

Surface Mobility of Re_2O_7 in the System $\text{Re}^{7+}\text{Pd}^0/\gamma\text{-Al}_2\text{O}_3$

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Effect of hydration on the mobility of Re_2O_7 on $\gamma\text{-Al}_2\text{O}_3$ in the system $\text{Re}^{7+}\text{Pd}^0/\gamma\text{-Al}_2\text{O}_3$ was investigated by TPR and XRD techniques. In samples dried at 110°C , reduction of Re_2O_7 takes place with $T_{\text{max}} = 47^\circ\text{C}$, i.e., at a temperature lower by ca. 400°C than that observed in the absence of metallic palladium. The low-temperature migration of Re_2O_7 to preexisting Pd^0 crystallites, where reduction takes place, is consistent with the Tamman temperature of Re_2O_7 . This mechanism is supported by the observed interaction between Pd and Re, manifested by the decreased formation of palladium hydride and by changes in the X-ray diffraction spectra. Dehydroxylation of alumina at 500°C causes interaction between Re_2O_7 and Al_2O_3 to occur, hindering the surface migration. In dehydrated samples most of the rhenium heptoxide is reduced away from Pd crystallites above 400°C . © 1986 Academic Press, Inc.

INTRODUCTION

Bimetallic catalysts containing rhenium, mostly $\text{Pt-Re}/\gamma\text{-Al}_2\text{O}_3$, have been extensively investigated in recent years. Controversy still exists as to the degree of alloying of the metallic components [literature supporting alloy formation, see Ref. (1); literature arguing against alloying, see Ref. (2)], and even as to the oxidation state of rhenium in the reduced catalyst (3, 4). In two recent papers (5, 6) in particular attention was focused on the mechanism through which reduction of Re_2O_7 is facilitated by the presence of the Group VIII metal. Wagstaff and Prins (5), and subsequently Isaacs and Petersen (6), concluded on the basis of temperature-programmed reduction (TPR) experiments that the degree of hydration has a decisive effect on the ease of reduction of Re_2O_7 in the $\text{Pt}^{4+}\text{-Re}^{7+}/\text{Al}_2\text{O}_3$ catalyst precursor. It was found that both metals are reduced to the zerovalent state, and exist as bimetallic clusters in samples that have not been dried extensively prior to reduction. A single reduction peak in the range $250\text{--}300^\circ\text{C}$ was observed by the above authors, "implying mobility of rhenium oxides on $\gamma\text{-Al}_2\text{O}_3$ surface above 250°C " (5).

However, analogous TPR profiles in the same system were more recently explained by Mieville (7) as a manifestation of hydrogen spillover. Clearly, one cannot distinguish between possible mechanisms which cause acceleration of reduction of Re^{7+} in bimetallic catalysts on the basis of TPR results alone. What is needed is an independent and unambiguous determination of interaction (or lack of it) between a Group VIII metal and Re in the reduced catalyst.

Easy formation of $\beta\text{-PdH}$, and the known dependence of the extent of hydride formation on the degree of Pd alloying, offers an unique opportunity to monitor alloying in the Pd-Re system. In this work supported and unsupported preparations containing heptavalent rhenium and zerovalent palladium were examined. The TPR results and measurements of the H/Pd ratio in palladium hydride were supported by *in situ* X-ray diffraction experiments. The experimental strategy was to first firmly establish the changes in hydride formation, and shifts in the X-ray diffraction pattern, associated with Pd-Re alloy formation. This was

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achieved using the unsupported Pd⁰-Re⁷⁺ mixtures. Then the effects of interaction between the metals in the 3% Re⁷⁺ 3% Pd⁰/γ-Al₂O₃ system were probed.

EXPERIMENTAL

The temperature-programmed reduction (TPR) apparatus was constructed following the concept proposed by Robertson, Jenkins, and co-workers (8, 9). Several modifications were made to allow for observation of not only temperature-programmed reduction, but also of reoxidation, absorption of hydrogen on cooling the sample directly after the TPR run in flow of H₂/N₂, and thermal desorption of hydrogen.

Reduction was carried out in a flow of 5% H₂ in N₂ (Air Products, Ultra Pure) dried and deoxygenated by passing through Alltech traps. Reoxidation runs were done in premixed 2% O₂ in He (Matheson certified). Flow rates were set at 60 ml/min (STP) using mass-flow controllers (Tylan, Model 260). The dead volume in the apparatus was minimized by using 1/8-in.-o.d. thick-wall stainless-steel tubing, quartz inserts in the reactor tube and crushed quartz in the cold trap. A low-mass heater was manufactured by winding 1/8-in.-o.d. rod heater (Aerorod, ARI Industries) around a brass cylinder fitted tightly on the 3/8-in. stainless-steel tube used as the reactor. Temperature of the catalyst was monitored by an internal thermocouple located axially and in contact with the catalyst bed, while a separate external thermocouple was connected with the temperature programmer (Valley Forge Instrument Co., Model PC 1180).

TPR experiments were carried out in the temperature range -40 to 650°C. Small sample size (typically 75 mg) and fast heating rate (50°/min) were used. It was demonstrated in separate experiments that the areas under the reduction profiles of Pd²⁺/Al₂O₃, recorded at five different heating rates between 5 and 50°C/min, agree to within ±7%.

