

The State of Rhenium in Pt/Re/Alumina Catalysts

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Received March 20, 1974

Various techniques were employed to characterize Pt/Re/alumina catalysts which had been reduced in hydrogen at 482°C. Upon leaching the reduced catalysts in HBF₄, most of the rhenium is found in the solution. Most of the platinum is found in the residue; its X-ray diffraction pattern shows no evidence for rhenium metal or Pt/Re alloy. Infrared spectra (in KBr) of these residues have a peak at 915 cm⁻¹ characteristic of Re-O bonds.

Pt/Re/alumina catalysts of varying promoter content were contacted with hydrogen at 482°C and 750 Torr. The initial disappearance of hydrogen is equivalent to reduction of platinum to metal, and to a change of three valence units of the rhenium, e.g., from Re³⁺ to Re⁴⁺. The subsequent rate of hydrogen adsorption is characteristic of adsorption by an oxide rather than by a metal. Furthermore, the slopes of the linear plots of adsorption vs log (time) are proportional to rhenium content.

Thus, rhenium is present in these catalysts as an oxide such as ReO₂, associated with the surface of the alumina. It is proposed that the hydrogenation activity of this oxide is responsible for reducing fouling due to coke during catalytic reforming, thereby accounting for the long-known ability of rhenium to increase catalyst stability.

INTRODUCTION

Alumina based hydrocarbon reforming catalysts including both platinum group metals and rhenium have long been known to minimize the catalyst activity loss during processing (1-3). Specifically, in work with platinum-rhenium-containing catalysts, it has been assumed by many that a Pt/Re alloy is the active species.

An experimental program was therefore undertaken to define the state of rhenium in these catalysts—the extent of alloying, if any, the state of subdivision, and the oxidation state.

EXPERIMENTAL

Catalysts

The high-purity aluminas used as catalyst supports were produced at the Engelhard Industries Division. They included: an η-alumina extrudate calcined at various temperatures to give BET surface areas varying between 180-430 m²/g; γ-alumina extrudates with areas from 239-256 m²/g; and a bead-form γ-alumina with a 264 m²/g area. The particular alumina used had no observable effect on the results reported here.

Catalysts were prepared from these aluminas by impregnation from solution, followed by oven-drying and calcination at 482°C in flowing dry air. Platinum was added as chloroplatinic acid, rhenium as ammonium perrhenate.

Hydrogen Consumptions

Hydrogen consumption measurements were made in a conventional volumetric adsorption apparatus which included a gas burette (B) constructed of carefully calibrated 5-ml bulbs and a burette-manometer (B-M) whose pressure side was calibrated from 0 to 5 ml, with graduations of 0.01 ml. The other side of the manometer was connected to another mercury manometer made of 15-mm bore tubing. Helium dead-spaces were run after degassing 16 hr at 482°C, to about 10^{-4} Torr or better. The catalyst samples (5–10 g) were immersed in a molten NaNO_3 - KNO_3 mixture, to minimize temperature gradients; the temperature was controlled by a Gardsman controller.

Hydrogen from a cylinder was admitted to the system by passage through 450°C copper turnings, Drierite, and P_2O_5 . Runs were started with a measured quantity of hydrogen in the B and B-M system by opening to the catalyst, still in the salt bath, at time = 0. Adjustments were made to the mercury levels in B and B-M to bring the internal pressure to 750 Torr, as closely as possible. At that time the two arms of the B-M were at the same level, and the pressure was read from the external manometer. The volume of the system was obtained from the position of the mercury in the B-M and the number of bulbs open in B. The quantity of hydrogen which has disappeared can then be calculated. The first reading for each run was obtained at 1.0 min, the second at 2–4 min; intervals between succeeding readings are progressively greater as the adsorption rate decreases. All readings were taken in the same manner as the first, with the two arms of B-M at the same level. When the volume in B-M had been exhausted, the mercury in B was elevated to fill one more bulb.

