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Alloy Formation and Metal Oxide Segregation in Pt–Re/γ-Al_2O_3 Catalysts as Investigated by Temperature-Programmed Reduction

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Temperature-programmed reduction has been used to characterize the finely dispersed metal compounds in a series of Pt–Re/γ-Al_2O_3 catalysts. Strong evidence has been obtained that zerovalent Pt and Re atoms are in intimate contact with each other after catalyst reduction. The formation of "bimetallic clusters" supports the "alloy" explanation for the improved performance of this type of bimetallic reforming catalyst. Treatment of the reduced catalysts with oxygen above about 200°C causes segregation of platinum and rhenium oxides. Adsorption of oxygen at temperatures up to 100°C leaves the bimetallic clusters largely intact, but subsequent high-temperature treatment in the absence of extra oxygen leads to segregation of Pt and Re species. This suggests that in the presence of adsorbed oxygen the Pt–Re clusters are thermodynamically unstable, but that under mild conditions the rate of segregation is slow.

INTRODUCTION

The advent of bimetallic reforming catalysts such as the Pt–Re/γ-Al_2O_3 system, has led to a reexamination of many ideas developed over the years to account for the catalytic properties of metals supported on acidic alumina. The most interesting feature of the bimetallic catalysts which distinguishes them from the monometallic Pt/γ-Al_2O_3 systems is the improvement in reforming stability. One of the theories put forward to explain the improved stability, the "alloy" model, attributes it to a modification of the catalytic properties of platinum when alloyed with a second metal (*1*).

The study of actual bimetallic reforming catalysts is hampered by the fact that the common methods of physical characterization are ineffective because of the very high degree of dispersion and the low metal loadings of these systems. Most investigators therefore use model systems such as bulk alloys or sintered metals on (nonacidic) supports. Only recently has the interaction between well-dispersed metals on alumina been discussed in the literature (*2*, *3*).

The present paper describes a study of home-made Pt–Re on chlorided γ-alumina catalysts (comparable to commercial Pt–Re reforming catalysts in terms of metals loading and dispersion) by the temperature-programmed reduction (TPR) technique. This sensitive technique comprises measuring the hydrogen consumption due to reduction of an oxidized metal surface while the catalyst sample is heated up with linear temperature programming, and is well suited to the examination of highly dispersed systems (*4*). In principle, it enables a distinction to be made between different surface species even at the low metal loadings of actual reforming catalysts.

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EXPERIMENTAL

Catalysts. Catalysts were prepared by (co) impregnating alumina powder of reforming grade quality (surface area = 180 m^2 g^{-1}, pore volume = 0.9 ml g^{-1}, Cl content = 0.45 wt%) with an aqueous solution of H_2PtCl_6, Re_2O_7, and HCl. The impregnated powder was dried in an oven at 120 to 150°C and pressed into tablets; the desired particle size was obtained by crushing and sieving. The fraction with 0.5 to 1.3 mm diameter was carefully calcined in circulating air at 525°C, this final temperature being maintained for 1 hr. The chloride content of the finished catalysts was about 0.7 wt% in all cases.

Measurements. The principles of the TPR method have been described previously (*4*). The automated equipment we used consisted of (a) pneumatic circuits for preparing 5 vol% H_2 in N_2 (TPR gas) and 5 vol% O_2 in He (oxidizing gas), (b) a reactor section comprising a quartz tube placed horizontally in a silver block oven with electrical heaters and a variable supply of liquid nitrogen coolant, and (c) a calibrated thermal conductivity (TC) detector connected to a recorder for measurement and display of hydrogen consumptions. The gas emerging from the reactor was dried over magnesium perchlorate before entering the TC cell.

Hydrogen was purified by diffusion through palladium. Nitrogen was passed over a bed of MnO on celite to remove traces of oxygen (*5*). Research grade helium and oxygen were used without further purification. The TPR and oxidizing gases were prepared *in situ* by injecting timed pulses of either hydrogen into a nitrogen stream or oxygen into helium, after which the mixture was passed into a large buffer vessel to permit homogenization.