Before each TPR run samples of catalyst were routinely dried *in situ* at 110°C for 30 min in a stream of dry nitrogen. Dehydration, when indicated in text, was done by passing dry nitrogen at 500°C for 2 h. Rehydration of the sample dried previously at 500°C was done by passing a stream of helium, saturated at room temperature with water vapor, through the catalyst bed at room temperature for 1 h.

The presence of palladium hydride can be detected directly in the TPR apparatus by following the hydrogen uptake observed during cooling of samples in a flow of H₂/N₂ immediately after the reduction run, and/or by thermal desorption of hydrogen associated with β-PdH. In the X-ray diffraction experiments the presence of hydride is easily observable due to the characteristic shift of Pd reflections to lower scattering angles.

Two channels of data were recorded and stored in the computer for each TPR run: a measure of imbalance of the thermal conductivity detector vs time, and internal thermocouple indications vs time. The data stored in the first channel allowed for integration of the area under the curve, while cross-plotting of the two data channels with elimination of the time variable gave the TPR profile.

All the catalysts contained nominally 3% (wt) of Pd and Re and were prepared by impregnation of Catapal γ-Al₂O₃ manufactured by Conoco (BET surface area 191 m²/g) with H₂PdCl₄ and Re₂O₇ solutions. The bimetallic catalyst was prepared by deposition of Pd²⁺, reduction to Pd⁰, and further impregnation with Re₂O₇ followed by drying at 110°C. The metals content in the bimetallic catalyst was measured to be 2.91% Pd and 3.04% Re. The unsupported preparations investigated included physical mixtures of Pd black with salts of Re⁷⁺ (both KReO₄ and Re₂O₇), and Re₂O₇ impregnated on Pd black. The atomic ratio of Pd to Re was close to 1:1 in all the cases. These preparations were used undiluted in XRD experiments, and diluted (1:1 by weight) with crushed quartz in the TPR runs.

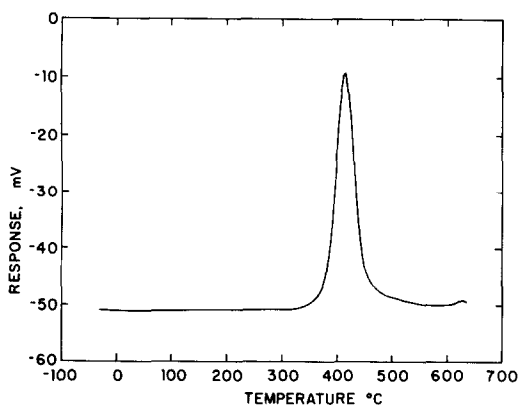


FIG. 1. TPR profile of Re_2O_7 supported on $\gamma\text{-Al}_2\text{O}_3$.

The *in situ* X-ray diffraction patterns of the catalysts were obtained from an automated microreactor, designed by Jones (10), attached to a microprocessor-driven Rigaku Theta-Theta wide angle goniometer. The reactor was operated in horizontal mode and controlled by an INTEL 8-bit SBC 80/204 single-board computer with 48K of RAM. The goniometer stepper motor drive, a Fluke temperature indicator, and an ECS temperature controller and soft-start power pack for reactor temperature control were integrated into a versatile data acquisition and display system through interface hardware and PLM software.

The wide-angle diffractometer was equipped with a long fine focus copper target, driven by a 3-kW Rigaku generator. All scans were collected at 40 kV and 25 mA with 2-degree divergence slits and 0.30-mm receiving slits.

The X-ray *in situ* microreactor can be heated to ca. 700°C. Two sheathed iron-constantan thermocouples referenced at 25°C were used as sensors for the temperature controller. The reactor can be operated under various reducing, inert, or oxidizing gas environments, at variable pressures and flow rates. Inert gas (nitrogen), and 4 and 8.5% H_2 in helium as the reducing medium, flowing at 15 ml min^{-1} , were used in experiments described in this work.

RESULTS

Temperature-Programmed Reduction

Rhenium heptoxide supported on Al_2O_3 and dried at 110°C undergoes reduction in a single-step event at temperatures around 450°C. This is shown in Fig. 1. The reduction profile is surprisingly narrow, and does not support a stepwise reduction mechanism with intermediate formation of several lower oxides of rhenium, each transition occurring at its own characteristic temperature. Contrary to this, it appears that a series of fast transitions between Re^{7+} and Re^0 takes place at and near the T_{max} .

In the presence of metallic palladium reduction of Re^{7+} is accelerated. Curve 1 in Fig. 2 shows the TPR profile of Re_2O_7 deposited on previously prepared $\text{Pd}^0/\text{Al}_2\text{O}_3$. A very strong catalytic effect of Pd^0 on the reducibility of Re^{7+} is observed. The T_{max} is now 47°C, and is shifted by close to 400°C from its position observed in the absence of palladium. Integration of the area of the main reduction peak indicates that about 90% of the overall Re^{7+} reduction takes place in the temperature range 0–100°C.