Pressure was never allowed to deviate from 750 Torr by more than 2%.

HBF_4 Leaching

In order to examine the X-ray diffraction (XRD) patterns of the metallic promoters it is necessary to remove the alumina support material. A fluoboric acid separation method was developed primarily for the determination of Pt crystallite size in reduced Pt/alumina catalysts. The mineral acid method solubilizes the alumina and collects the metallic Pt, without alteration, on 100 nm, 24-mm diam millipore filter paper. Later Pt/Re/alumina catalysts were included in the scope of the method. In addition, the procedure provides a means for determining percent soluble Pt and Re in virgin and reduced catalysts.

Among the elemental and oxide species examined for solubility behavior metallic Pt and Re were found to be insoluble in fluoboric acid but oxide forms of Re were very soluble.

Unless the unreduced catalyst were to be examined directly, the samples were first reduced under flowing hydrogen at 482 or 625°C. The latter temperature provides maximum conversion of Pt to the metallic state without alteration of the crystallite size. Leachings were carried out as follows:

Two grams of reduced catalyst are placed in a mixture of 20 ml 48% HBF_4 and 60 ml distilled water and held at 70°C with stirring until the alumina is dissolved and the metallic particles have agglomerated. The acid concentration is flexible but the minimum acid required to dissolve the alumina is suggested as a precautionary measure to avoid any Pt reduction in the solution through impurities present in the acid. The solution is removed by centrifugation and decantation; the insolubles are finally transferred to distilled water for filtering through a millipore assembly. The insolubles are thoroughly washed and dried. After drying, the residues are examined by XRD using $\text{CuK}\alpha$ radiation in a Phillips Norelco Diffractometer.

The combined solutions and wash-waters were analyzed by colorimetric method for platinum, and an X-ray fluorescence

(XRF) procedure for rhenium. In the latter method, rhenium was precipitated by H_2S in the presence of cellulose pulp and an internal standard; the solids were dried and formed into a disc for XRF examination. This method for rhenium analysis tends to give results which are too high. An improved procedure has been devised involving XRF examination of the solution, in comparison with standard solutions.

Estimates of the Pt/Re ratios in these leached residues were obtained by X-ray fluorescence. This is a relatively simple method, involving the ratio of intensities at two X-ray frequencies, with a suitable correction factor. Infrared spectra of leached residues were obtained using the KBr disc technique, with a Beckman IR-9.

RESULTS

When a Pt/alumina catalyst is reduced at $482^\circ C$ in hydrogen, then leached as described in the experimental section, the XRD pattern of the residue is that of platinum; relatively little of the platinum appears in solution. The same is true of platinum in Pt/Re/alumina catalysts, but not for the rhenium. Table 1 shows that the Pt/Re ratios in the residues are substantially greater than the Pt/Re ratios in the catalysts. Since substantially all of the

platinum is in the residues, this means very little rhenium in the residues. Analyses of the solutions confirm this conclusion, although there is not a very good rhenium balance in these results.

The XRD patterns for three of the Table 1 catalysts in Fig. 1 have Pt lines at 39.8° and at $46.2^\circ (2\theta)$, corresponding to d/n values of 2.26 and 1.96 Å, respectively. The crystallite sizes calculated from line-broadening range from 25–35 Å. Rhenium metal has three strong diffraction lines in this region, at 37.6° , 40.4° , and $42.9^\circ (2\theta)$, corresponding to d/n values of 2.39, 2.23, and 2.11 Å, respectively. No evidence for these lines is apparent in Fig. 1, largely, of course, because there is little rhenium present. These patterns are typical of many of this type which have been obtained.

