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Platinum–Rhenium Interaction: A Temperature-Programmed Reduction Study

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A study of Pt, Re, and Pt–Re on γ-alumina catalysts was made by temperature-programmed reduction (TPR). As observed by others, an interaction occurs with Pt and Re when Pt–Re catalysts are preoxidized at 300°C or below; Re reduces at lower temperatures compared to Re/Al_2O_3. At 500°C preoxidation, TPR profiles of Pt–Re show no interaction and are similar to superimposed additions of Pt and Re spectra. Return of Re to the uncatalyzed state occurs on reoxidation at 500°C of Pt–Re catalysts previously exhibiting catalytic reduction. Intimate mixtures of Pt/Al_2O_3 and Re/Al_2O_3 particles, preoxidized at 300°C, also exhibit reductive interaction; however, loose mixtures of relatively large particles do not. It is proposed that H_2 spillover initiates Re oxide reduction by creating nuclei of Re which then catalyze the reduction of the remaining oxide. The overall mechanism is controlled by the rate of spillover which in turn is determined by the degree of hydration of the alumina surface.

INTRODUCTION

The activity decline rate of $Pt–Re/Al_2O_3$ reforming catalysts is lower than with Pt/Al_2O_3 (*1*). Several suggestions have been made for the increased resistance to deactivation of Pt in the presence of Re (*2–4*) and perhaps the most popular is the "alloy" theory (*2*) which proposes that Pt is modified by the intimate contact of Re in some form of mixed metal clusters. Some evidence for this has been provided by several techniques, including temperature-programmed reduction (TPR) studies (*5–7*). The TPR evidence is based on the observation that both Pt and Re reduce in a combined low-temperature peak when the Pt–Re catalyst has been dried below about 200°C, while Re, when present separately on the same alumina support, will reduce at a much higher temperature (approx 500°C). However, McNicol has shown (*7*) that Pt–Re, preoxidized at the operating temperature of reforming, 500°C, will reduce in two separate peaks similar to superimposed TPR profiles of Pt/Al_2O_3 and Re/Al_2O_3. Reasons for the catalyzed reduction of Re at lower drying temperatures have been ascribed to the high mobility of hydrated ReOx species which migrate to Pt centers (*6, 8*). Presumably at higher predrying temperatures the ReOx dehydrates and "alloy" formation is suppressed. However, infrared studies by Peri (*9*) showed no evidence for alloy formation with Pt–Re catalysts.

Also, Bertolacini and Pellet have shown that the enhanced performance of Pt–Re cosupported catalysts can also occur with mechanical mixtures of Pt/Al_2O_3 with Re/Al_2O_3 (*10*). They suggest that Re acts independently by reacting with certain coking intermediates which would otherwise deactivate Pt.

In light of this, a fresh TPR study has been made of the Pt–Re system which also includes an investigation into various mechanical mixtures.

METHODS

The TPR experimental procedure used was essentially that previously described by McNicol (*7*). The most significant modification was an *in situ* adsorbent trap of γ-

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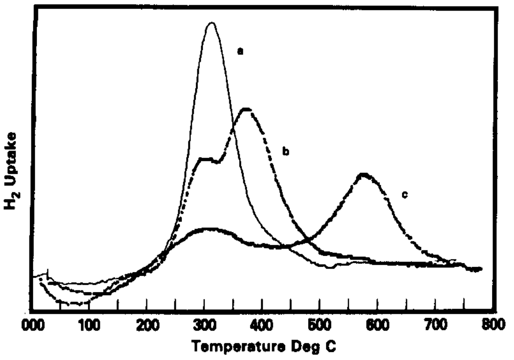

FIG. 1. Effect of preoxidation temperature on Pt–Re TPR. 0.35 wt% Pt–0.35 wt% Re/Al_2O_3. Preoxidized at (a) 100°C, (b) 300°C, (c) 500°C.

alumina and an oxygen adsorbent (Alltech's Oxy-Trap) housed in the reactor tube upstream of the catalyst and surrounding furnace. This addition was found essentially to remove last traces of O_2 and H_2O from the carrier gas.

Catalysts used in this work were prepared by impregnation of Cyanamid's Aero 1000 γ-alumina (14–20 mesh) with aqueous solutions of chloroplatinic and perrhenic acid, dried at 120°C, and then calcined for 2 h at 500°C. After calcination, all catalysts were aged for at least a week at room temperature to allow equilibration with atmospheric water vapor before use.