This situation is, however, completely altered if the sample has been extensively dehydrated (2 h in flow of dry nitrogen at 500°C) prior to reduction, as shown in curve 2 of Fig. 2. The uptake of hydrogen

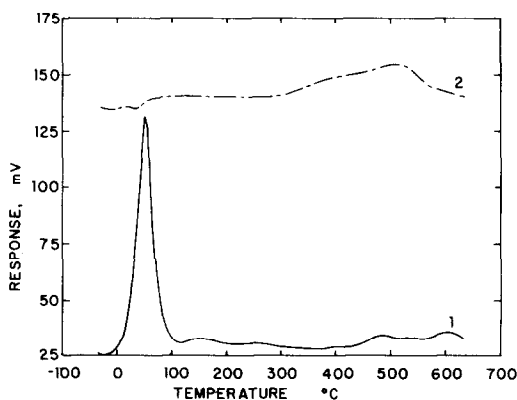


FIG. 2. TPR of $\text{Re}^{7+}\text{Pd}^0/\text{Al}_2\text{O}_3$. (1) Dried at 110°C; (2) dried at 500°C.

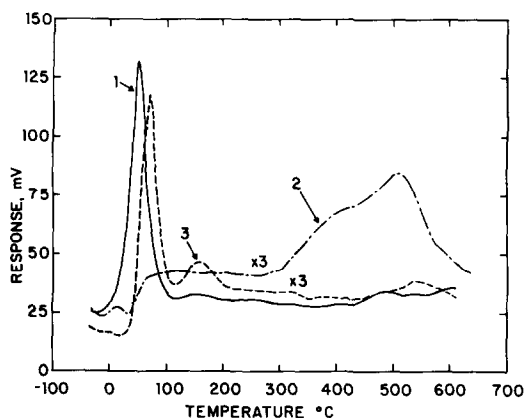


FIG. 3. Effect of dehydration and rewetting on TPR of $\text{Re}^{7+}\text{Pd}^0/\text{Al}_2\text{O}_3$. (1) The original sample, dried at 110°C ; (2) after drying at 500°C ; (3) after drying at 500°C and rehydration at room temperature. The Y coordinate is magnified by a factor of 3 in curves 2 and 3.

starts above 50°C and continues, at a low rate and without distinct maxima, above 300°C . Only a broad reduction peak appears, with a shoulder at 400°C , and a maximum at ca. 510°C . This is better visible in Fig. 3, where the Y coordinate of curve 2 is magnified by a factor of 3. Extension of the main reduction peak to temperatures higher than the T_{max} observed for $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ (Fig. 1) is most likely associated with the presence of smaller crystallites of Re_2O_7 , produced by spreading of the oxide during the drying step.

Figure 3 gives also a direct comparison of the TPR profiles of the original sample, the sample after drying for 2 h at 500°C , and the sample that was dried as above and subsequently rehydrated by passing water-saturated helium at room temperature through the bed for 1 h. The reduction profile of the rehydrated sample is also enlarged $3\times$ along the Y axis for better comparison. Clearly, exposure of the dried sample to water vapor at room temperature is sufficient for partial (at least) restoration of the TPR profile observed before the 500°C drying process.

The TPR profile of Pd black impregnated

with Re_2O_7 and dried at 110°C is shown in Fig. 4. All of the rhenium heptoxide is reduced below 200°C , i.e., well below the temperature of reduction of Re^{7+} in the absence of palladium, but above the temperature range in which most of Re_2O_7 was reduced when both Pd^0 and Re_2O_7 were deposited on $\gamma\text{-Al}_2\text{O}_3$. The catalytic effect of Pd^0 on reducibility of Re^{7+} is further decreased in the case of physical mixtures. Figure 5 shows the reduction of an equimolar physical mixture of Pd black and KReO_4 , diluted with an equal weight of quartz. The negative peak around 75°C corresponds to evolution of hydrogen associated with decomposition of $\beta\text{-PdH}$. The T_{max} for reduction of KReO_4 is lower by ca. 100°C comparing to the reduction of $\text{KReO}_4 + \text{quartz}$ (curve 2 in Fig. 5).

Palladium Hydride Formation

The other pertinent information comes from the measurement of absorption of hydrogen observed when the sample is cooled in flow of 5% H_2 in N_2 directly after the TPR run. Palladium hydride is unstable above ca. 50°C at the partial pressure of H_2 used. The uptake of hydrogen by metal particles, produced in the preceding reduction, gives rise to a peak which must be associated with formation of palladium hydride, as confirmed by XRD results (compare Fig. 8).

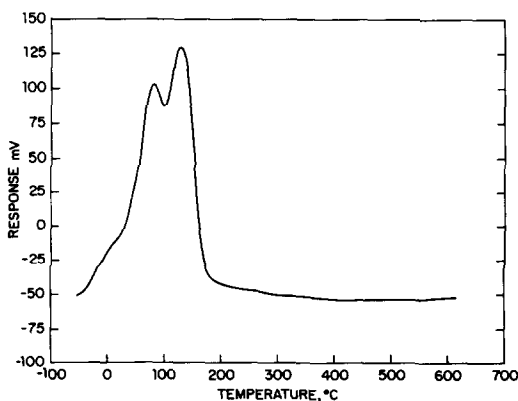


FIG. 4. TPR profile of Re_2O_7 impregnated on Pd black.