Figure 2 contains corresponding XRD patterns for two residues from a reduced 0.6% Re/ γ -alumina. These residues were grayish in appearance; X-ray fluorescence identified the presence of rhenium in the residue, although most of the rhenium appeared in solution, as with the catalysts of Table 1. Neither pattern contains the three diffraction lines for rhenium metal in this region. Increasing the reduction temperature from 482 to $625^\circ C$ increased the intensity of the broad pattern which is ob-

TABLE I
LEACHING OF REDUCED Pt/Re/ALUMINA CATALYSTS

No.	Catalyst		Residue		Solution		
	Support	Area (m ² /g)	% Pt	% Re	Pt/Re	% Soluble Pt	% Soluble Re
18299	η -alumina	354	0.59	0.59	26	0.01	0.56
18228	η -alumina	(198) ^a	0.31	0.26	7.2	0.01	0.21
18172	η -alumina	189	0.61	0.66	11	0.02	0.51
18300	η -alumina	180	0.65	0.63	17	0.04	0.47
18322	γ -alumina	253	0.61	0.61	10	0.01	0.61
18216	γ -alumina	244	0.60	0.65	10	0.01	0.54
18358	γ -alumina	262	0.66	0.20	110	0.20	0.15
18360	γ -alumina	(262) ^a	0.62	0.40	20	0.05	0.57
18367	γ -alumina	(262) ^a	0.62	0.61	17	0.01	—
18372	γ -alumina	(262) ^a	0.61	0.89	11	0.02	0.87
18377	γ -alumina	(262) ^a	0.61	1.18	13	0.02	1.09

^a Estimated from other preparations using the same support.

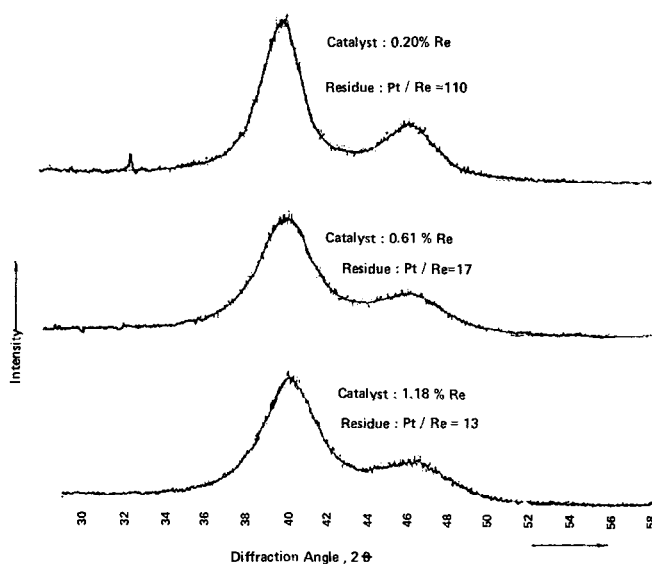


FIG. 1. XRD patterns of leached residues: 0.6% Pt/Re/ η -Al₂O₃, reduced at 482°C in H₂.

served. In addition to the 41° peak shown ($d/n = 2.15$), there is another broad band at about 22° ($d/n = 4.0$); these correspond to no rhenium compound listed in the ASTM XRD file.

Similar results were obtained when reductions were carried out at pressures as high as 300 psig of hydrogen. For example, a catalyst containing 0.32% Pt and 0.35% Re was treated at 510°C with hydrogen at 350 psig for 176 hr. After leaching this cat-

alyst, the residue again contained most of the platinum, with a crystallite size of 23 Å, and the solution contained most of the rhenium.