An electronic programming unit was provided for switching of the various gas streams to the reactor or via bypasses, control of the reactor temperature, and balancing of the TC cell, where necessary. A desired sequence of steps, such as repetition of several redox cycles, could be programmed in this way. The standard program comprised the following steps:

(i) Drying the sample at 180°C for 1 hr (5 vol% O_2 in He).

(ii) First TPR measurement from −50 to 500°C and a 1-hr isothermal reduction ("finishing off") at 500°C (5 vol% H_2 in N_2).

(iii) Reoxidation for 1 hr (5 vol% O_2 in He).

(iv) Second TPR measurement as in (ii) (5 vol% H_2 in N_2).

Standard heating and cooling rates were 5°C min^{-1} throughout, and gas flow rates were 300 N ml h^{-1}. The catalyst sample weighed about 0.5 g. Gas pressures were about 1.5 bar abs, the H_2 partial pressure during reduction amounting to about 0.075 bar.

In the TPR profiles presented, the peak at ca. −40°C is an artefact caused by a surge of physically adsorbed nitrogen desorbing from the sample at the start of the temperature-programmed heating. It can be neglected in all cases.

RESULTS AND DISCUSSION

Pt/Al_2O_3 and Re/Al_2O_3

In order to assign the TPR peaks of Pt–Re/Al_2O_3 catalysts it was necessary to compare TPR profiles for the bimetallic systems with those for the corresponding monometallic catalysts, recorded after identical oxidative pretreatment.

Reduction profiles for Pt on chlorided γ-alumina are given in Fig. 1. Oxidic platinum in the calcined catalyst shows a characteristic TPR curve with a maximum rate of reduction at 250°C and a reduction tail up to about 500°C. The total hydrogen consumed corresponds to an overall reduction stoichiometry of $Pt^{4+} \rightarrow Pt^0$. The platinum(IV) species formed during calcination and reduced during the TPR measurement is a highly dispersed form of the metal oxide, presumably complexed with oxygen atoms from the alumina carrier. No particles were detected in our catalysts by X-ray or electron microscopic techniques either before or after reduction in this manner. This puts the maximum particle size at ca. 1 nm, which corresponds to a metal "cluster" of 10 to 15 atoms only. The complex of Pt(IV) in the calcined catalyst probably represents a situation approaching an atomic dispersion of metal ions on the carrier, as suggested by the relatively difficult reducibility of the species (bulk H_2PtCl_6 decomposes in hydrogen at considerably lower temperatures). A relationship between the amount of platinum oxide or oxychloride complexed with the alumina (sometimes termed "soluble" platinum) and the final dispersion of catalysts after reduction has been indicated in the literature (*6, 7*).

After reduction and a 1-hr reoxidation at 180 to 400°C platinum is found in a more easily reducible state (Fig. 1), and the reduction stoichiometry is 1 H_2/Pt, in agreement with the accepted stoichiometry for the hydrogen titration of adsorbed oxygen (*8*).[2] Interestingly, the reduction peak shifts to progressively higher temperatures with increasing temperature of oxidation (oxygen adsorption), while the stoichiometry remains constant. This suggests an increasing degree of interaction of the platinum–oxygen species with the alumina.

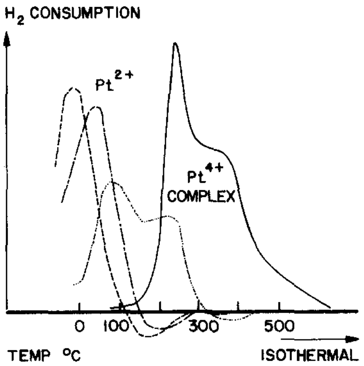

FIG. 1. TPR profiles for 0.75 wt% $Pt/Cl/Al_2O_3$: ——— fresh, calcined; - - - - - reduced, reoxidized for 1 hr at 180°C; – —– reduced, reoxidized for 1 hr at 300°C; . . . . . . reduced, reoxidized for 1 hr at 500°C.

