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On the Mechanism for the Platinum-Catalyzed Reduction of Rhenium in PtRe/γ-Al_2O_3

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The formation of mixed PtRe clusters and of separate clusters of Re and Pt has been studied by temperature-programmed reduction (TPR) for PtRe/Al_2O_3 catalysts of low metal loading. Mixed PtRe clusters are reliably detected by their specific catalytic selectivity for deep hydrogenolysis. Deuterium exchange of cyclopentane is not ensemble-specific and, therefore, useful to normalize the hydrogenolysis rates for extent of reduction and percentage metal exposed. It is concluded that formation of mixed clusters is highest if the Re precursor migrates over the support surface and becomes reduced in contact with a prereduced Pt particle. Hydrogen spillover appears to be limited to this direct contact of the reducible Re species with a Pt cluster. No catalytic effect of Pt on the reduction of Re is observed if the rhenium oxide is immobilized by the formation of a surface compound with γ-Al_2O_3. Upon hydrolysis of this surface compound, Re oxide regains its surface mobility and can, again, be reduced at significantly lower temperatures. © 1989 Academic Press, Inc.

INTRODUCTION

The superior performance of PtRe/γ-Al_2O_3 catalysts in naphtha reforming has stimulated considerable research effort. Numerous results indicate that these catalysts contain mixed clusters of Pt and Re atoms (*1–14*) and that the surface of these "alloy" particles is partially covered with sulfur atoms under industrial reforming conditions (*6, 11–14*). In 1975 Bolivar *et al.* (*1*) had shown with physical mixtures of Pt/α-Al_2O_3 and Re/α-Al_2O_3 that after reduction Re was detectable also on those support particles which initially contained only Pt. This result suggested a considerable mobility of Re or its precursors over the surface of these supports. In conformity with this, Bertolacini and Pellet (*15*) reported in 1980 that catalysts which were initially prepared as physical mixtures of separately supported platinum or rhenium displayed virtually the same steady-state performance as did samples which had been prepared by coimpregnation of both metals on the same support. Even more extensive migration over the support surface was indicated for zeolite-supported samples (*16*): a catalytic hydrogenolysis probe revealed that a physical mixture of Pt/NaHY and Re/NaHY after treatment under relatively mild conditions displays an activity which is similar to that of well-defined PtRe alloys or a PtRe/NaHY catalyst prepared by coimpregnation, but vastly different from that of either of the two separated metals. In this case, the chances for the migrating species to encounter their future alloy partner could be drastically lowered by simply diluting the physical mixture with an excess of inert silica. This dilution reduced the hydrogenolysis activity to a negligible level.

Conceivably related to the mobility of the oxidic rhenium precursor over the surface of its support is the phenomenon of Pt-catalyzed reduction of rhenium. Several reports show that under certain conditions, Re is reduced at a lower temperature and more extensively in the presence of platinum than in its absence (*1, 5, 7, 16–19*). It is also well documented that hydroxyl groups

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on alumina aid in this catalyzed reduction (*4, 7, 8*), although, thermodynamically, water should inhibit it.

Two mechanisms have been proposed to rationalize these observations. The first assumes that Pt activates H which spills over to the alumina support, diffuses to a Re_xO_y center, and reduces it (*17, 18, 20*). Indeed, it appears that hydrogen spillover is enhanced by a high concentration of surface hydroxyls on Al_2O_3 (*21, 22*). The effect of H spillover has also been claimed to be quite long range (*23*). On the other hand, it has also been proposed that an oxidic Re species first migrates to a Pt^0 nucleation center, where it is preferentially reduced (*5, 7*). It has been shown with Mössbauer spectroscopy that when Pd catalyzes the reduction of cosupported Fe, the small fraction of Fe which is reduced to the zero valent state is located only in bimetallic particles. This suggests that Fe is fully reduced only when its oxide is in direct contact with Pd^0 nucleation centers (*24*). In addition to this, many authors have shown the surface migration of oxidic species, such as MoO_3, WO_3, or Re_2O_7 over Al_2O_3 to be rapid, resulting in spontaneous monolayer dispersion at temperatures well below their respective melting points (*25, 26*).

In order to decide which of these mechanisms predominates during Pt-catalyzed reduction of Re/Al_2O_3 it is relevant to understand whether, in the reduced state, the metals are intimately associated. For if hydrogen spillover is significant, and the Pt and Re precursors are well separated, a majority of the Re species would be reduced in a position well removed from the Pt activator. This would result in a low concentration of bimetallic particles. On the other hand, if migration of an oxidic Re species to a Pt nucleation center is necessary for the enhanced reduction of Re, then the concentration of bimetallic particles would be very high; in fact, this concentration should equal the concentration of catalytically reduced Re. Experimental verification of either of these predictions is difficult; for $PtRe/Al_2O_3$, catalysts of industrial relevance contain less than 1 wt% total metal with an average metal particle of less than 2 nm. Consequently, typical physical methods of catalyst characterization are of limited applicability. Recently, however, we have developed a unique and very sensitive technique which can be used to detect the presence of PtRe bimetallic particles in these catalysts by making use of highly site-specific catalytic reactions (*19, 27*).

