysts were studied recently by Bouwens et al [9] using Mo K-edge EXAFS. Vissers et al [3] studied the differences of carbon and alumina supported catalysts by combined dynamic oxygen chemisorption (DOC), X-ray photoelectron spectroscopy and thiophene HDS. They found that carbon supported MoS_2 catalysts possessed a higher HDS activity per active site than the alumina supported catalysts.

Hydrodeoxygenation (HDO) has also received [10-12] increased recent attention due to the presence of organooxygen compounds in coal derived liquids, shale oil and petroleum feedstocks. Sulphided catalysts of molybdenum/tungsten promoted with cobalt/nickel are found to be commonly employed for this process. It is generally believed that HDO takes place on the same sites as HDS. However, there is no study so far concerning carbon supported Mo and Co-Mo catalysts for the HDO process. An attempt has been made for the first time in this communication using carbon supported MoS_2 catalysts towards HDO of furan. A comparison is also made with conventional alumina supported catalysts and commercial hydrotreating catalysts towards HDO activity and dispersion of the molybdenum sulphide phase.

It has been reported [13] that Mo-oxide forms a monolayer at 8 wt.% of Mo on a $\gamma\text{-Al}_2\text{O}_3$ support. However, the monolayer formation depends on the surface area of the carrier material. Therefore, in this study a comparison is made between conventional alumina and carbon supported MoS_2 catalysts with respect to their activity and dispersion at this composition. Unpromoted Mo/C (8% w/w of Mo) catalyst was prepared by incipient wetting of the carbon support (Lurgi, S.A. 1160 $\text{m}^2 \text{g}^{-1}$) using an aqueous solution containing ammonium heptamolybdate. Cobalt (3% w/w) and nickel (3% w/w) promoted molybdena catalysts were prepared by impregnation of 8% Mo/C

(w/w) catalyst using aqueous solutions containing cobalt nitrate and nickel nitrate, respectively. Unpromoted $\text{Mo}/\text{Al}_2\text{O}_3$ (8% w/w of Mo) catalyst and Co or Ni promoted catalysts were prepared in an identical manner using a $\gamma\text{-Al}_2\text{O}_3$ support (Harshaw, S.A. 234 m^2g^{-1}). The samples were subsequently dried and calcined in air at 540°C for 16 h. No calcination was done in the case of carbon supported catalysts. Oxygen chemisorption measurements were performed on presulphided catalysts at -78°C using a static high vacuum adsorption unit following the method of Parekh and Weller [14]. The details of the experimental procedure are described elsewhere [13]. Activity measurements for HDO of furan were carried out at 400°C on presulphided (using a $\text{CS}_2 + \text{H}_2$ mixture) catalysts 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 gas chromatography.

The results of oxygen chemisorption and HDO activities of carbon and alumina supported catalysts are given in Table 1. It is found that oxygen chemisorption capacities of Mo/C catalysts are higher than those of the corresponding alumina supported catalysts. The dispersion ($\text{O}/\text{Mo} \times 100$) of molybdenum sulphide calculated from oxygen chemisorption capacities is found to be 0.199 for 8% Mo/C and 0.073 for 8% $\text{Mo}/\text{Al}_2\text{O}_3$ catalysts. Thus molybdenum sulphide is found to disperse better on a carbon support than on the alumina surface. It is generally accepted that coordinatively unsaturated sites (CUS) on partially reduced $\text{Mo}/\text{Al}_2\text{O}_3$ and Co-Mo/ Al_2O_3 catalysts are the active sites for hydrogenation and hydrogenolysis reactions. Oxygen selectively chemisorbs on these sites at -78°C and offers a quantitative estimation of them. These CUS are located on the MoS_2 phase as a 'patchy-monolayer' on the surface of alumina [15].

The oxygen chemisorption capacities of cobalt and nickel promoted catalysts were found to differ marginally from those of unpromoted MoS_2 catalysts. However, the HDO activities of the promoted catalysts appears to be four times higher than those of unpromoted catalysts. Interestingly, the HDO activities of carbon supported Co-Mo and Ni-Mo catalysts are much higher than those of the corresponding alumina supported catalysts and also than those of commercial Co-Mo and Ni-Mo catalysts. However, it should be pointed at this juncture that there is a considerable debate about the applicability and significance of oxygen chemisorption to HDS reactions [16,17,18]. A similar observation has been found by Zmierczak et al [16] wherein the cobalt promoted $\text{Mo}/\text{Al}_2\text{O}_3$ catalysts showed 5-6 times higher activity than the unpromoted $\text{Mo}/\text{Al}_2\text{O}_3$ catalysts towards hydrodesulphurisation (HDS) of thiophene. Therefore it appears from the results that the role of the promotor is mainly to increase the intrinsic activity of the HDO sites and not to increase the number of active sites responsible

Table 1

Results of Oxygen Chemisorption and Furan Hydrodeoxygenation (HDO) Activities of Various Catalysts

Catalyst	Composition wt%			Oxygen uptake μ moles g^{-1} catalyst	HDO rate/ 10^{-3} mole g^{-1} catalyst h^{-1}
	Mo	Co	Ni		
Mo/C	8	-	-	83.00	11.29
Co-Mo/C	8	3	-	90.57	41.07
Ni-Mo/C	8	-	3	86.55	39.32
Mo/Al ₂ O ₃	8	-	-	32.26	6.24
Co-Mo/Al ₂ O ₃	8	3	-	35.15	26.62
Ni-Mo/Al ₂ O ₃	8	-	3	38.90	23.50
Harshaw (HT-400)	9.86	2.52	-	35.70	27.55
Ketjenfine-124	7.73	3.26	-	33.46	30.02
Ketjenfine 802	7.67	-	4.09	47.02	29.78
Harshaw (HT-500)	9.93	-	2.51	36.22	36.85

for HDO of furan.

Thus carbon supported molybdenum sulphide catalysts are found to show better dispersion of the MoS₂ phase and HDO activities than the corresponding alumina supported catalysts.

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