Another residue from leaching reduced Re/alumina, having an XRD pattern similar to those depicted in Fig. 2, was examined by infrared spectroscopy. In the 500–1200 cm⁻¹ region only one distinctive absorption occurred at about 915 cm⁻¹. This band was observed in a sample of ReO₃; it

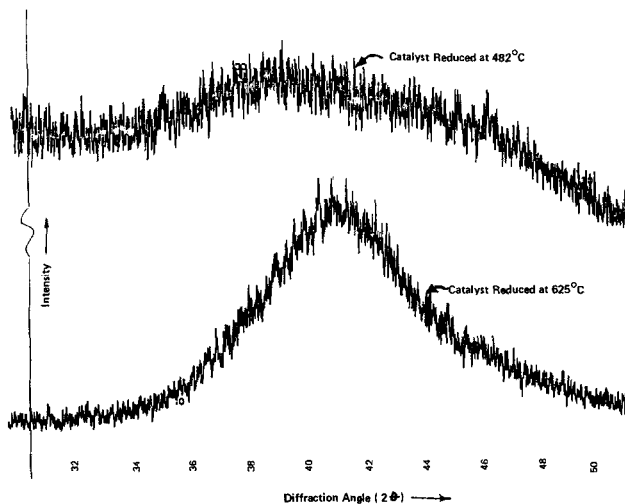


FIG. 2. XRD patterns of leached residues: 0.6% Re/ η -Al₂O₃, reduced in H₂ as shown.

is similar to the Re-O band reported for some perrhenic acid salts and for ReO_2 (4).

No absorptions were observed in the 620–780 cm^{-1} region which would have been indicative of undissolved alumina.

This residue therefore appears to be an insoluble oxide of rhenium, poorly crystal-lized, which represents a small fraction of the total rhenium content. It must have an oxidation state below Re^{+7} , since Re_2O_7 is water-soluble; otherwise it has not been identified.

Some typical hydrogen consumption results at 482°C and 750 Torr are in Fig. 3. In all cases there is an initial rapid disappearance of hydrogen largely due to reduction of the promoter metal oxides; this process is nearly complete at 482°C by the 1.0 min reading. The subsequent adsorption process follows the Elovich equation. Note that the same slope is obtained for the two 0.6% Re catalysts; the intercepts differ because of the platinum in one catalyst and not the other.

Rhenium was added to these catalysts as perrhenate ion, having Re in the +7 state. Calcination of perrhenic acid, or of lower oxides, at an elevated temperature yields Re_2O_7 (5). Therefore, the Re in the calcined catalysts will be +7. If it were to be reduced to metal, seven atoms of hydrogen per atom of rhenium would be required. Bulk Re_2O_7 is reduced to ReO_2 by hydrogen at 300°C, and to metal at 400°C (5). If the oxide is stabilized by incorporation into the alumina lattice, it would therefore not be

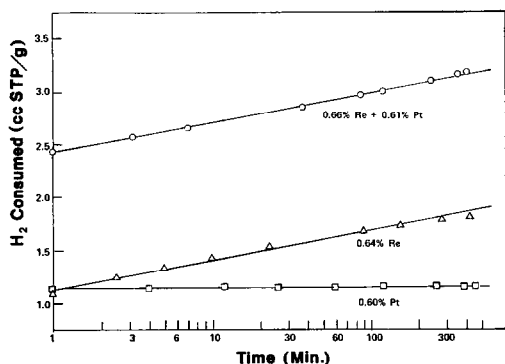


FIG. 3. Rates of hydrogen consumption at 482°C, 750 Torr, by catalysts supported on $\eta\text{-Al}_2\text{O}_3$.

too surprising to find that reduction to metal at 482°C is difficult, as indeed we observe.

Figure 4 is a plot of rhenium content vs hydrogen disappearance at 750 Torr and 482°C, at the arbitrary time of 1.0 min. The conclusions would not be altered if adsorption at a somewhat different time were chosen. To a first approximation this parameter represents the hydrogen consumed in reducing the platinum or rhenium oxides. It is estimated that the water of reduction will be absorbed by the catalyst, with a residual pressure of 0.1 Torr, and therefore is not a significant source of error. The lines are drawn to give the best fit of the data assuming a slope equivalent to $\text{H}/\text{Re} = 3$. As is evident, the data are quite consistent with that slope. It is therefore clear that Re^{7+} is reduced to Re^{4+} by hydrogen at 482°C.