The effectiveness of this probe can be rationalized by considering that the activity of a heterogeneous catalyst can be best correlated with its ability to form chemisorption bonds. For catalytic reactions that require many contiguous active metal atoms, a mixed PtRe ensemble is particularly favorable, because it displays an intermediate heat of adsorption between Pt and Re. Hydrogenolysis of cyclopentane (CP), an ensemble-specific reaction, proves to be an excellent probe for the formation of bimetallic particles. The turnover frequency of this reaction is considerably greater for bimetallic catalysts prepared by coimpregnation onto the same support relative to physical mixtures of separately prepared monometallic catalysts. To ascertain whether the enhanced hydrogenolysis activity is related to the interaction of Pt and Re or a result of some other effect, such as changes in the percentage of metal reduced or exposed, a second reaction, which is catalyzed by a very small ensemble of active metal atoms and thus insensitive to the formation of bimetallic particles, is studied. The deuterium exchange of CP was shown to be such a reaction. The TOF is equal for the bimetallic catalyst relative to a physical mixture (*27*).

The primary objective of this work is to decide whether the formation of bimetallic PtRe clusters, as determined by the hydrogenolysis activity, correlates with the extent of Pt-catalyzed reduction of Re. We therefore combine temperature-programmed reduction (TPR) studies with catalytic tests for samples which have been treated under systematically varied prereduction conditions.

EXPERIMENTAL

All supported catalysts are prepared by the incipient wetness impregnation method. Cyanamid PHF γ-Al_2O_3 (surface area 180 m^2/g, pore volume 0.5 cm^3/g; mesh size 60–80) is the catalyst support. Solutions of $Pt(NH_3)_4(NO_3)_2$ (Alfa No. 88960) and NH_4ReO_4 (Aldrich No. 20416-1) in doubly distilled water are used for impregnation. In the case of the alumina-supported bimetallic catalyst, coimpregnation makes use of a solution containing both the Pt and the Re compound. After impregnation, the alumina-supported catalysts are dried at 120°C in an oven overnight, calcined at 500°C in flowing dry air for 2 h, and stored in bottles before use. The final loadings of the catalysts are 0.35 wt% Pt/Al_2O_3, 0.20 wt% Re/Al_2O_3, and 0.33 wt% Pt–0.22 wt% Re/Al_2O_3. These catalysts will be grouped together, for future reference, according to the technique used to prepare the bimetallic catalyst, which we have termed "coimpregnation."

The second preparation method started with impregnation of Pt onto γ-Al_2O_3 followed by calcination and reduction as above. The sample was then saturated with NH_4ReO_4 and dried overnight at 120°C and allowed to pick up moisture from the atmosphere for 1 week. The purpose of this is to avoid any high-temperature calcination step with supported Re prior to catalyst *in situ* treatments. The catalysts prepared in this way are 0.32 wt% Pt/Al_2O_3, 0.18 wt% Pt/Al_2O_3, 0.14 wt% Re/Al_2O_3, 0.41 wt% Re/Al_2O_3, 0.32 wt% Pt–0.14 wt% Re/Al_2O_3, and 0.18 wt% Pt–0.41 wt% Re/Al_2O_3. We will refer to this group of catalysts by the term "successive deposition" or, for brevity, "novel catalysts." Two samples, which were prepared in a similar manner but on Davidson Grade 62 SiO_2, had loadings of 0.86 wt% Re/SiO_2 and 0.43 wt% Pt–0.86 wt% Re/SiO_2.

Temperature - programmed reductions were done with a 5% H_2/95% Ar gas mixture. The temperature range was −80 to 550 or 700°C with a ramp of 8°C/min. The H_2 uptake was monitored by a Gow-Mac thermoconductivity detector (TCD) which was interfaced to a Zenith 158 personal computer for data collection and analysis. A molecular sieve trap, kept at −80°C, was placed after the catalyst and before the sample side of the TCD in order to trap out water before detection.

