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Use of Dynamic Oxygen Chemisorption for the Characterization of Partially Deactivated (Coked) Hydrotreating Catalysts

Coke is a ubiquitous contaminant of solid catalysts used for hydrocarbon reactions. Its general effect, as is well known, is to decrease catalytic activity, presumably by covering the active sites or rendering them inaccessible by other means such as pore blocking. The quantitative relationship between coke deposition and activity decline is, however, a complex affair and depends upon many factors.

Chemisorption should be able, in principle, to attack some important questions relating to coked catalysts. What, for example, are the relationships between amount of deposited coke, change in chemisorption capacity, and decrease in activity? Nevertheless, the application of chemisorption procedures to coked catalysts has been widely avoided. This may well reflect an apprehension that coke will itself adsorb appreciable amounts of the adsorbate in question, and thus destroy any correlation between chemisorption and catalytic properties. Alternatively, it may be suspected that appreciable coke loadings would essentially eliminate adsorption even if activity remained, especially since experimental conditions for chemisorptions and reactions are usually very different.

This report describes the application of chemisorption (specifically, dynamic oxygen chemisorption) to partially deactivated (coked) hydrodesulfurization catalysts. In this case (and probably in others as well) there are practical incentives to characterize such catalysts. Thus, commercial hydrotreating units often employ several reactors in series. It is very difficult to estimate the degree of deactivation in individual reactors at a given time. Such knowledge can be important, however, as it indicates when a given reactor requires regeneration.

Dynamic oxygen chemisorption (DOC) has previously been described as a promising technique for characterizing hydrotreating catalysts in their working (sulfided) state. An initial study (*1*) dealt with unsupported MoS_2. It was shown that the catalytic activity for the hydrodesulfurization of dibenzothiophene correlated linearly with DOC uptake, despite the absence of correlation with total surface area. More recently we have described results with sulfided cobalt–molybdena–alumina (*2*) which are catalysts commonly used in commercial hydrotreating applications. In the preparation of large-scale batches, poor distribution of the supported phases often occurs, leading to significant activity differences for samples of the same composition. DOC uptake was found to correctly predict the hydrodesulfurization activity in this circumstance.

To extend the application of the DOC technique to coked hydrotreating catalysts, we have studied nickel–molybdena–alumina catalysts which had been used in

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TABLE 1

Chemical Analyses of Spent Hydrofiner Catalysts (wt%)

	Bed		
	2	3	4
Carbon	4.5	7.5	8.6
MoO_3	12.3	13.5	15.1
Ni	3.3	2.3	2.4
Fe	1.7	0.77	0.56
V	0.95	0.063	0.011

TABLE 2

Relative Activities and DOC Uptakes of Partially Deactivated Hydrofining Catalysts (%)

	Bed		
	2	3	4
Relative hydrodesulfurization activity	66	69	63
Relative DOC Uptake	61	71	61

a commercial hydrofiner unit for the desulfurization of 45/55 liquid volume percent blend of heavy coker and virgin gas oils (650–1050°F boiling point cut). The unit consisted of four catalyst beds in series; Bed 1 (inlet) . . . Bed 4 (outlet). However, samples could only be obtained from Beds 2–4. Table 1 shows the results of chemical analyses of these samples.

It is seen that significant amounts of coke had been deposited in all three beds. There is, however, a clear trend towards increased coke deposition in the downstream reactors. This can be explained on the basis of the observed gradient of deposited metals. Bed 2 had accumulated 1.7% iron as well as 1% each of vanadium and excess nickel. The accumulation of the latter two metals decreased sharply in the downstream beds, while iron concentration decreased more gradually. These metals catalyze hydrocracking reactions which reduce coke levels.

Recovered samples were tested in two ways. Their hydrodesulfurization activities were measured in a laboratory unit on the same feed as in the commercial unit. The activity of fresh catalyst of the same composition on this feed was also determined. In addition, DOC measurements were performed on the three partially deactivated samples and on the corresponding fresh catalyst. Details of the procedure are given in Ref. (*2*). The samples (1-g, 1/16-in extrudates) were freshly ovendried. This was found to be an important preliminary step. They were then sulfided with 15% H_2S/H_2 *in situ* at 350°C, for 45 min, cooled under H_2S/H_2 to ambient temperature and purged with argon. O_2 pulses (20.5 μmoles O_2/pulse) were delivered at 2-min intervals until the effluent peaks were essentially constant in size. Taking this peak size to represent 20.5 μmoles O_2, the amounts adsorbed from the earlier pulses were calculated and summed to give the cumulative uptake.[1]

Table 2 lists the relative (to fresh catalyst) hydrodesulfurization activities and relative DOC uptakes of samples removed from Beds 2, 3, and 4. The DOC uptake of the fresh nickel-molybdena–alumina catalyst was 143 μmoles O_2/g.

Based on the varied amounts of coke and deposited metals indicated in Table 1, one might anticipate significant activity differences between the three catalysts. Table 2 indicates that they are, however, closely comparable, underscoring the difficulty of predicting activity based on such analyses. The DOC measurements are nevertheless clearly consistent with the observed activities, as shown in Table 2. Thus, the DOC-activity correlation has remained intact despite these appreciable amounts of coke and deposited metals.

It need hardly be mentioned that cata-

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[1] See Ref. (*2*) for necessary corrections.

lytic cokes vary widely and that systems can undoubtedly be found in which activity-chemisorption correlations will prove impossible. The above results demonstrate, however, that such correlatabilities cannot be ruled out in advance of experiment.

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