

Use of Dynamic Oxygen Chemisorption for the Characterization of Sulfided Cobalt-Molybdena-Alumina Catalysts

In recent years the chemisorption of oxygen has been used to characterize reduced molybdena-containing catalysts. Parekh and Weller (1) studied reduced molybdena-alumina and cobalt-molybdena-alumina catalysts and used their results to derive equivalent molybdena surface areas. Hall and Millman (2) have stressed the site-specificity of O₂ chemisorption in these systems and have correlated this with anion vacancy concentration, as well as catalytic activity for propylene hydrogenation. Similarly, Vyskocil and Tomanova (3) have correlated O₂ chemisorption with cyclohexane hydrogenation activity for reduced cobalt-molybdena-alumina catalysts.

In the present report we describe the application of O₂ chemisorption to cobalt-molybdena-alumina catalysts in the sulfided state, which prevails under hydrodesulfurization reaction conditions. We have found that the catalytic activity for this reaction correlates with O₂ chemisorption data.

In a recent report (4) we have described the characterization of molybdenum disulfide using the method of dynamic oxygen chemisorption (DOC). The dynamic technique, in which intermittent pulses of adsorbate are added to a carrier gas and rapidly traverse the catalyst bed, was chosen in order to minimize subsurface oxidation of the metal sulfide. In a study involving many samples of MoS₂, a linear correlation was found between hydrodesulfurization activity and DOC uptake in contrast to the absence of any correlation with BET surface area (4). MoS₂ has a layered structure, and the correlation was explained on the basis of the *edge plane* being the site of both oxygen chemisorption and hydrodesulfurization activity.

Industrial hydrotreating catalysts present a more complex situation. The active (sulfide) phases are supported on alumina.

O₂ has the important attribute of not chemisorbing on this carrier. Chemisorption does occur on cobalt (or nickel) sulfide; however, this does not preclude the possibility of an effective correlation between DOC and hydrodesulfurization activity. The present report describes experiments designed to investigate this relationship.

Two nominally identical cobalt-molybdena-alumina calcined catalysts, designated A and B, with composition 4.5% CoO, 15.9% MoO₃, 0.8% P₂O₅, balance Al₂O₃, were selected for this study. Pilot plant tests with a light Arabian 343-565°C vacuum gas oil feed established a 30% hydrodesulfurization activity advantage for B over A. The general procedure described in (4) was used. Samples (1.0 g, 1/8-in. extrudates) of calcined catalysts were charged into a U-configuration glass cell and were sulfided *in situ* with 15% H₂S/H₂, usually at 350°C for 45 min. Raising the sulfiding temperature to 400°C had no discernible effect. The samples were then cooled to ambient temperature under the sulfiding gas and the system was purged with argon at ~125 cm³/min for 10 min. At this point, effluent gas from the catalyst bed was routed into the sample chamber of a thermal conductivity cell (carrier gas entered the system through the reference chamber) and the purge continued at a lower flow rate (~25 cm³/min) until a reasonably stable baseline was indicated on the recorder. This required ~15 min; as pointed out in (4) the duration of the purge was not found to be a critical parameter. The measurement ensued with the addition, at 2-min intervals, of 5-cm³ increments of 10% O₂/argon (each pulse = 20.5 μmole O₂) with the aid of a microsampling valve (Carle Co., Anaheim, Calif.). The first few pulses were completely adsorbed (see Table 1) and then O₂ peaks began to emerge and grow to fairly constant size. The run

was completed upon the appearance of two consecutive pairs of peaks, whose average sizes differed by less than 1%. At this point the catalytically active sites were considered to be saturated. This does not actually signify total saturation of the catalyst. A small residual uptake (a few percent of each pulse) continued in a quasi-invariant manner. This behavior contrasts with the earlier stages of the run in which the percentage adsorbed drops sharply from pulse to pulse. This quasi-invariant uptake apparently represents some secondary process, e.g., oxidation of sulfur or a small amount of sub-surface penetration of O₂. In any case, it seems reasonable to exclude these sites from the chemisorption-activity correlation.

Table 1 presents the data representing eight runs (all separate samples) from Batch A and six runs (three separate samples) from Batch B. It can be seen that the DOC

results are in close agreement with the catalytic data. Thus, a 30% advantage for both activity and DOC uptake was found for Batch B over Batch A. The clear advantage of B is likewise indicated by the relative numbers of completely adsorbed pulses.

Another important consideration pertains to reproducibility. The total O₂ uptake results obtained with Batch A were quite precise, showing an average deviation of 4.5 μmole O₂/g (3.6% of the mean). The precision was poorer with respect to Batch B. Still, the average deviation is 6.4% of the mean. Thus, the precision, which can be expected to improve with further experience, is adequate for dealing with activity differences of the magnitude dealt with here.

In conclusion, we believe dynamic oxygen chemisorption to be a promising technique for the characterization of sulfided cobalt-molybdena-alumina catalysts. It affords data which are reasonably precise and which conform well with hydrodesulfurization activity. It may thus be capable of supplanting costly, time-consuming activity tests for this purpose.

TABLE 1
O₂ Chemisorption

Batch	Uptake (μmole O ₂ /g)	Pulses completely adsorbed ^a
A ^b	129	4
	115	4
	119	4
	131	4
	129	4
	129	4
	125	4
	123	4
Average ad	125 4.5	
B ^b	157	6
	149	6
	155 ^c	6
	186	6
	160 ^c	5
	172 ^c	5
Average ad	163 10.5	

^a Each pulse contains 20.5 μmole O₂.

^b Batch B was 30% more active for the hydrodesulfurization of vacuum gas oil.

^c Sample used in previous run was resulfided.

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