

## Effect of Sulfidation on the Dehydrogenation Activity of a Bimetallic Reforming Catalyst

Several commercial reforming processes have start-up procedures involving sulfidation of the catalysts. Controlled sulfidation is said to improve the stability and life of the catalysts apart from increasing the  $C_5+$  yield. Pfefferle (1) has observed that the presence of sulfur in the feed decreases the aging rate of the catalyst while increasing the  $C_5+$  yield. Very recently Hayes *et al.* (2) have also reached the same conclusions based on their studies using sulfided and nonsulfided Pt-alumina catalysts with naphtha, *n*-heptane and cyclohexane as feed materials. They have found that coke lay-down on sulfided catalyst is about half that on unsulfided catalyst. In our present work, we have used a bimetallic reforming catalyst and have studied the intrinsic ability of the metal surface to dehydrogenate cyclohexane, coupling  $H_2$  adsorption studies with reaction data.

The reforming catalyst used in the present study had Pt as the major constituent. The support was a high purity alumina and had about 100 ppm of Fe. Sample A was reduced and sulfided by passing a mixture of  $H_2$ - $CS_2$  at  $250^\circ C$  for 10 hr at a pressure of 5 kg/cm<sup>2</sup>. Sample B was a sulfided catalyst removed from a bench-scale reactor after 75 hr on a naphtha feed under typical reforming conditions. Sample C was a freshly reduced and unsulfided catalyst. All the three samples were reduced again at  $500^\circ C$  before  $H_2$  chemisorption measurements were made according to the procedure of Spenadel and Boudart (3). Cyclohexane dehydrogenation experiments were carried out in a vertical flow reactor at conditions such that the conversions were mostly below 10%.

Table 1 lists the data obtained over the catalyst samples. The dehydrogenation efficiency expressed in terms of turnover number is defined as the number of molecules of benzene produced per hour per exposed metal atom. This was obtained by dividing the total number of molecules of benzene produced in 1 hr on a certain amount of catalyst by the number of atoms of hydrogen adsorbed by the same amount of catalyst. The ratio of adsorbed hydrogen atoms to the total number of metal atoms in the catalyst (H/M ratio) is also presented in Table 1.

The sulfided samples have a smaller value of H/M ratio compared to the unsulfided sample. Similar results have been obtained by Zaidman *et al.* (4). This is mostly due to the S blocking off of the adsorption sites. The used sulfided sample (B) has a slightly larger H/M value than the fresh sulfided catalyst (A). This is due to removal of part of the sulfur from the metal surface during the high pressure reforming reaction. It is found that the turnover number is higher (880 at  $275^\circ C$ ) for the unsulfided sample than for the sulfided catalyst (200 at  $275^\circ C$ ). The used sample (B) also has a small turnover number (190 at  $275^\circ C$ ), about the same magnitude as that of the fresh sulfided catalyst. The same trend is observed at other temperatures also. The lower dehydrogenation efficiency in the case of sulfided catalysts cannot be explained on the basis of surface-structural rearrangements caused by the chemisorbed sulfur, since hydrogenation-dehydrogenation reactions are likely to be structure insensitive. While it is possible that sulfur may drastically alter the

TABLE I  
H/M RATIOS AND TURNOVER NUMBERS OF  
THE REFORMING CATALYST SAMPLES

Sam- ple	Pretreatment	H/M ratio	Temp (°C)	Turnover No.
A	Reduced and sulfided (fresh)	0.13	275	200
			250	<100
B	Reduced and sulfided (used)	0.36	275	190
			250	<100
			225	<50
C	Reduced (fresh, unsulfided)	0.64	275	880
			250	400
			225	160

path of catalytic reactions by direct chemical interactions with the adsorbed molecules instead of by inducing surface recrystallization (5), the smaller turnover number could be ascribed to either one or both of the following two reasons: (a) more than one site might be necessary for the dehydrogenation of cyclohexane (6) and the presence of sulfur might exclude certain sterically favorable multiple sites essential for the reaction to take place; (b) the added sulfur might alter the electronic properties of the metal surface itself.

Both catalyst samples A and B have nearly similar turnover numbers. This

shows that sulfidation of a fresh catalyst brings down the intrinsic dehydrogenation activity of the metal surface to a stable level. An unsulfided catalyst possesses very high dehydrogenation activity and leads to easy production of coke on the metal surface due to excessive dehydrogenation of the adsorbed species. Thus, an unsulfided catalyst reaches quickly an activity level lower than the stable level of the sulfided sample.

#### REFERENCES

1. Pfefferle, W. C., *Amer. Chem. Soc. Div. Petrol. Chem. Prepr.* **15**, A 21 (1970).
2. Hayes, J. C., Mitsche, R. T., Pollitzer, E. L., and Homeier, E. H., *Amer. Chem. Soc. Div. Petrol. Chem. Prepr.* **19**, 334 (1974).
3. Spenadel, L., and Boudart, M., *J. Phys. Chem.* **64**, 204 (1960).
4. Zaidman, N. M., Krasilenko, N. P., Kefeli, L. M., and Ratner, I. D., *Kinet. Catal. (USSR)* **11**, 604 (1970).
5. Somorjai, G. A., *J. Catal.* **27**, 453 (1972).
6. Germain, J. E., "Catalytic Conversion of Hydrocarbons." Academic Press, New York, 1969.

S. SIVASANKER  
A. V. RAMASWAMY

*Indian Institute of Petroleum*  
*Dehradun, India*  
*Received August 21, 1974*