The hydrogenolysis of cyclopentane was done with a flow-type microreactor at atmospheric pressure, and products were analyzed with a Hewlett–Packard gas chromatograph. The reaction was carried out at 240°C, with a hydrogen-to-cyclopentane ratio of 9. The values reported in the tables were taken at 10 min time on stream. The deuterium exchange reaction was done in a batch-type microreactor at a pressure of 26 Torr and was constantly monitored with a Dycor mass spectrometer. The catalyst was kept at a temperature of 100°C, and the deuterium to cyclopentane ratio was 25. Metal surface areas were measured via hydrogen–deuterium titrations in the batch-type reactor. Details of the procedures, reagents, and equipment used have been outlined previously (*27*).

RESULTS

Catalysts Prepared by Coimpregnation

Previously we had shown (*16*) that the reduction profile of a coimpregnated catalyst preoxidized at 500°C resembles a superposition of the TPR profiles for the two monometallic samples. The reduction peak of Pt was at approximately 290°C, while the Re peak was located at 560°C, whereas, after a 100°C oxidation, Re was clearly reduced at lower temperatures, and the reduction profile was of two convoluted peaks at 205 and 275°C with a shoulder above 390°C. If it was assumed that all the Pt was reduced below 390°C, then a lower limit of 25–30% of the Re was reduced from the 7+ state to zero in these coreduction peaks. The total area of each profile showed that about 80% of the metals were reduced to zero from their highest oxidation state.

Catalysts Prepared by Successive Deposition

The TPRs of these samples were recorded either after drying in Ar at 500°C for 1 h or with no drying step at all. The Pt sample, in this case, had been prereduced and allowed to oxidize under ambient conditions. Its reduction profile is presented in Fig. 1, the upper trace is of the 0.18 wt% Pt and the lower is the 0.32 wt% sample. Two sets of peaks are obtained, a group is found at ~120°C and a single peak is at 380°C. The Pt is in the 4+ state and totally reduced. After an *in situ* oxidation step at 210°C for 1 h the reduction peaks shift to lower temperatures and the areas correspond to a reduction of Pt from the 2+ state.

Figure 2 shows the reduction profiles of NH_4ReO_4/Al_2O_3. For samples that had not been dried (upper trace), two reduction peaks, at 520 and 575°C, are visible. The integrated peak area corresponds to reduction from Re^{4+} to Re^0. This consumption agrees with the results of Coeffier *et al.* (*28*) who showed that, in a closed system, NH_4ReO_4 decomposes upon heating to yield ReO_2; i.e., the hydrogen of the ammonium cation participates in the reduction process. This does not occur in the 500°C Ar drying step, after which the TPR profile (lower trace) resembles that obtained after oxidation at 500°C (*16*). The hydrogen consumption, in this case, is adequate to reduce 82% of Re from 7+ to zero.

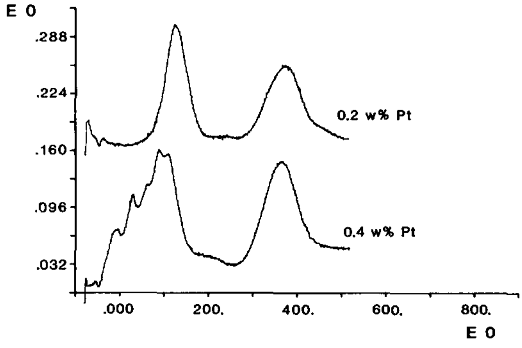

FIG. 1. TPR profile of prereduced Pt/Al_2O_3 which had been reoxidized under ambient conditions for at least 1 week. Upper trace is of 0.2 wt% sample; lower trace is of 0.4 wt% sample.

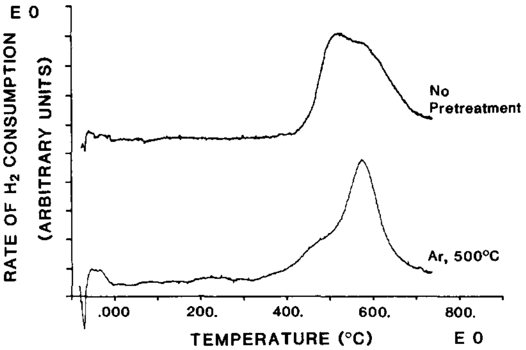

FIG. 2. TPR profile of 0.42 wt% Re/Al_2O_3. Directly reduced (upper trace) or after treatment in flowing Ar for 1 h at 500°C (lower trace).