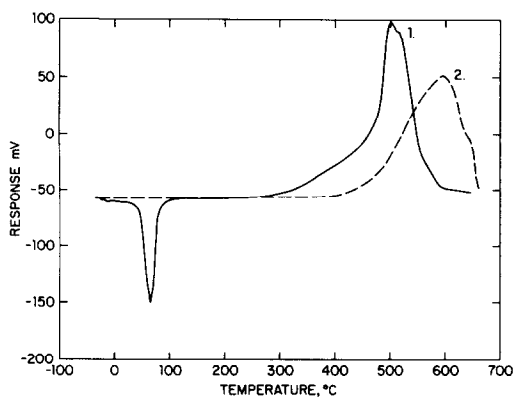


FIG. 5. TPR profiles of a physical mixture of 10 mg Pd black + 10 mg KReO₄ + 50 mg of quartz (continuous line), and 10 mg KReO₄ diluted with 50 mg of quartz (dashed line).

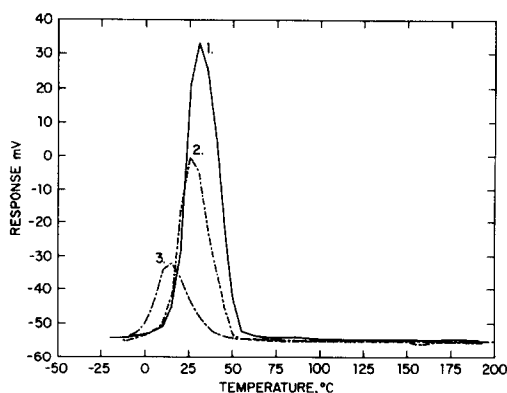


FIG. 6. Curves of hydrogen uptake associated with β -PdH formation, measured directly after a TPR run. Each sample contains 10 mg of Pd black. (1) Pd black; (2) physical mixture Pd + KReO₄; (3) Re₂O₇ impregnated on Pd black.

In bulk palladium, including Pd black, values of $H/Pd \approx 0.65$ were measured by the above technique. We know, however, that very small palladium particles ($d < 2.6$ nm) do not form β -PdH (11), and that hydride formation is hindered in palladium alloys (12). The effect of alloying on the extent of β -PdH formation is illustrated in Fig. 6, which shows the hydrogen uptake for Pd black (curve 1), Pd + KReO₄ (curve 2), and Pd impregnated with Re₂O₇ (curve 3). Each sample contains 10 mg of Pd black. Palladium-rhenium alloys indeed are formed during reduction of the physical

mixture of Pd + KReO₄, and Pd black impregnated with Re₂O₇. The XRD evidence will be presented below.

On the basis of TPR profiles (Figs. 4 and 5) one can postulate more extensive interaction between Pd and Re in the case of Pd impregnated with Re₂O₇ than for the physical mixture of Pd + KReO₄. This is reflected in the extent of suppression of β -PdH formation shown in Fig. 6. Simultaneously, we observe a systematic shift in thermal stability of the hydride toward lower temperatures.

The results for the Re⁷⁺Pd⁰/Al₂O₃ cata-

TABLE I

Hydrogen Uptake Measured Directly After TPR

Sample treatment	Peak area (mV min)	H/Pd ^a ratio
Pd/Al ₂ O ₃		
Dried 110°C	83	0.4
Dried 500°C	104	0.53
RePd/Al ₂ O ₃		
Dried 110°C	5	0.02
Dried 500°C	35	0.17
Rewetted after 500°C drying	23	0.11

^a Assuming that all the palladium can participate in PdH_x formation. $H/Pd = 0.65$ can be achieved in bulk palladium under analogous conditions.

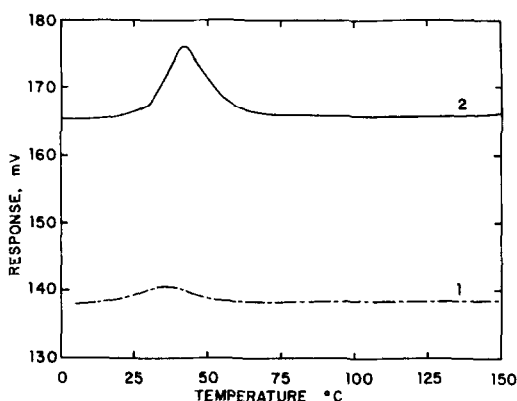


FIG. 7. Hydrogen absorption. (1) RePd/Al₂O₃; (2) Pd/Al₂O₃.

lyst are given in Table 1, and are partially illustrated in Fig. 7. The last column of Table 1 gives the H/Pd ratio calculated from the hydrogen uptake and the nominal load of Pd (3% wt). It is assumed that all of the palladium deposited on the support can participate in hydride formation. For the samples dried at 110°C, the H/Pd ratio decreases from 0.4 to 0.02 due to interaction of Re with Pd. After drying of the Re⁷⁺Pd⁰/