The 1.0 min hydrogen consumptions attributable to reduction of platinum in Figs. 3 or 4 are equivalent to $\text{H}/\text{Pt} = 3.65\text{--}3.7$. A ratio of 4.0 is expected if all the platinum were in the 4+ oxidation state, and would be completely reduced.

Further hydrogen consumption rate data are in Fig. 5, for a series of $\gamma\text{-alumina}$ catalysts with 0.6% Pt varying in % Re from

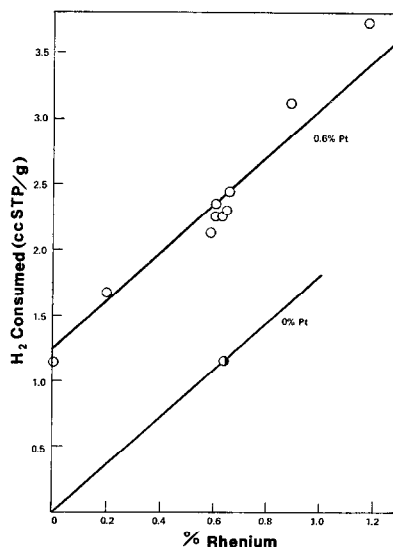


FIG. 4. Effect of rhenium content on H_2 consumed at 1.0 min, 750 Torr, 482°C.

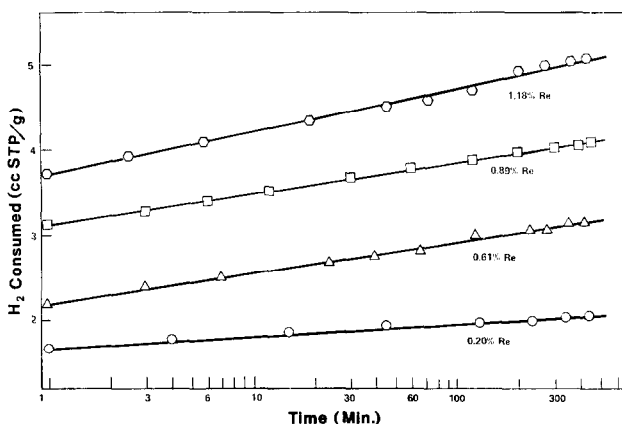


FIG. 5. Rates of hydrogen consumption at 482°C, 750 Torr, by catalysts containing 0.6% Pt and supported on η -Al₂O₃.

0.2 to 1.2%. Not only is there an upward shift due to hydrogen consumed by reduction, but there is also an increased slope. The effect of increasing rhenium content on rate of hydrogen adsorption is more clearly shown in Fig. 6 for all of the catalysts studied. Clearly, the rate increases as rhenium content increases. It is very nearly independent of platinum content and of support.

DISCUSSION

It is clear from the foregoing that the rhenium in Pt/Re/alumina or Re/alumina is not reduced to metal at the conditions

of normal usage in a catalytic reforming process. Furthermore, it is quite probable that most of the reduction which occurs does not proceed below the Re⁴⁺ state. Confirmation of this conclusion was obtained by one ESR experiment with the 0.64% Re sample of Fig. 3: in the calcined state only weak resonances due to impurities were observed, whereas reduction at 482°C produced a strong resonance signal. Re⁷⁺ and metallic Re have no unpaired electrons; Re⁴⁺ has unpaired electrons, and should therefore give a strong resonance signal.

Furthermore, the hydrogen adsorption rate data are not characteristic of adsorption by metallic surfaces, which adsorb hydrogen quite rapidly. On the other hand, hydrogen is adsorbed slowly over oxides of transition elements. The adsorption behavior shown here is similar to what the author has observed for MoO₃/alumina catalyst in which the Mo is known to exist in an oxidized form even after prolonged exposure to hydrogen at elevated temperatures.