Figure 3 represents profiles of the coreduction of Pt and Re in both the 0.18 wt% Pt–0.416 wt% Re (upper trace) and the 0.32 wt% Pt–0.14 wt% Re (lower trace) for the samples which were not dried. For both traces there are groups of low-temperature peaks located below 120°C resembling the low-temperature peaks of the respective Pt spectra (Fig. 1), except the areas of the peaks are increased. The maximum of the second peak is located in the 260–280°C range, and there is a shoulder above 390°C. The occurrence of two peaks and their positions are similar to what was observed by Wagstaff and Prins (*5*) after a gentle reoxidation of PtRe. If three hydrogen atoms from each equivalent of NH_4^+ are counted in the total hydrogen uptake, the consumption corresponds to a complete reduction of Pt from the 4+ state and Re from the 7+ state. The amounts of hydrogen consumed in the two coreduction peaks below 390°C correspond to 100% of the Pt reduction and about 90% of the Re reduction. The other 10% of Re reduction occurs in the high-temperature shoulder.

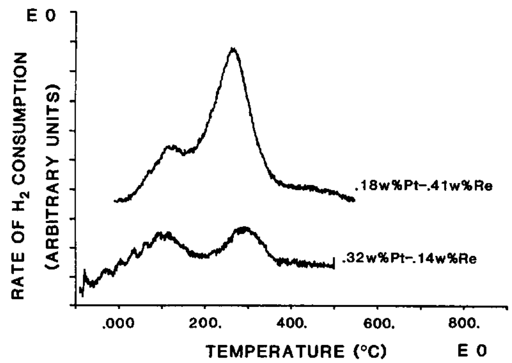

FIG. 3. TPR profile of PtRe catalysts prepared by successive impregnation and not dried prior to reduction. Upper trace is of 0.18 wt% Pt–0.41 wt% Re, and lower trace is of 0.32 wt% Pt–0.14 wt% Re (lower trace).

The profile of $Pt(NH_4ReO_4)/Al_2O_3$, predried at 500°C, is also very similar to the reduction spectra of severely calcined Re/Al_2O_3 (Fig. 4, upper trace). Little Pt reduction is seen. This has tentatively been ascribed to Pt reduction, prior to the TPR, by the decomposition of ammonium ion. This was checked by studying the decomposition of NH_4ReO_4/Al_2O_3 in Ar with a mass spectrometer as a function of temperature. The results are presented in Fig. 5. H_2 and N_2, resulting from NH_4^+ decomposition, were both detected in the gas phase. Decomposition reached its maximum rate at 180°C and was completed at 250°C. When Pt was present on the sample, H_2 evolution was completely suppressed. Yet the presence of this reduced Pt in these catalysts prepared by successive impregnation does not affect the reduction of Re. However, if this catalyst is allowed to be oxidized and rehydrated under ambient conditions for 1 week, the Re peak position shifts to 275°C due to an apparent Pt-catalyzed reduction of the Re (Fig. 4, lower trace).

We had also done a study with a similar catalyst, but using SiO_2 as a support. In this case both the bimetallic and the monometallic Re samples were dried for 1 h in Ar at 500°C, and yet, for this sample, Pt clearly catalyzed the reduction of Re (*16*).

Reoxidation Studies

Some reoxidation studies were done in order to determine the role of water in the reduction of Re. The results of these studies are presented in Fig. 6. After a reduction similar to that represented in Fig. 3 the catalyst was allowed to cool in H_2. It was then reoxidized at 210°C for 1 h and the TPR shown in Trace A was taken. In this profile the catalyzed reduction of Re is, again, apparent with most of the reduction occurring below 500°C, including a peak appearing at 390°C. The cooling step in H_2 after the first reduction results in atomic H adsorbed on the metal crystallites. This will lead to the formation of water during oxidation. In order to determine whether this water could play a role in the oxidation and subsequent reduction of the Re, a drying step in Ar at 500°C for 1 h was introduced between the first reduction and the reoxidation. The subsequent profile is shown in Trace B. It looks very similar to the previous TPR with the exception that the low-temperature peak ($<120°C$) grows at the expense of the species reducing at 390°C. The H_2 consumptions of each of these reductions correlate to full reduction of Pt from 2+ and Re from 4+ to zero. If the order of the drying and oxidation steps is reversed

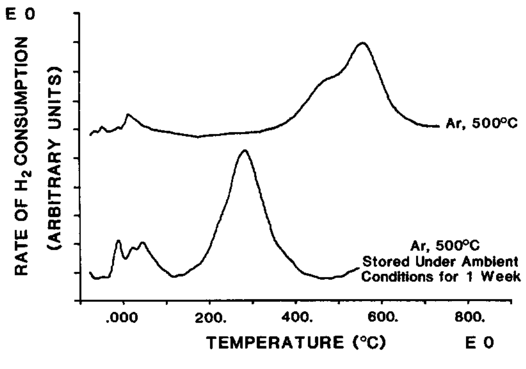

FIG. 4. TPR profile of 0.18 wt% Pt–0.41 wt% Re catalysts prepared by successive impregnation. The upper trace is after drying in Ar at 500°C for 1 h. The lower trace is after a 1-h drying at 500°, reduction, and storage under ambient conditions for at least 1 week.