Pretreatment, in all cases, unless otherwise stated, was to heat each catalyst sample (approx 0.1 g) in dry air for 30 min to the specified temperature, cool in air to room temperature, regenerate the adsorbent trap, and then to switch to a mixture of 1% H_2 to Ar before running the TPR. The trap was regenerated by heating to 400°C in a reverse flow of H_2. The program heating rate was 20°C/min.

Calibration of H_2 uptake was made from the reduction profile of known amounts of pure RuO_2. Generally, TPR profiles accounted for 100% of the metal oxides present, assuming a +4 oxidation state for Pt and a +7 oxidation state for Re.

RESULTS

Pt–Re/Al_2O_3

The effect of the preoxidation temperature on the TPR profiles of a Pt–Re (0.35, 0.35 wt%) cosupported on alumina catalyst is shown in Fig. 1. The Re peak, initially at 560°C, moves to increasingly lower temperatures as the preoxidation temperature decreases, and eventually at 100°C preoxidation the Re peak merges completely with the Pt. Measurements of H_2 uptake indicates that the extent of reduction increases from approx 70% to approx 100% as the preoxidation decreases from 500 to 100°C.

Pt/Al_2O_3 and Re/Al_2O_3

The effect of 300 and 500°C preoxidation temperature of the TPR profile of a Pt/Al_2O_3 catalyst is shown in Fig. 2. Both

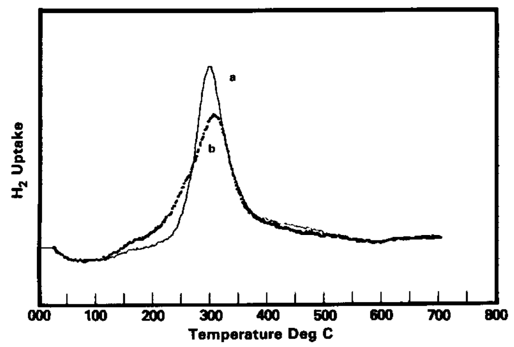

FIG. 2. Effect of preoxidation temperature on Pt TPR. 0.40 wt% Pt/Al_2O_3. Preoxidized at (a) 300°C, (b) 500°C.

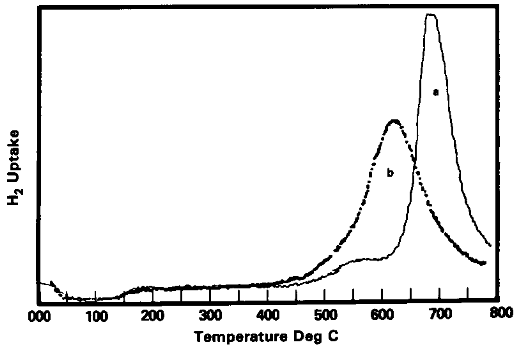

FIG. 3. Effect of preoxidation temperature on Re TPR. 0.35 wt% Re/Al_2O_3. Preoxidized at (a) 300°C, (b) 500°C.

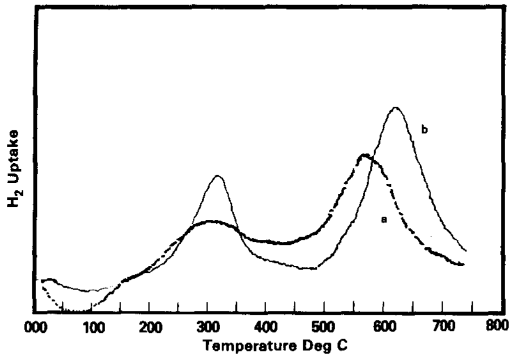

FIG. 4. TPR of Pt–Re vs superimposed Pt + Re. (a) 0.35 wt% Pt–0.35 wt% Re/Al_2O_3. (b) 0.4 wt% Pt/Al_2O_3 and 0.35 wt% Re/Al_2O_3. Preoxidized at 500°C.

peaks occur at about 300°C and there is a small broadening at the lower pretreatment temperature. Similar spectra are shown in Fig. 3 for a Re/Al_2O_3 catalyst, and in this case, differences are more pronounced with a shift to higher temperatures (80°C) at the lower preoxidation temperature; however, this slight shift to higher temperatures is in sharp contrast to the major shift to lower temperatures when Pt is present.

Comparison between Pt–Re/Al_2O_3 and a superimposed addition of Pt/Al_2O_3 and Re/Al_2O_3 run after the same preoxidation temperature of 500°C is shown in Fig. 4, and essentially these spectra are the same.