One of the functions of platinum in a Pt/alumina reforming catalyst is to reduce the rate of deactivation by coke formation. Presumably, it does this by virtue of its ability to catalyze the hydrogenation of coke precursors. We have shown that the rhenium in a reduced Pt/Re/alumina exists as a lower oxide, probably ReO₂, distributed over the surface of the alumina.

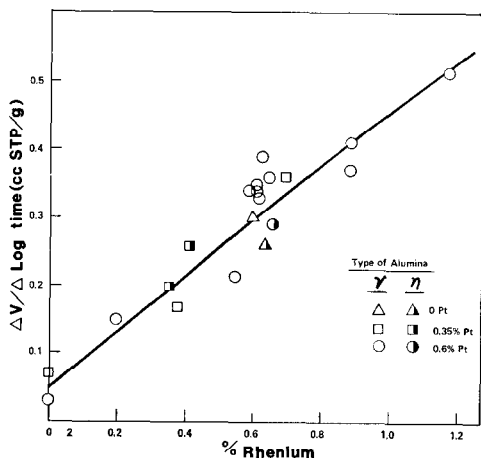


FIG. 6. Effect of rhenium content on rate of hydrogen adsorption, 482°C, 750 Torr.

Since rhenium oxides are known to have hydrogenation activity (6, 7), it seems reasonable to suppose that the surface oxide functions as a hydrogenation catalyst for specific coke precursors under conditions of catalytic reforming.

The ionic rhenium dispersed over the support is more available for catalysis than it would be if it were agglomerated into crystallites, as is the platinum. This view is supported by the relationship between rate of hydrogen adsorption and rhenium content, which suggests that all of the rhenium in these catalysts is accessible for activation of hydrogen.

The existence of rhenium in a two-dimensional phase, complexed with the alumina surface, has previously been suggested by Freel (8). The present work confirms his finding that reduction at 500–600°C does not produce metallic rhenium. On the other hand, Freel finds that the H₂–O₂ adsorptive behavior of Pt/Re/alumina is not additive with respect to Pt/alumina and Re/alumina. There is no suggestion of nonadditivity in the present work.

ACKNOWLEDGMENTS

The author is indebted to H. Erickson for the catalyst preparation, to A. W. Crowley for the

infrared and ESR data, to R. L. Terry for X-ray fluorescence results, to J. R. Hoffman and W. E. Kreger for assistance with other experimental work, and to J. Mooi for valuable discussions.

REFERENCES

1. CIAPETTA, F. E., AND WALLACE, D. N., *Catal. Rev.* **5**, 67 (1971).
2. NEVISON, J. A., DALSON, M. H., AND MOOI, J., *Prepr. Proc. Amer. Petrol. Inst. Div. Refining* (May, 1970).
3. RYASHENTSEVA, M. A., MINACHEV, KH. M., AND AFANASEVA, YU. A., *Neftekhimiya*, **2**, 37 (1962).
4. JEZOWSVA-TRZEBIATOWSKA, B., HANUZA, J., AND BALUKA, M., *Spectrochim. Acta* **27A**, 1753 (1971).
5. COLTON, R., "The Chemistry of Rhenium and Technetium." Interscience Publishers, New York, 1969.
6. DAVENPORT, W. A., KOLLONITSCH, V., AND KLINE, C. H., *Ind. Eng. Chem.* **60**, 10 (1968).
7. (a) BROADBENT, H. S., CAMPBELL, G. C., BARTLEY, W. H., AND JOHNSON, J. H., *J. Org. Chem.* **24**, 1847 (1955).
(b) BROADBENT, H. S., AND JOHNSON, J. H., *J. Org. Chem.* **27**, 4400 (1962).
(c) BROADBENT, H. S., AND SEEGMILLER, D. W., *J. Org. Chem.* **28**, 2347 (1963).
8. FREEL, J., *Prepr. Amer. Chem. Soc. Div. Petrol. Chem.* **18**, No. 1, 10 (1973).