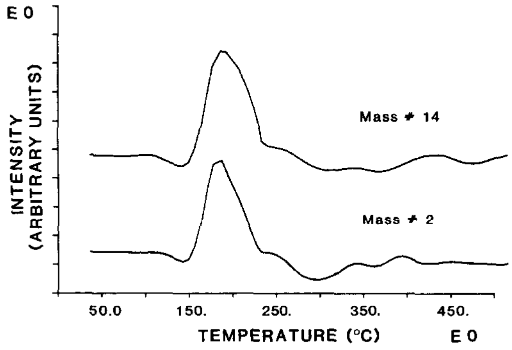

FIG. 5. Temperature-programmed decomposition of NH_4ReO_4/Al_2O_3. The upper scan is of mass number 14 (N), and the lower scan is of mass number 2 (H_2).

then the profile in Trace C results. In this profile the uncatalyzed Re reduction is again apparent.

Trace D in this figure is of a sample which had been treated in a fashion similar to that of Trace C, the difference being that before reduction an Ar stream which had been saturated with water at 0°C was passed over the catalyst for 3.5 min at a flow rate of 30 ml/min. In total, 25.9 μmol of water (three times the number of moles of Re on the surface) contacted the catalysts. It can be clearly seen that a large portion of the reduction peak of Re again shifts to lower temperatures.

Catalytic Studies

The catalysts were reduced prior to these studies according to information gained in the TPRs and thus the conditions were varied with different calcination pretreatments. All samples were reduced for 2 h. For the coimpregnated catalysts the first hour involved a temperature ramp from room temperature to 550°C, where the temperature was held for the next hour. In the case of the catalysts prepared by successive impregnation with no pretreatment, the temperature was ramped to 500°C in 1 h and held constant for the next hour; when they were dried at 500°C in Ar the reduction step consisted of 2 h at 500°C in flowing H_2. Metal surface area measurements via hydrogen–deuterium titrations (Table 1) indicate that after each treatment a comparable amount of active metal surface is produced, although after the 500°C calcination the measured metal dispersion is typically larger. The rates of the deuterium exchange of CP are presented in Table 1 along with the dispersion measurements. Previously we had shown that these reactions were ensemble nonspecific (*19, 27*). Again, in this study we see that the observed rates per gram catalyst change in a manner similar to that of the dispersion data, such that the turnover frequencies for the deuterium exchange of CP change very little with different pretreatment temperatures. The TOF will change, however, from sample to sample, because the relative amounts of reduced Pt and Re are different and these metals display a different intrinsic rate of exchange (*27*).

The TOFs for the hydrogenolysis reactions are very sensitive to the temperature of the oxidation/drying step. As shown before (*16*), for the coimpregnated catalysts the TOFs of overall hydrogenolysis and methane production were a factor of about 2 higher when the catalyst was preoxidized at 100°C than when the temperature of the

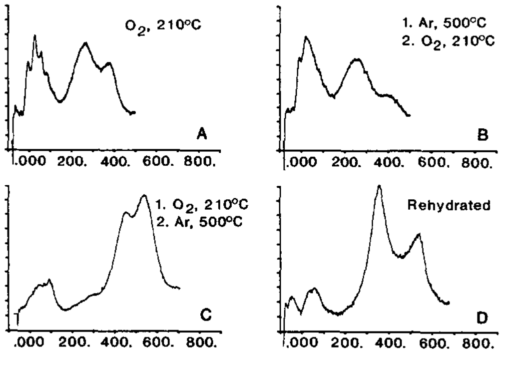

FIG. 6. Reoxidation studies of 0.18 wt% Pt–0.41 wt% Re prepared by successive oxidation. Trace A is after reoxidation at 210°C for 1 h; Trace B is after 1 h in flowing Ar at 500°C and 1 h in flowing O_2 at 210°C; Trace C is after 1 h in flowing O_2 at 210°C and then 1 h in flowing Ar at 500°C; Trace D is after 1 h in flowing O_2 at 210°C, 1 h in flowing Ar at 500°C, and rehydration with moist Ar for 3.5 min.

