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Characterization of Unsupported Ni–Mo Hydrodesulfurization Catalysts by Oxygen Chemisorption

I. INTRODUCTION

The use of molybdenum- and tungsten-based catalysts for the hydrodesulfurization and hydrodenitrogenation of petroleum feedstocks is well known. In the future it is expected that such catalysts will become even more important for removal of sulfur and nitrogen in the production of synthetic fuels from coal and oil shale. The use of reliable characterization techniques is therefore of great importance in the development of catalysts with greater selectivity and activity.

Recently O_2 chemisorption using a pulse flow technique has been employed for the characterization of hydrodesulfurization catalysts (*1–4*). O_2 chemisorption on unsupported MoS_2 catalysts (*1*), sulfided Co–Mo/Al_2O_3 (*2*), and sulfided Ni/Al_2O_3 (*4*) catalysts has been shown to correlate with desulfurization activity. O_2 chemisorption has also been shown to correlate with activity on coked Ni–Mo/Al_2O_3 hydrotreating catalysts (*3*).

The purpose of this study was to investigate the oxygen uptake on a series of unsupported nickel–molybdenum catalysts. The nickel content of the catalysts ranged from 0 to 100 at.% nickel. Their activities for thiophene hydrodesulfurization (HDS) along with X-ray diffraction and transmission electron microscopy (TEM) data were previously reported (*5, 6*). The application of O_2 chemisorption to the characterization of the nickel–molybdenum system, i.e., particularly to a series of catalysts covering a wide range of compositions, has not been previously reported. It was therefore decided to investigate the oxygen adsorption using two different techniques. In previous studies the dynamic (pulse flow) adsorption method was shown to provide reproducible uptake data (*1–4*), and this technique was therefore employed in this study. There are no reports of using a conventional volumetric system to obtain oxygen uptake on metal sulfides. This is probably due to problems associated with exothermic subsurface penetration of the oxygen, at least at room temperature or higher temperatures. However, it has been shown that oxygen adsorption at −78.5°C on reduced molybdenum oxide/alumina catalysts is a reliable method of characterization (*7, 8*). Recently we found that static O_2 adsorption on molybdenum sulfides at low temperatures results in reproducible uptake data which compare favorably with the flow uptake data obtained at room temperature, while static adsorptions at room temperature apparently result in bulk oxidation (*9*).

II. EXPERIMENTAL

The preparation of the Ni–Mo catalysts in the oxide form was described previously (*5*). For each chemisorption 0.5 to 1.0 g of the calcined catalyst was placed in a Pyrex glass chemisorption cell and pretreated under a flowing mixture of 10% hydrogen sulfide in hydrogen for 4 h at 400°C. After this pretreatment the catalysts were prepared for flow oxygen adsorption measurements by purging the catalyst sample with 60 cm^3/min of purified helium at 350°C for 1 h, after which the cell was cooled to ambient temperature and the helium flows were reduced to about 25 cm^3/min. The effluent gases from the chemisorption cell were then passed through a thermal conductivity de-

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tector. After obtaining a steady baseline, 1-cm^3 pulses of 10% O_2/He were injected into the helium carrier gas with a gas sampling valve before entering the chemisorption cell. The oxygen leaving the catalyst was then detected by the thermal conductivity detector. When the oxygen peaks reached essentially constant size, the catalyst was assumed to be saturated. From the areas under the effluent peaks the oxygen uptake was then calculated.

To measure the oxygen adsorption using the static, volumetric technique a conventional all-glass adsorption apparatus was used. Pressure measurements were made using a Texas Instruments precision pressure gauge. The H_2S/H_2-treated catalysts were evacuated at 350°C for approximately 1 h to below 5×10^{-5} Torr (1 Torr = 133.3 N/m^2). After evacuation, the catalyst was cooled to −78.5°C by immersion in a dry ice–acetone bath. Oxygen was then admitted to the chemisorption cell at a pressure of 300 Torr. The catalyst sample was allowed to equilibrate 1 h before a desorption isotherm was measured. The linear portion of the isotherm was extrapolated to zero pressure to give a measure of combined chemical and physical adsorption. The catalyst sample was then evacuated at −78.5°C for 1 h to remove physically adsorbed oxygen. A second isotherm was then produced using the above procedure giving the amount of physically adsorbed oxygen. The difference in the two uptakes was assumed to be the amount of chemisorbed oxygen. After determining the oxygen uptake, the catalyst sample was evacuated and the BET surface area was determined by argon adsorption at −195°C.

III. RESULTS AND DISCUSSION

Table 1 lists the previously determined rate constants (*5*), BET surface areas, and oxygen uptakes for the eight catalysts studied. Previous O_2 adsorptions on MoS_2 (*1*) were done by cooling the sample to ambient conditions and purging with Ar, while in this work the H_2 and H_2S were removed at 350°C either by purging with He or by evacuation. The purpose of the evacuation or purge at 350°C was to provide a surface free from adsorbed H_2S and H_2 species. It has been shown that the amount of O_2 adsorbed on sulfided Ni/Al_2O_3 varies with the length of purge time at elevated temperature which was explained to be due to H_2S on the surface (*4*). Moreover, a recent paper concerning H_2S chemisorption on WS_2 (*10*)

TABLE 1

Rate Constants, BET Surface Areas, and O_2 Uptakes for Ni–Mo Catalysts

Catalyst	$\frac{Ni}{Ni + Mo}$	k^a (μmole/sec g)	Surface area[b] (m^2/g)	Oxygen uptake (μmole/g)	
				Pulse flow[c]	Volumetric[d]
A	0	10	5.1	0	1
B	0.30	128	18.0	5.2	11.4
C	0.41	228	31.1	11.9	14.3
D	0.55	263	45.8	25.8	19.1
E	0.73	366	39.1	9.1	25.0
F	0.79	302	32.8	10.8	25.7
G	0.92	139	25.7	27.8	40.8
H	1.00	4.2	8.0	35.5	55.6

[a] Rate constants for HDS of thiophene from Ref. 5.