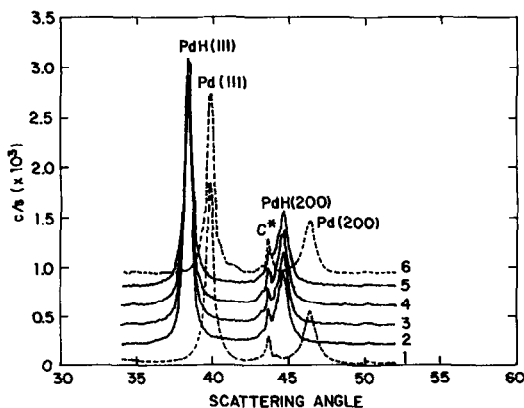


FIG. 8. XRD spectra of formation and decomposition of β -PdH on exposure of Pd black to a flow of 8.5% H₂/He under equilibrium conditions. Scan in N₂ is added for comparison. (1) N₂ at 25°C. All the following in H₂/He: (2) at 25°C; (3) at 30°C; (4) at 35°C; (5) at 40°C; (6) at 70°C. C* is the standard (diamond powder).

Al₂O₃ preparation prior to reduction this interaction is partially suppressed (H/Pd = 0.17), but increases again for the sample re-wetted after drying. Note also that drying of the Pd/Al₂O₃ preparation at 500°C results in some sintering of metal crystallites (H/Pd = 0.53).

X-Ray Diffraction

Test reactions of the *in situ* apparatus were conducted with palladium black (Alfa Inorganics) deposited on a 316 stainless-steel sample support. Figure 8 shows the X-ray diffraction pattern of palladium black in N₂ at 25°C, and after equilibration at several temperatures in the range 25 to 70°C in a hydrogen atmosphere (8.5% H₂ in He). The palladium phase disappears and is totally converted to PdH_{0.7} in the presence of hydrogen. The (111) and (200) reflections of

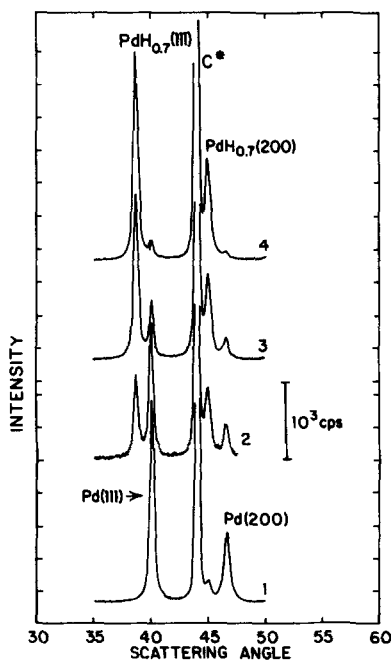


FIG. 9. Formation of PdH_{0.7} during exposure of palladium black to H₂ under dynamic conditions. (1) XRD spectrum of Pd black in N₂ at 26°C; (2) recorded at 26°C after switching to H₂/He (temperature programming was started at that moment); (3) at 35°C in H₂/He; (4) at 43°C in H₂/He. Temperature was programmed at 10°C/min. C* is the internal standard.

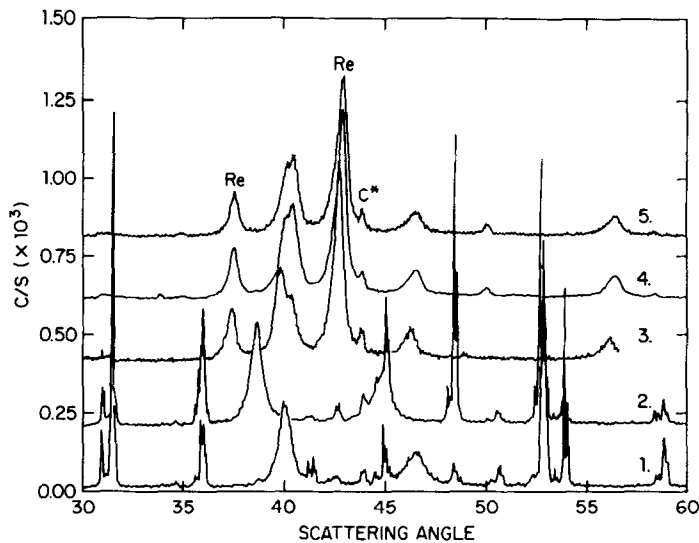


FIG. 10. XRD spectra of a physical mixture of Pd black + KReO_4 . (1) At 25°C in N_2 ; (2) at 25°C in H_2 ; (3) at 550°C in H_2 ; (4) cooled down to 25°C in H_2 ; (5) at 25°C in N_2 after reduction. C* is the diamond standard.

palladium are shifted to lower scattering angles, characteristic of β -PdH (change of the lattice parameter from $a_0 = 0.389$ nm to $a = 0.4025$ nm). The hydride is, however, thermally unstable at the partial pressure of hydrogen used, and disappears at 70°C. The dynamics of the $\text{Pd} \rightarrow \text{PdH}$ phase transition under non-equilibrium conditions is shown in Fig. 9. Here, after recording the diffraction pattern of Pd black in flowing N_2 at 1.2 atm and 26°C (curve 1), gas flow was switched to 8.5% H_2/He , and programming of the sample temperature at 10°C/min was started. Curve 2 was measured at 26°C, and curves 3 and 4 were recorded when the sample temperature reached 35 and 43°C, respectively, in the hydrogen-containing flow.