TABLE 1

Deuterium Exchange of Cyclopentane

Pretreatment	H/M	Disappearance of light cyclopentane H(μ-mole/g-cat.-s)	Exchange TOF (molecule/M_s-s)
0.32 wt% Pt, 0.14 wt% Re on γ-Al_2O_3, novel preparation			
(Ar, 500°C)	1.17	1.19	4.25×10^{-2}
No pretreatment	0.92	0.88	3.99×10^{-2}
0.18 wt% Pt, 0.41 wt% Re on γ-Al_2O_3, novel preparation			
(Ar, 500°C)	0.93	1.76	6.06×10^{-2}
No pretreatment	0.69	1.45	6.73×10^{-2}

Note. P_{D2} = 25 Torr; P_{CP} = 1 Torr; temperature = 100°C.

oxidation was 500°C. With the sample prepared by successive impregnation (Table 2), this increase is much greater, viz. a factor of at least 10 for overall hydrogenolysis and over 20 for methane production.

DISCUSSION

Temperature-Programmed Reduction

According to previous studies (*5, 7, 17, 18*) and from the present TPR results, it appears that Pt does not catalyze the reduction of Re in cases where the γ-Al_2O_3-supported bimetallic catalyst is pretreated at 500°C. This remains true notwithstanding whether the catalyst is treated in O_2 or Ar, and it is insensitive to the relative loadings of the metals and preparation conditions. The only decisive factor is the temperature of pretreatment.

Our results and those of other authors consistently show that coreduction does occur if the catalyst has not been pretreated, or was dried at a low temperature, before reduction. All these studies agree that coreduction takes place in the 250–300°C range (*5, 7, 17, 18*). Reduction of the catalysts prepared by successive impregnation is unique in that there is an additional coreduction peak at ~120°C (Fig. 3). The presence of this additional peak coincides well with the low-temperature reduction of Pt, which is observed in comparable monometallic Pt catalysts (Fig. 1).

All Pt samples treated at temperatures below 500°C before reduction exhibit two well-separated TPR peaks (Fig. 1). The low-temperature peak is located below 300°C, while the high-temperature peak is always located very close to 380°C. Two reduction peaks for Pt have been reported before for Pt supported on γ-Al_2O_3 (*29*). These have been attributed to two different phases of Pt, viz. a three-dimensional PtO_2 phase (low-temperature peak) and a two-dimensional oxide phase which interacts strongly with the support surface (high-temperature peak). The Pt in this surface oxide may be in the 4+, 2+, or zero valent state (*29, 30*). For mildly calcined bimetallic catalysts, the peak position of the Pt reduction of this two-dimensional oxide is shifted from 380 to <280°C. It appears that the strong interaction of platinum oxide with the support is decreased when rhenium oxide is present.

Catalytic Activity

As was stated above, the effectiveness of the probe reactions is based on the observation that the catalytic activity of a metal surface is closely related to the ability of that surface to form and break chemisorption bonds. Pt forms relatively weak chemisorption bonds with hydrocarbons, and

TABLE 2

Hydrogenolysis of Cyclopentane TOFs
(10^{-3} molecule/M_s-s)

Pretreatment	Cyclopentane consumption	Methane production	Enhancement in methane rate[a]
0.32 wt% Pt, 0.14 wt% Re on γ-Al_2O_3, successive impregnation			
(Ar, 500°C)	3.44	0.46	1.70
None	52.7	10.3	38.1
Physical mixture	6.14	0.27	1.00
0.18 wt% Pt, 0.41 wt% Re on γ-Al_2O_3, successive impregnation			
(Ar, 500°C)	15.7	1.97	5.97
None	155.	44.4	135.
Physical mixture	3.43	0.33	1.00
0.18 wt% Pt, 0.41 wt% Re on γ-Al_2O_3, reoxidized and reduced			
(O_2, 210°C; Ar, 500°C)	2.15	0.34	1.03
(Ar, 500°C; O_2, 210°C)	32.7	10.8	32.7
2.9 wt% Pt, 4.7 wt% Re on SiO_2			
Alloy	1780	1650	42.6
Physical mixture	69.7	38.7	1.00

Note. P_T = 1 atm; H_2/CP = 9; temperature = 240°C.

[a] Relative to physical mixture.

thus, the overall rate of conversion is limited by a low concentration of surface intermediates. With Re, on the other hand, the chemisorption bonds are rather strong, so that desorption limits the rate. When both metals combine to form a multiatomic site each atom will contribute to its overall nature, resulting in a composite heat of chemisorption intermediate between that of Pt and Re. The rate of a reaction which is catalyzed by a large ensemble of surface atoms, such as hydrogenolysis, should be sensitive to this effect and be faster on such a site exposing both Pt and Re atoms. Conversely, a reaction requiring small sites, consisting of only a few surface metal atoms, should be insensitive to bimetallic cluster formation. Deuterium exchange of hydrocarbons is a reaction of this type, so its rate should depend only on the number of exposed metal atoms.