The observed difference in the Re reduction when Pt is present and after a 300°C preoxidation, could be due to the occupation of special Al_2O_3 sites by Pt which otherwise Re might interact; therefore, a series of TPR profiles were obtained with Re/Al_2O_3 catalysts at three different loadings of Re (0.35, 0.8, and 1.1 wt%) after a 300°C preoxidation. Results in Fig. 5 show that a shift in Re reduction does occur to lower temperatures from 670 to 520°C as the Re concentration increases from 0.35 to 1.1 wt%, but that this change does not explain the gross change when Pt is present (see Fig. 1). Measurements of the extent of reduction show an increase from approx 80% for 0.35 wt% Re to approx 100% for the 1.1 wt% Re catalyst.

Reoxidation

The reversibility of the catalyzed reduction of Re (after 300°C preoxidation) by reoxidizing at 500°C was also investigated. Reoxidation has previously been shown by Wagstaff and Prins (*6*) to decrease the reduction temperatures of both Pt and Re; consequently, a reference pair of runs (shown in Fig. 6) was made on a Pt–Re catalyst initially oxidized at 500°C and then reoxidized at the same temperature. On reoxidation, it is observed that the Pt reduction peak has moved from 300 to 150°C while the Re peak has shifted from 580 to 400°C. Figure 7 shows the corresponding results on the same catalyst after an initial oxidation of 300°C and a reoxidation of

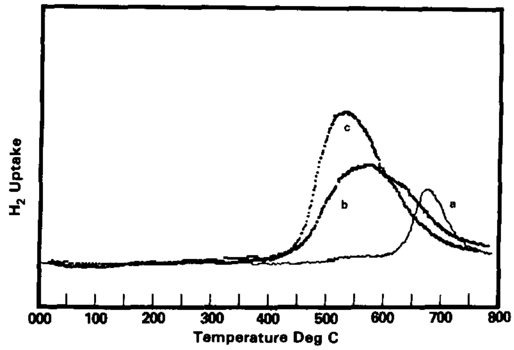

FIG. 5. Effect of Re concentration on Re/Al_2O_3 TPR. (a) 0.35 wt% Re/Al_2O_3, (b) 0.8 wt% Re/Al_2O_3, (c) 1.1 wt% Re/Al_2O_3. Preoxidized at 300°C.

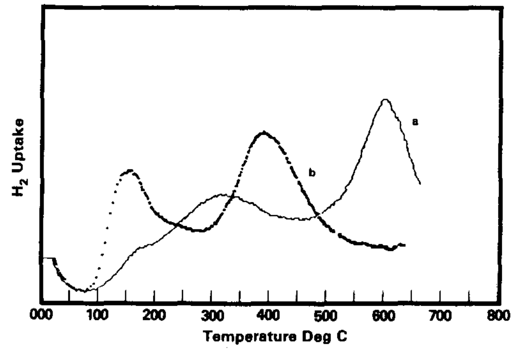

FIG. 6. TPR effect of reoxidation after initial oxidation at 500°C on Pt–Re. 0.35 wt% Pt–0.35 wt% Re/Al_2O_3. (a) Oxidized at 500°C; (b) reoxidized at 500°C.

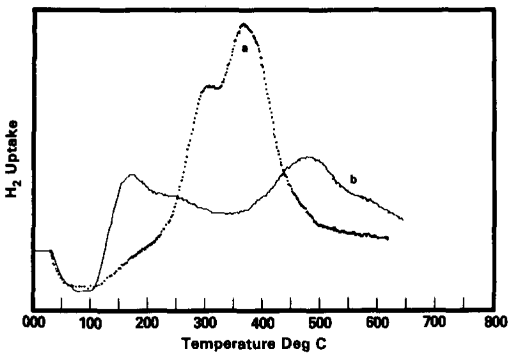

FIG. 7. TPR effect of reoxidation after initial oxidation at 300°C on Pt–Re. 0.3 wt% Pt–0.3 wt% Re/Al_2O_3. (a) Oxidized at 300°C; (b) reoxidized at 500°C.

500°C. Reoxidation again reduces the temperature of the Pt peak by the same amount; however, the Re peak has segregated from its combined state to a higher temperature of 470°C.

Pt and Re Mixtures

Figure 8 shows the TPR profiles after 300 and 500°C of a Pt and Re mixed catalyst system as prepared by Pellet and Bertolacini and quoted in their original paper (*10*). The catalyst was a 50/50 intimate mixture of 0.8 wt% Pt/Al_2O_3 with 0.8 wt% Re/Al_2O_3 to give an overall loading 0.4 wt% Pt and 0.4 wt% Re. The results show that after a 300°C preoxidation, the same catalyzed reduction of Re occurs as in the cosupported Pt–Re.