Reduction of equimolar physical mixtures of Pd black with KReO_4 and Re_2O_7 was examined. Figure 10 shows transformations observed in the Pd + KReO_4 system. Initially, the lines of Pd and KReO_4 are seen; in hydrogen at room temperature PdH is formed, but potassium perrhenate is not reduced. At 550°C only the reflections of rhenium, and palladium-rhenium alloys

are seen. On cooling in hydrogen atmosphere a phase transformation of the Pd-Re alloys takes place, resulting in changes of relative intensity of the components (compare curves 3 and 4 of Fig. 10). Palladium hydride is not observed at room temperature in H_2 . The region of interest is enlarged in Fig. 11. Detailed analysis yields two mean populations of alloy, having lattice parameters $a_0 = 0.3839$ nm and $a_0 = 0.3881$ nm, respectively. Reduction of the

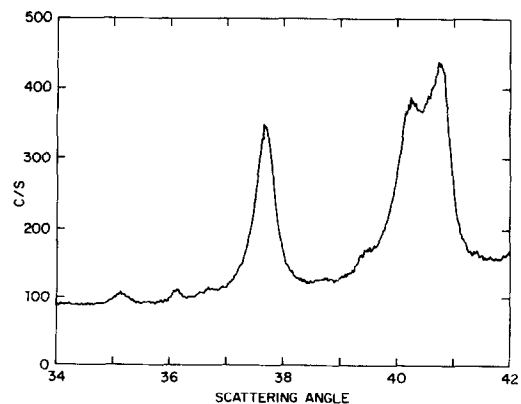


FIG. 11. Enlarged portion of scan 4, Fig. 10.

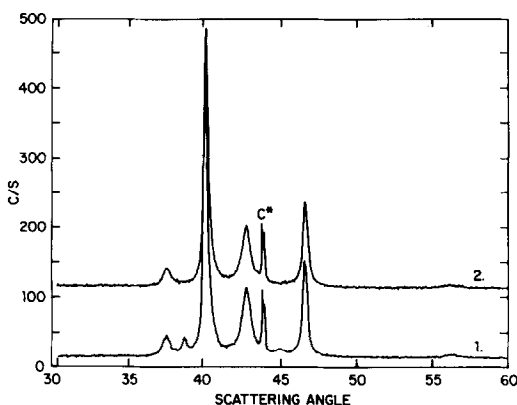


FIG. 12. XRD spectra of a physical mixture of Pd + Re_2O_7 after reduction *in situ* at 500°C . Measured at 25°C in: (1) 4% H_2 ; (2) N_2 .

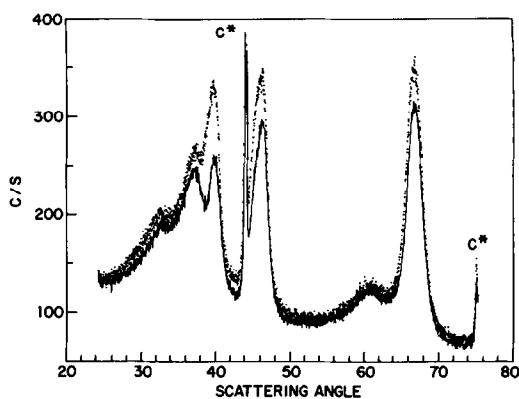


FIG. 13. XRD spectra of $\text{Re}^{7+}\text{Pd}/\gamma\text{-Al}_2\text{O}_3$, after drying *in situ* at 500°C , recorded at 25°C in a flow of nitrogen (line), and 8.5% H_2/He (points). C* is the diamond standard.

physical mixture of Pd black and Re_2O_7 at 500°C yields principally palladium-rhenium alloy of lattice parameter $a_0 = 0.3883$ nm and some unalloyed palladium. Indeed, a small peak of PdH is observed when the sample is cooled to room temperature in H_2/He (curve 1 in Fig. 12). The yield of rhenium is about 1/3 of that observed in the Pd + KReO_4 experiment, probably due to the low sublimation temperature of Re_2O_7 .

Investigation of supported catalysts by X-ray diffraction is more difficult because $\gamma\text{-Al}_2\text{O}_3$ itself is a strong X-ray scatterer. In another series of experiments the $\text{Re}^{7+}\text{Pd}^0/\text{Al}_2\text{O}_3$ catalyst was dried *in situ* in flowing nitrogen by a programmed temperature ramp from 25 to 500°C . Programmed heating in nitrogen yielded an apparent increase in palladium particle size, but did not introduce changes indicative of new phases. As seen in Fig. 13, behavior typical for unalloyed palladium is observed in hydrogen atmosphere at 25°C : the intensity of the (111) peak increases, and a shoulder indicative of $\beta\text{-PdH}$ is formed on the low-angle side of the Pd peak. These features were not observed in N_2 atmosphere (line in Fig. 13).