[b] Argon adsorption using 0.146 nm^2/argon atom.

[c] At 25°C using 10% O_2 in He.

[d] At −78°C using pure O_2 at 300 Torr.

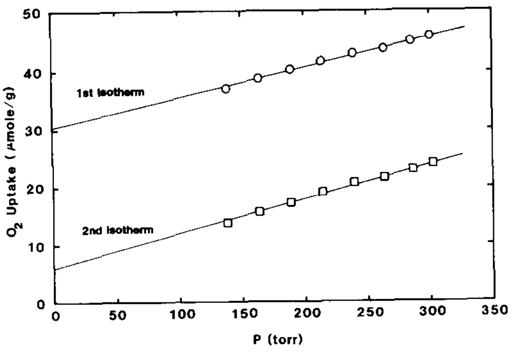

FIG. 1. Double isotherm for catalyst E at −78.5°C.

suggests that H_2S and O_2 may be absorbing on the same sites.

Figure 1 shows a typical pair of O_2 desorption isotherms. The isotherms are seen to be linear from 300 Torr down to at least 120 Torr. For the catalysts with the lowest surface areas, the uptake measured by the second isotherm was found to be negligible.

Figure 2 is a plot of the hydrodesulfurization rate constant vs oxygen uptake. Both the pulse flow method and the low-temperature volumetric method give similar volcano-type curves. Indeed, there is good correlation between increasing O_2 adsorption determined by either technique and increasing activity with addition of Ni until the maximum activity is reached. While this activity–O_2 uptake correlation is similar to that obtained by previous workers for unsupported MoS_2, Co–Mo/Al_2O_3, and partially deactivated Ni–Mo (*1–3*), the data in this study are the first to show that such a correlation exists over a reasonably wide range of nickel contents (up to about 60%). Moreover, the data are quite consistent with those previously reported for the same catalysts (*5*, *6*) showing similar volcano plots for activity vs nickel content and vs BET surface area.

For those catalysts with high Ni content the activity decreases with increasing oxygen uptake. However, these catalysts are effectively Mo-promoted Ni catalysts rather than Ni-promoted Mo catalysts. Thus increasing Ni content ceases to have a promotional effect; indeed, the decrease in Mo content has the opposite effect (*5*). The high O_2 adsorption on the high-Ni catalysts may be due to the predominance of adsorption sites significantly less active for hydrodesulfurization than those in MoS_2 or nickel-promoted MoS_2 (*1*, *5*).

The fact that similar correlations between HDS activity and oxygen chemisorption are observed for MoS_2, Co–Mo, and Ni–Mo catalysts suggests that the same kind of specific catalytic sites are involved in all three kinds of catalysts and that these particular sites selectively adsorb oxygen. Indeed, Millman and Hall have discussed and demonstrated the site specificity of O_2 adsorption in these systems and have correlated this behavior with anion vacancy concentration (*11*). However, recent correlations of oxygen adsorption with hexene hydrogenation activity of sulfided Mo/Al_2O_3 and Co–Mo/Al_2O_3 catalysts (*12*) and CO hydrogenation activity of MoS_2 catalysts (*13*) provide evidence that O_2 chemisorption may not be specific to sites for HDS as previously suggested (*1–3*), but rather may provide a measure of dispersion of the active sulfide phase(s) (*12*). Nevertheless, the ongoing controversy regarding the precise nature of these sites (*12*, *14–16*) indicates that further work is needed to resolve this question.

In conclusion, our results indicate that both dynamic and static oxygen adsorption measurements can be used to characterize

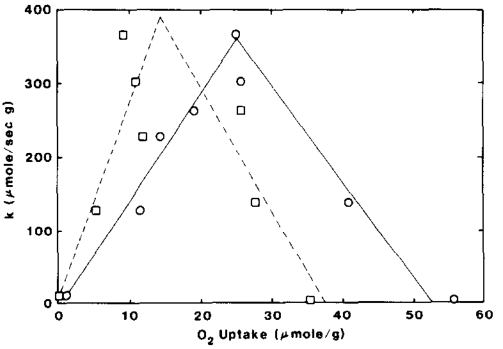

FIG. 2. Rate constant vs oxygen chemisorption. ○—Volumetric system, −78.5°C (——). □—Flow system ambient temperature (– – –).

active surface areas of Ni–Mo catalysts over a fairly wide range of nickel contents (0–60%). Moreover, our results when compared with previous work suggest that the active sites in Ni–Mo HDS catalysts may be the same as those in MoS_2 and Co–Mo HDS catalysts since very similar correlations are observed for all three systems.

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