Other mixtures were also prepared. First, a loose mechanical mixture of relatively large particles (14–20 mesh) of Pt/Al_2O_3 and Re/Al_2O_3 showed no reductive interaction after 300°C oxidation. Attempts at making smaller particle mixtures resulted in a messy spectra due to the high pressure generated in the flow system from the tightly packed bed sample. However, to overcome this problem, a technique was devised consisting of compacting the smaller particles in a disk and then regranulating the sample to a 14–20 mesh size. Figure 9 shows the TPR of two such mixtures after 300°C oxidation which originally were made from 20–80 mesh and 200–320 mesh cuts, respectively. Both mixtures gave almost identical results, which shows that catalyzed reduction of Re had occurred in the same manner as in the cosupported catalyst. This method of preparing mixtures was tried on two different-colored Al_2O_3 particles. Microscopic examination of the final particles revealed that the integrity of the size, if not the shape, of most of the original particles was maintained.

DISCUSSION

It is evident from the results obtained and from previous work that the reduction characteristics of both Pt and Re on Al_2O_3 are very sensitive to the pretreatment conditions of which the preoxidation tempera-

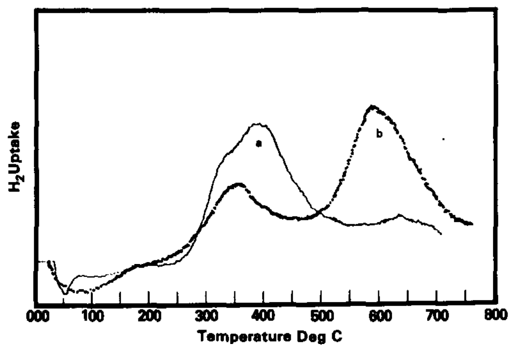

FIG. 8. Effect of preoxidation temperature on the TPR of a Pt and Re mixture. 0.8 wt% Pt/Al_2O_3 mixed 50/50 with 0.8 wt% Re/Al_2O_3. Preoxidized at (a) 300°C, (b) 500°C.

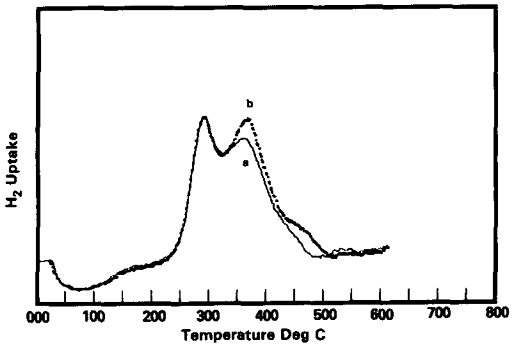

FIG. 9. TPR of Pt and Re mixtures at two different particle sizes. 0.3 wt% Pt/Al_2O_3 mixed 50/50 with 0.3 wt% Re/Al_2O_3 (0.2 g). Preoxidized at 300°C. (a) 20–80 mesh, (b) 200–325 mesh.

ture appears critical. It is believed that the main function of this preoxidation step is to dry the surface up to a certain level of dehydration while maintaining the metals present in their oxide form.

The reducibility of Re in the presence of Pt depends significantly on the preoxidation temperature as seen in Fig. 1. This is mainly in agreement with previous work (*5–8*) where interpretations of this effect tend to favor the theory based upon hydrated ReOx migration to Pt sites. Evidence to support this is given in the study by Bolivar *et al.* (*5*), who showed that a transfer of some Re to Pt particles occurred with mixtures of the two metals supported on Al_2O_3. In contrast, Bertolacini and Pellet (*10*) found no transport of metals occurring between particles of similar mixtures. However, the type of alumina support used can probably account for the discrepancy. Bolivar had used a low-area α-Al_2O_3 where possible vapor phase transfer of volatile Re_2O_7 had occurred, while Bertolacini had used a more typical high-area γ-Al_2O_3 where the support interaction would be significantly stronger.