Reduction of that sample was carried out *in situ*, in a flow of 8.5% H_2/He at 1.25 atm reactor pressure, using the same programmed temperature ramp as described

above. The XRD scans recorded at 25°C in H_2/He , for the reduced (curve 1) and unreduced (curve 2) sample are shown in Fig. 14. Vertical bars on the plot indicate the expected line positions associated with the presence of Re. Thus reduction at 500°C results in formation of metallic rhenium, and possibly Pd-Re alloy. The detailed analysis is, however, difficult due to the strong background of $\gamma\text{-Al}_2\text{O}_3$ itself. Figure 15 shows the spectrum of the reduced

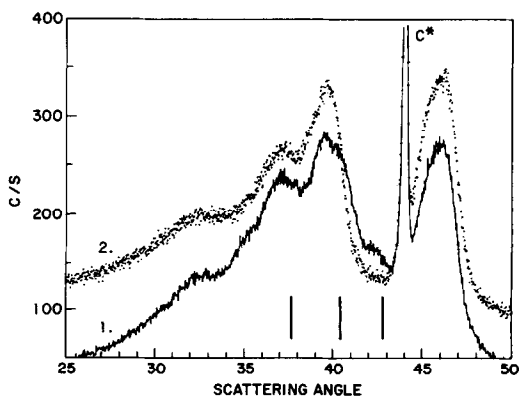


FIG. 14. XRD spectrum of $\text{RePd}/\gamma\text{-Al}_2\text{O}_3$ after *in situ* reduction at 500°C (curve 1). Vertical bars indicate the expected α_1 lines of Re. Scan of the same sample before reduction (curve 2) is shown for comparison. Both scans recorded at 25°C in H_2/He flow. C* is the diamond standard.

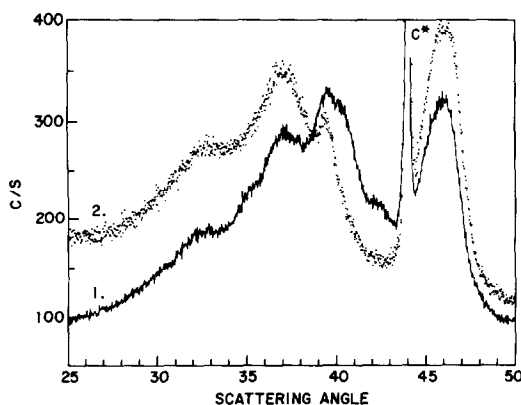


FIG. 15. XRD spectra of $\text{RePd}/\gamma\text{-Al}_2\text{O}_3$ (curve 1) and $\gamma\text{-Al}_2\text{O}_3$ (curve 2). C^* is the diamond standard.

$\text{PdRe}/\text{Al}_2\text{O}_3$ preparation (curve 1), and that of the $\gamma\text{-Al}_2\text{O}_3$ used as support (curve 2).

This interpretation is also supported by examination of the same sample after described sequence of treatments in a scanning transmission electron microscope (STEM). Using the X-ray microanalysis capability of the microscope, we were able to identify rhenium and palladium crystallites, as well as bimetallic Pd–Re particles.

DISCUSSION

Effect of Group VIII Metals on Reducibility of Re^{7+}

The TPR results described above are similar in their qualitative aspect to the findings of earlier investigators (5–7) for the $\text{Pt}^{4+}\text{Re}^{7+}/\gamma\text{Al}_2\text{O}_3$ system. The observed acceleration of reduction of Re^{7+} in the presence of Pt was explained as a manifestation of migration of rhenium oxides toward Pt (5, 6), or alternatively as a manifestation of hydrogen spillover on alumina (7).

While migration of rhenium heptoxide at temperatures close to 300° (6) seems a plausible explanation of changes in the TPR profile of Re^{7+} caused by the presence of Pt, there exists a strong instinctive resistance for such mechanism being operational in the $\text{Re}^{7+}\text{Pd}^0/\text{Al}_2\text{O}_3$ system. In our work the rhenium heptoxide was deposited on alumina already containing metallic pal-

ladium. Consequently, reduction of Re_2O_7 occurs with the maximum rate at ca. 50°C (see Fig. 2). By implication, the migration of rhenium oxides must take place at low temperatures.

Mechanisms Not Involving Re_2O_7 Migration

Two alternative mechanisms were considered: (a) rhenium heptoxide is deposited preferentially on, or in the immediate vicinity of the existing palladium crystallites, (b) reduction of Re^{7+} takes place via spillover of hydrogen on alumina.

(a) One can assume that in the sample which was dried at 110°C prior to TPR, most of the Re^{7+} is intimately associated with palladium crystallites to the extent that ca. 90% of the Re_2O_7 can be reduced below 100°C (observed $T_{\text{max}} = 47^\circ\text{C}$). There is almost complete suppression of palladium hydride formation in such catalysts (see Table 1). This means that bimetallic clusters of Pd and Re are formed, or that palladium crystallites are covered by a layer of rhenium. No lines assignable to metallic rhenium were detected in the X-ray diffraction spectrum at that stage.