With this in mind, the final state of each of these catalysts can be evaluated in terms of the normalized rates compiled in Ref. (*16*) and Table 2. When catalysts which have been prepared using different pretreatment conditions are compared, the rates of the hydrogenolysis reaction are markedly different. Catalysts which have undergone a less severe drying or oxidizing procedure display a higher hydrogenolysis rate than those catalysts which were pretreated at 500°C. We conclude that a larger amount of Re is intimately associated with Pt in the former case. The enhancements in rates are also greater with the catalysts prepared by successive impregnation than for those prepared by coimpregnation. This corresponds well with the observation that coreduction of Re with Pt is more pronounced for the novel catalysts (90%) than for the coimpregnated ones (25–30%). Enhancement factors for methane production relative to the physical mixture catalysts are also included in Table 2. For a high loading and extensively alloyed PtRe/SiO_2 catalyst (as determined by XRD), the enhancement factor for methane production, when compared to a sample where the Pt and Re were supported on different SiO_2 supports and physically mixed, was 42.6 for methane production when the TOFs were normalized with the H_2/D_2 titrations. With the novel preparations, which have not been dried, the enhancement factors are similar to or even larger than this. Therefore, we conclude that the Pt-catalyzed reduction of Re is a result of rhenium oxide migration prior to reduction.

It is also apparent from Table 2 that an increase in hydrogenolysis TOFs relative to corresponding physical mixtures is detected for both bimetallic catalysts that were calcined at 500°C. In these cases it seems likely that bimetallic cluster formation occurred after initial reduction by migration and agglomeration of unlike metal atoms, or particles, as has been previously postulated (*16*).

Factors Affecting Re Reduction

The nature of the oxidic Re species on the surface of Al_2O_3 has been studied extensively by several groups using a variety of spectroscopic techniques (*26, 31–37*). There seems to be general agreement that on a hydrated alumina surface the immediate symmetry of Re^{7+} resembles that of aqueous ReO_4^-, regardless of whether the rhenium precursor is Re_2O_7 or NH_4ReO_4 (*26, 34–36*). When the temperature of the catalyst is raised to 500°C the ReO_4^- tetrahedra are distorted, due to an increased interaction with the surface (*26, 34–37*). This behavior is reversible, such that when the surface is rehydrated ReO_4^- tetrahedra are again detected (*26, 34–37*). These results indicate that the free energy of the Re^{7+} species on a dehydroxylated surface is lowered by the formation of Re–O–Al bonds (*26, 33–35*). These bonds form an energy barrier for migration and cause Re to be more resistant toward coreduction with Pt than in either Re_2O_7 or NH_4ReO_4. When water is present, these bonds are hydrolyzed, and the Re species becomes more mobile.

The existence of these Re–O–Al bonds

implies that a rhenium/aluminum mixed oxide is formed at higher temperatures, although the precise nature of this species is still unclear. Edreva-Kardjieva and Andreev showed that the diffuse reflectance spectrum of this "surface compound" was similar to that of $Ba_3(ReO_5)_2$, but attempts to synthesize the corresponding aluminum mesoperrhenate proved unsuccessful (*34*). Baud and Capestan (*38*) synthesized Al $(ReO_4)_3$ from Re_2O_7 and α-Al_2O_3 at 450°C in N_2. This compound was thermally unstable in both H_2 and O_2 and decomposed well below 500°C.

The conditions necessary for the formation of the Re species resistant to migration, and, consequently, resistant to Pt-catalyzed reduction in our samples, were studied. This species does not form for a SiO_2-supported sample after a 500°C drying step (*16*). Figure 4 shows the reversibility of forming the migrating species from a strongly bound Re by simply allowing the catalyst to rehydrate and reoxidize under ambient conditions for 1 week. This is in full accordance with previous results (*26, 31–37*). We also see that there is a considerable energy barrier to forming this strongly bound Re. It has not been observed after a predrying temperature of 100°C (*16*) or a reoxidation temperature of 210°C (Fig. 6, Trace A). But Re needs to be in an oxidized state during the high-temperature treatment. The strongly bound Re cies is not formed when the reduced catalyst is subjected to flowing Ar at 500°C for 1 h (Fig. 6, Trace B). In addition, even though water appears to play a role, the large amounts of water produced during reduction of a metal oxide appear to not affect the reducibility of Re when in the presence of Pt (*16*). These data indicate that, for our samples, the Re–O–support bond is established:

(i) on γ-Al_2O_3,

(ii) prior to reduction, and

(iii) resulting from severe predrying, in which Re was in an oxidic state.

