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LETTERS TO THE EDITORS

Reducibility of Supported Rhenium

Interest in the reducibility of rhenium supported on alumina stems from the use of this element in bimetallic platinum/alumina reforming catalysts and the question of its role in such catalysts. Reduced rhenium would more likely be associated with the platinum while an oxidized form would probably interact with the alumina. Johnson and LeRoy (*1*) have reported that rhenium on alumina is reduced by hydrogen to the Re^{4+} state exclusively. Their conclusion is not consistent with the results of our experiments in which alumina-supported rhenium has been found to be completely reducible.

In the work reported here the extent of reduction was determined by hydrogen consumption and by oxygen taken up in reoxidation. Hydrogen was circulated over the catalyst in an all-glass system which included a trap at -196°C to remove water. A pressure of approximately 400 Torr (1 Torr = 133.3 N m^{-2}) was maintained by appropriately reducing the volume in a gas buret attached to the system. Reduction was carried out initially at 400°C followed by a period at 450°C as shown in Table 1. For reoxidation, the reduced and degassed catalyst was exposed to a measured amount of oxygen at 200 Torr, the temperature held at 400°C until the pressure remained constant, and the amount of oxygen was remeasured.

Samples were prepared by impregnating alumina (American Cyanamid Aero 100, surface area 227 m^2/g) with an aqueous solution of perrhenic acid, drying at 107°C for 16 hr, and calcining in flowing air at 482°C for 2 hr. The sample for a second trial was additionally calcined at 500°C for 3 hr.

The average of all nine values appearing in Table 1 is 7.0 ± 0.2 equiv/Re, which corresponds to $99.6 \pm 3.0\%$ reduction. The largest source of error is probably the rhenium analysis; however, the standard

TABLE 1
RESULTS

Trial:	I				II	
Sample wt (g)	5.00				5.14	
Re (%)	3.42 ± 0.03				3.64 ± 0.08	
Theor H_2 reqd (cc)	72.0 ± 0.6				78.8 ± 1.7	
Reduction	1st		2nd		1st	
Temp (°C)	400	450	400	450	400	450
Time at temp (hr)	19	4	69	24	26	41
Measd H_2 consum (cc)	72.2	73.4	71.2	72.3	74.3	77.5
Reduction (%)	100.3	101.9	98.9	100.4	94.3	98.4
Equiv/Re	7.0	7.1	6.9	7.0	6.6	6.9
O_2 consum (cc equiv H_2)	—	76.2	—	71.6	—	76.7
Reduction (%)	—	105.8	—	99.4	—	97.3
Equiv/Re	—	7.4	—	7.0	—	6.8

deviation (of triplicate determinations) is less than 3% in the worst case. The results shown in Table 1 have been corrected for the following blanks (for 5 g samples); H_2 consumed by the alumina alone, 1.5 cc at 400°C, 3.4 cc at 450°C; O_2 consumed by alumina alone after 450°C reduction, 2.0 cc; H_2 adsorbed by reduced catalyst, 1.8 cc; and O_2 adsorbed by oxidized catalyst, 0.6 cc. Adsorptions were determined at the conditions of reduction and oxidation.

Several possible reasons could be suggested for differences between these results and those of Johnson and LeRoy. Low concentrations of nonnoble metal oxides on refractory supports are known to be difficult to reduce; however, if as much as 1.18% Re (the concentration used by Johnson and LeRoy) reduced only to Re^{4+} and the remainder to Re^0, the average extent of reduction would have been only 81%. The higher concentrations of rhenium used in this work may have been present as larger particles, less influenced by the support, and therefore more easily reduced to Re^0. It should be noted that the sample for trial II, which had been more severely calcined, was definitely more difficult to reduce. Another and perhaps more significant difference is that Johnson and LeRoy used a static reduction with product water remaining in the system, whereas in this work the hydrogen was circulated with continuous removal of water. Yates and Sinfelt (*2*) also succeeded in completely reducing supported rhenium in flowing H_2 at 500°C. In their case, however, the catalyst was 10% rhenium on silica rather than alumina, another factor contributing to ease of reduction.

REFERENCES

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2. Yates, D. J. C., and Sinfelt, J. H., *J. Catal.* **14**, 182 (1969).

A. N. WEBB

Texaco Research Center
Beacon, New York 12508

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