After extensive drying (500°C for 2 h) of the same preparation prior to TPR experiment, the effect of Pd on the reducibility of Re_2O_7 is largely eliminated. Most of the Re^{7+} is now reduced at higher temperature, comparable to that of reduction in the absence of metallic palladium. Formation of palladium hydride is observed again (Table 1). Although the H/Pd ratio observed is lower than that measured for pure 3% Pd/ Al_2O_3 (in spite of the apparent increase of particle size), it can be argued that drying at elevated temperatures causes migration of Re_2O_7 away from the Pd crystallites; that assumption indeed could account for part of the observed phenomena. But it cannot explain the effect of rehydration (at room temperature) of the previously dried sample on the subsequent TPR profile. After rehydration approximately 30% of the Re_2O_7 is reduced below 100°C (Fig. 3), i.e., restored

to its strong interaction with Pd crystallites that existed before the high-temperature drying. This is reflected in both the area of the low temperature TPR peak, and the amount of palladium hydride formed (by implication the amount of unalloyed palladium). The balance of Re^{7+} is reduced at higher temperatures.

(b) The second mechanism assumes a random distribution of Pd^0 and Re_2O_7 particles on the support surface. Hydrogen would dissociate on Pd crystallites, spill over onto the support, and migrate to Re_2O_7 particles, where reduction takes place. The beneficial effect of the presence of water on hydrogen spillover is well documented (16). Isaacs and Petersen (6) have demonstrated, on the basis of data of Kramer and Andre (15), that the number of hydrogen atoms spilled over up to 400°C is insufficient to account for the reduction of rhenium heptoxide present in the investigated sample. This argument is even more valid here because the rate of hydrogen spillover is temperature dependent (15), and most of the Re_2O_7 is reduced below 100°C in our system.

The most important deficiency of the H_2 spillover mechanism is that it does not account for the apparent alloying of the metals—as manifested by suppression of palladium hydride formation (see Table 1 and changes in the X-ray diffraction spectra)—in the hydrated samples.

Mechanism Based on Re_2O_7 Migration

Thus, after careful consideration, we must reject both of the alternative mechanisms that could be responsible for the effect of palladium on the reducibility of Re^{7+} in our system. We are left with the migration of Re_2O_7 (dependent on the degree of hydroxylation of Al_2O_3) toward the preexisting Pd crystallites. What is surprising, though, is that this mechanism is operative at such low temperature: the process starts at subambient temperatures, and reaches the maximum rate around 50°C.

Baker (13) observed by electron micros-

copy temperatures of the onset of mobility for several metal and metal oxide particles deposited on a noninteracting support (graphite). These results correlate very well with the corresponding Tamman temperatures. When the published (14) value of the melting point of Re_2O_7 is superimposed on Baker's plot, the corresponding Tamman temperature ca. 17°C is obtained. This value is lower than the observed T_{max} for reduction of Re_2O_7 in the nondehydrated $\text{Re}^{7+}\text{Pd}^0/\text{Al}_2\text{O}_3$ catalyst. Hence, migration of Re_2O_7 particles on a noninteracting support is possible at relatively low temperatures. It is reasonable to assume that fully hydroxylated alumina represents a noninteracting surface for rhenium heptoxide particles. After dehydration at 500°C, i.e., removal of approximately 10^{15} OH/cm² of Al_2O_3 (17), Re_2O_7 interacts strongly with the support, and its mobility is hindered due to strong oxide-oxide interaction. This approach explains also the observed partial restoration of the original reduction profile by rehydration of the previously dried sample.

The authors of the two related papers (5, 6) invoked the possibility of mobility of Re_2O_7 being dependent on the degree of hydration of the molecules of rhenium heptoxide. While we can offer no evidence for or against such a dependence, there is nothing in the limited knowledge of physicochemical properties of dispersed rhenium heptoxide to support this assumption. The concept of mobility related to the Tamman temperature of Re_2O_7 on noninteracting surfaces seems to be adequate to account for the observed phenomena.

The possibility of PdO (formed by oxidation of Pd^0 during the preparation and handling in air) being the mobile species must be rejected. No evidence of bulk PdO was found in this work. Any superficial PdO that can be formed undergoes immediate reduction at subambient temperatures in the presence of hydrogen (18).

We do not pretend to have the last word in the controversy over the mechanism and

extent of rhenium reduction in the practical reforming catalyst. It can be argued that the oxide-oxide interaction is much stronger at low concentrations of Re_2O_7 prevailing in the commercial $\text{PtRe}/\text{Al}_2\text{O}_3$ catalysts than in our preparations. Indeed the TPR data of Mieville (7) and Arnoldy *et al.* (19) indicates that the reducibility of $\text{Re}^{7+}/\text{Al}_2\text{O}_3$ increases with increasing rhenium load, which can be taken as a manifestation of decreasing interaction. But, at least for the 3% Pd^0 3% $\text{Re}^{7+}/\text{Al}_2\text{O}_3$ and unsupported preparations of zerovalent palladium and heptavalent rhenium, we were able to demonstrate the *consequences* of Re_2O_7 migration, namely alloying of Pd and Re.

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