Three functions which water can serve in facilitating the mobility of Re on γ-Al_2O_3 have been investigated. First, extensive work by Peri shows that if alumina is treated at temperatures of 100°C or below, there will exist at least a monolayer of OH groups on the surface. When the temperature of dehydroxylation is 500°C, more than 70% of this water is desorbed from the surface, via condensation of the hydroxyl groups, leaving exposed Al^{3+} behind (*39*). Consequently, it may be thought that surface water renders the Al_2O_3 surface less reactive by passivating the Al^{3+} Lewis acid centers, so they cannot form Re–O–Al bonds. Second, it has been postulated (*7*) that, since Re_2O_7 is very hygroscopic, a solvated complex may be formed on a hydrated surface which would facilitate migration by limiting the interaction of the rhenium species with the support surface. Or, third, as has been indicated by spectroscopic data (*26, 31–37*), the presence of water may prevent a Re–O–Al bond from forming or hydrolyze it once it has been formed.

If a reduced 0.18 wt% Pt–0.41 wt% Re catalyst is reoxidized in flowing O_2 at 210°C, the reduction pattern (Fig. 6, Trace A) is very similar to the initial TPR of this catalyst (Fig. 3, upper trace). The differences are that the low-temperature peaks are more pronounced, and a new feature at 390°C appears. The similarities between this profile and that of Fig. 3 indicate that during this oxidation significant segregation of the two metal oxides takes place, but the species responsible for the TPR peak at 250°C, that has been attributed to a Pt-catalyzed reduction of Re, is again visible in the profile. There are no peaks at temperatures >450°C that are typical for Re reduction in a monometallic sample.

In the reduction represented in Fig. 6, Trace A, a small amount of water, in excess of the water produced from reduction, should be present early in oxidation, since the catalyst was allowed to cool in H_2 prior to oxidation, and the alumina surface should be fairly well hydroxylated. In order to drive off the small amount of chemisorbed H_2 and put the support in a partially dehydroxylated state similar to that in the severely calcined samples, the catalyst was held at 500°C for 1 h in flowing Ar prior to reoxidation. Trace B of Fig. 6 results. There is little difference in the reduction profile respective of Trace A. There are also considerable enhancements in hydrogenolysis activity for a catalyst prepared in this way relative to a physical mixture (Table 2). This indicates that neither hydroxyl passivation of Al^{3+} centers nor significant hydration of the oxidic Re species is important for Re migration to occur. Yet, if only the order of the drying and oxidation steps is reversed, the strongly bound Re–O–Al species, characterized by reduction peaks above 450°C, is formed (Fig. 6, Trace C). The evidence from the reaction studies also supports this conclusion, for the hydrogenolysis activity of this catalyst, reported in Table 2, is rather low. If this catalyst is hydrated prior to reduction with a very small amount of water, a majority of the Re–O–Al bonds appear to be hydrolyzed, the oxidic Re species is again mobile, so that the reduction of Re can, again, be catalyzed by Pt (Fig. 6, Trace D).

CONCLUSIONS

From TPR results and reaction studies we conclude that the Pt-catalyzed reduction of Re results in the formation of a significant number of zero-valent PtRe clusters, and, as more Re is coreduced with Pt, there are more bimetallic clusters formed. This follows from the comparison of the sample prepared by successive impregnations with a coimpregnated catalyst. We propose that the mechanism of PtRe coreduction involves migration of an oxidic Re species over the support surface to a zero-valent Pt center, where it can be reduced by activated hydrogen. This view is substantiated not only by the results in Table 2 but also by the rates of deuterium exchange of CP. Enhanced surface migration of Re implies that fewer and larger metal particles are formed. Indeed, measured rates of deuterium exchange per gram of catalyst indicate that the metal particles are larger in the catalysts where Re reduction takes place at a lower temperature due to the presence of Pt (Table 1).

These conclusions agree with those of Wagstaff and Prins (*5*) and Isaacs and Petersen (*7*) as well as with the results of Ziemecki *et al.* who have studied the catalyzed reduction of Re in $PdRe/Al_2O_3$ catalysts and concluded that mixed metal crystallites are formed due to the migration of Re to Pd nucleation centers during reduction (*40*).

Spectroscopic studies and the present TPR results are in full accordance, suggesting that a treatment at 500°C causes a strong interaction between rhenium oxide and the Al_2O_3 (*26, 31–37*). The formation of the surface complex inhibits the migration of Re. Water will hydrolyze the surface-to-Re bond (*26, 31, 34, 36*) so that the Re species becomes mobile and can migrate to Pt nucleation centers where it can be reduced at a lower temperature. Water is not needed for this purpose if formation of the strongly bound Re species is prevented by avoiding high-temperature treatments with oxidic Re supported on γ-Al_2O_3.

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