Other factors to consider in the possible migration of Re are the TPR profile at the 300°C preoxidation or intermediate condition in Fig. 1. If Re migration occurs, it would be expected that between the two extremes of Pt–Re segregation and aggregation, an inversion in the size of peaks would occur as Re moves from its difficult to its easy-to-reduce position. However, the results show that no size inversion occurs, and that only the reducibility of the total Re peak changes. Similar conclusions about the lack of Re mobility may be reached from the results of reoxidizing at 500°C a previously "interacting" Pt–Re catalyst which shows peak separation occurring (Fig. 7). While it is possible that Re moves to Pt sites under hydrated conditions, it is less likely that these clusters, once formed, will separate again after a brief oxidation at 500°C.

While several interpretations of this data are certainly possible, a reasonable explanation for the catalyzed Re reduction might be that H_2 activated by reduced Pt moves to Re oxides sites via some undefined spillover mechanism which is dependent on the degree of hydration of the alumina surface (*12, 13*). A small fraction of the oxide contained in rafts or clusters becomes reduced to the metal. The Re metal nuclei then catalyzes the reduction of the remaining oxide. Catalyzed reduction of Re oxide by Re metal has been observed in other systems (*5, 14*). The whole process is dependent on the slowest step, probably the rate of H_2 spillover while the amount of active H_2 necessary to nucleate the reduction may be quite small. However, the results on the Pt and Re mixtures (Figs. 8 and 9) indicate that the active H_2 has to move relatively large distances to accomplish this reduction, and since the mixed particles have to be in close contact, movement of H_2 has to occur across the surface.

This proposed mechanism infers that Pt need be present at only low concentrations to catalyze the reduction of Re, and in fact it has been observed in a separate experiment that a catalyst containing 0.35 wt% Re and 0.01 wt% Pt will lower the reduction temperature maximum of Re to 410° compared to the reduction temperature maximum of 370° for a catalyst containing 0.35 wt% Pt after a 300°C preoxidation treatment. Taking the value of 28.5 kcal/mole for the activation energy for the rate of diffusion for H_2 spillover over an alumina surface (*15*), this equates to an approximate factor of 4 in difference in rates. This compares well with the difference in H_2 spillover rates of 3 observed for catalysts at 0.5 and 0.02 wt% Pt loadings by Ambs and Mitchell (*13*).

Isaacs and Petersen (*8*) have made a good argument against hydrogen spillover as a cause for this reduction effect, namely, that insufficient active H_2 can be generated under these conditions as calculated from kinetic data obtained by Kramer and Andre (*15*); however, the mechanism that is presented here requires only sufficient active H_2 to nucleate a small portion of the Re oxide.

The proposed nucleation or autocatalytic theory of Re reduction assumes ReOx to be present in some aggregated cluster. Freel has suggested the ReOx is present in Pt–Re reforming catalysts in a two-dimensional raft (*16*) and Yao and Shelef have provided both TPR and ESR evidence that these two-dimensional forms interact strongly with the Al_2O_3 surface and are hard to reduce (*17*). Programming the TPR at lower heating rates may lower this autocatalytic reduction of Re sufficient for it to become rate determining. This should be tried in a future study.

In the absence of Pt and the spillover effect, such variations of Re reduction that are observed in Fig. 3 can probably be ascribed to changes in the interaction between ReOx and the Al_2O_3 surface, although changes in the ReOx two-dimensional form might also vary the reducibility. These results indicate that reduction is facilitated a small degree when the surface is more dehydrated. Under the hydrated conditions, bridging between adjacent hydroxyl groups on Re and Al oxides may occur on dehydration during the reduction process resulting in stronger interaction (*18*).

The shift to lower temperatures of Re reduction, in the absence of Pt, shown in Fig. 5, on increasing the Re loading from 0.35 to 1.1 wt%, indicates that incremental Re is occupying Al_2O_3 sites of decreasing interaction energies. Measurements of the extent of reduction also suggest that at the low loading, a fraction of the Re is unreduced which could be ascribed to partial incorporation of Re to the Al_2O_3 support at the sites of highest interaction.

In summary, the presence of Pt causes catalytic reduction of Re when cosupported on γ-Al_2O_3 and preoxidized below 300°C, while reversal from catalytic to noncatalytic reduction occurs when Pt–Re is reoxidized at 500°C. However, the interactive reduction also occurs with intimate mixtures of Pt/Al_2O_3 and Re/Al_2O_3. A mechanism has been proposed containing the following four steps:

1. Activation of H_2 by reduced Pt.
2. Active H_2 transfer to ReOx aggregates across a hydrated Al_2O_3 surface (spillover).
3. Reduction of a small fraction of ReOx to Re metal.
4. Re metal nuclei catalyzing the reduction of the remaining oxide.

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