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LETTER TO THE EDITORS

The Reducibility of Rhenium in Re on γ-Alumina and Pt–Re on γ-Alumina Catalysts

There has been considerable interest and controversy regarding the reducibility of rhenium when supported on γ-alumina, both in the presence and in the absence of platinum. The prime reason for the interest has been the desire to obtain an understanding of the nature and the role of the rhenium component in bimetallic reforming catalysts. Bolivar *et al.* (*1*) and Webb (*2*) have claimed that rhenium supported on γ-alumina is completely reduced to the zerovalent state by hydrogen at temperatures ranging from 400 to 550°C. Bolivar *et al.* (*1*) also found that platinum strongly catalyzes the reduction of Re_2O_7 supported on alumina. On the other hand Johnson and LeRoy (*3*) reported that rhenium on alumina is reduced by hydrogen to the Re^{4+} state exclusively. Explanations put forward (*2, 4*) to explain these discrepancies have been based on the different metal loadings and different conditions of reduction used by the various authors.

In most modern bimetallic reforming catalysts the total metal loading is $<1\%$w, yet in the reported work on the reducibility of rhenium (*1–3*) the metal loading is in excess of this value. In the work reported here the reducibility of Re on alumina, Pt on alumina and Pt–Re on alumina was investigated with metal loadings considerably less than 1%w total metal. The technique of temperature-programmed reduction (TPR) was used, a technique previously described in detail (*5*) for the characterization of Cu–Ni on silica catalysts. About 0.5 g of catalyst was required for each measurement. The sample was heated between 25 and 700°C at a programmed heating rate of 6°C/min. The reducing gas, a mixture of 6%v hydrogen in nitrogen, was passed through the reference compartment of a thermal conductivity cell, then through the catalytic reactor and finally via a cold trap through the other compartment of the thermal conductivity cell. In this way a profile of hydrogen consumed as a function of temperature was obtained. Specific species being reduced showed up as peaks in the profile. γ-Alumina spheres or powder were used as support for the catalyst. A catalyst of composition 0.2%w Re/alumina was prepared by impregnation of the alumina with perrhenic acid solution, one of 0.375%w Pt/alumina by impregnation with chloroplatinic acid solution, and one of 0.375%w Pt–0.2%w Re/alumina by coimpregnation with a solution of chloroplatinic and perrhenic acids. All catalysts were dried at 120°C and calcined at 525°C for 2 hr. Prior to TPR measurement all samples were dried at 400°C in nitrogen.

The Pt/alumina catalyst reduced in a single peak at 280°C and the Re/alumina in a single peak at 550°C. The Pt catalysts consumed 4 equiv of hydrogen and the Re catalysts 7 equiv of hydrogen, thus indicating that both Pt and Re were reduced in the monometallic catalysts to the zerovalent state. In the Pt–Re/alumina catalyst the TPR profile was simply the additive of the two profiles of the monometallic catalysts. Complete reduction of both

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metals to the zerovalent state was again found. However, since the TPR profile was identical to the additive of the two separate profiles it was concluded that no interaction between the Pt and the Re had occurred in this sample. This is a similar finding to the results for Cu–Ni on silica (*5*) where no interaction between Cu and Ni occurred in calcined catalysts which had been dried at 400°C in nitrogen prior to measurement, yet both metals could be completely reduced to the zerovalent state. However, as discussed below, the catalytic influence of metals such as Pt and Cu on the reduction of other metals depends critically on the catalyst preparation conditions.

It is difficult to relate TPR directly to the conditions used in reducing a typical reforming catalyst since TPR is a *dynamic* technique involving continued programmed heating at a rate of 6°C/min or higher while reducing. Thus we have reduced the Pt–Re/alumina catalyst at a series of fixed temperatures between 200 and 550°C but using the same detection system to monitor the reduction. The results are shown in Table 1. It is clear from these results that only a small fraction of the Re is reduced below 500°C within 60 min, in line with the TPR results. At 500 and 550°C the reduction of the catalyst is 81 and 95%, respectively, after 60 min.

TABLE 1

Isothermal Reduction of 0.375%w Pt–0.2%w Re on Alumina Calcined at 525°C

Temp (°C)	Extent of reduction[a] (%)		
	15 min	30 min	After 60 min
200	11	20	34
300	57	65	72
500	70	75	81
550	84	89	95

[a] Assuming that Pt and Re are in the 4+ and 7+ valency states, respectively, in the calcined catalyst.

TABLE 2

Dynamic Temperature-Programmed Reduction (TPR) of 0.375%w Pt–0.2%w Re on Alumina, Calcined at 525°C (Heating Rate 1°C/min)

Temp range (°C)	Hydrogen consumption (ml/g)	Extent of reduction[a] (%)	
		Pt	Re
25–300	0.9	100	0
25–500	1.5	100	76
25–700	2.2	100	100

[a] Assuming Pt and Re are in the 4+ and 7+ valency states, respectively, in the calcined catalyst.

We have also measured the reducibility of the Pt–Re/alumina catalyst using TPR over the range 25–700°C but with an extremely slow heating rate, namely 1°C/min; the results are given in Table 2. The results are in quite good agreement with the fixed temperature reducibilities given in Table 1. At 500°C approximately 80% of the Re is completely reduced to the zerovalent state. Bearing in mind the fact that a dilute hydrogen gas stream (6%v hydrogen in nitrogen) was used in these experiments and that Bolivar *et al.* (*1*) showed that the hydrogen pressure had a positive influence on the reduction of Re, it seems that with 100% hydrogen the remaining small amounts of unreduced Re would be reduced to the metal at such temperatures.

There remains an apparent discrepancy between our work and that of Bolivar *et al.* (*1*) regarding the influence of Pt on the reduction of Re. They found a marked positive influence of Pt on the reduction of Re, while in this work we found no such influence. Now the work reported here was done on catalysts calcined at 525°C and subsequently dried in nitrogen at 400°C and cooled in nitrogen prior to TPR measurement, whereas in the work of Bolivar *et al.* (*1*) the catalysts had only been dried at 110°C after impregnation. From previous work on Cu–Ni on silica (*5*) it was clear that samples that had been only dried at 100°C or which had been calcined at high temperature and allowed to cool in air gave different reduction profiles from samples which had been calcined then dried in nitrogen at 400°C and cooled in this gas to the temperature at which TPR measurement commenced. It seems that the degree of hydration of a metal oxide has a marked influence on its ease of reduction (*5*). Thus the difference in the case of reduction of the Re component in the catalysts described here and in the catalysts used by Bolivar *et al.* (*1*) might simply reflect the difference in the degree of hydration of the metal species in both types of catalyst.

Thus it is concluded that for low-load Re/alumina and Pt–Re/alumina catalysts at the reduction temperatures commonly used in the preparation of Pt–Re/ alumina reforming catalysts, the Re component is completely reduced to the zerovalent state.

REFERENCES

1. Bolivar, C., Charcosset, H., Frety, R., Primet, M., Tournayan, L., Betizeau, C., Leclercq, G., and Maurel, R., *J. Catal.* **39**, 249 (1975).

2. Webb, A. N., *J. Catal.* **39**, 485 (1975).

3. Johnson, M. F. L., and LeRoy, V. M., *J. Catal.* **35**, 434 (1974).

4. Johnson, M. F. L., *J. Catal.* **39**, 487 (1975).

5. Robertson, S. D., McNicol, B. D., De Baas, J. H., Kloet, S. C., and Jenkins, J. W., *J. Catal.* **37**, 424 (1975).

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