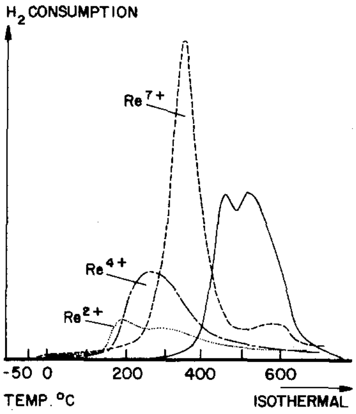

FIG. 2. TPR of 0.7 wt% Re/Al_2O_3: ——— fresh, calcined; . . . . . . reduced, reoxidized at 100°C; – —– reduced, reoxidized at 180°C; - - - - - - reduced, reoxidized at 300°C.

After oxidation at 500°C the TPR peak of the fresh calcined catalyst reappears and at oxidation temperatures above 500°C and/or treatments for several hours the profile becomes similar to that of the calcined catalysts, the Pt(IV) complex being formed again.

Rhenium in fresh, calcined $Re/\gamma\text{-}Al_2O_3$ (0.45 wt% Cl) is more difficult to reduce than platinum in $Pt/\gamma\text{-}Al_2O_3$, as can be seen in Figs. 1 and 2. The TPR measurements showed that ca. 90% reduction of Re^{7+} to Re^0 took place up to 600°C. On reoxidation of the reduced rhenium the

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[2] At low temperatures the accepted stoichiometry (*8*) is $PtO + \frac{3}{2} H_2 \rightarrow PtH + H_2O$. Under TPR conditions, however, the adsorbed hydrogen desorbs during the temperature-programmed heating. The overall net reaction becomes $PtO + H_2 \rightarrow Pt + H_2O$ if allowance is made for the desorbing hydrogen by subtracting the negative part of the signal in Fig. 1 from the positive part. This has been done in the present work.

associated TPR spectra exhibit a shift to higher temperatures with increasing oxidation temperature, as was the case for platinum. With rhenium, however, the oxidation state changes: upon oxidation at 100°C it is two, at 180°C it is four and at 300°C it is seven (see Fig. 2). It may well be that the Re(II) state reflects oxygen chemisorption, while the Re(IV) and Re(VII) states represent real rhenium oxides on support.

Pt–Re/Al_2O_3 in the Reduced State

TPR profiles of a series of fresh (calcined) Pt–Re on chlorided γ-alumina catalysts with varying Pt/Re ratio are shown in Fig. 3 and the associated reduction data in Table 1. At about 250°C considerable amounts of rhenium reduce simultaneously with platinum whereas in catalysts containing Re only reduction takes place at much higher temperatures (cf. Fig. 2). Apparently Pt catalyzes the reduction of Re. The data of Table 1 demonstrate that at a Pt load of 0.35 to 0.38 wt% up to about 0.2 wt% Re is completely reducible to the metallic state, but for Re loads of 0.3 wt% and higher this is no longer so. Thus at Re/Pt ratios below about 0.6 the composition of the metals on the catalyst after reduction is identical to the overall Re/Pt composition, while at higher Re/Pt ratios a fraction of the Re remains unreduced under our reduction conditions. The fact that in the low-Re-load catalyst rhenium is completely reduced from Re^{7+} to Re^0 suggests that we should regard all reduction data in terms of the stoichiometry $Re^{7+} \rightarrow Re^0$. In the case of incomplete reduction of the higher Re-load samples we therefore assume that part of the Re_2O_7 has been reduced to metallic rhenium while the rest is still present as Re^{7+}.

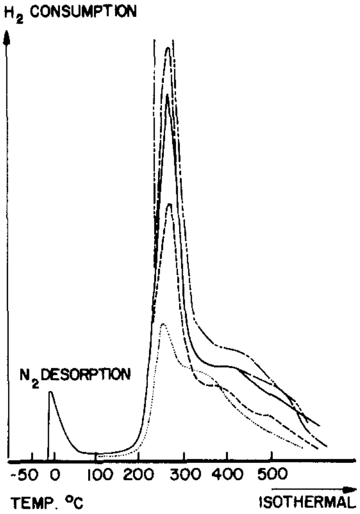

FIG. 3. TPR of fresh, calcined Pt/Re/Cl/Al_2O_3. Pretreatment, dried at 180°C: ...... 0.35 Pt; ----- 0.35 Pt/0.1 Re; ——— 0.38 Pt/0.2 Re; – – – – 0.35 Pt/0.3 Re; – – —— – – 0.35 Pt/0.6 Re.

TABLE 1

Reduction Data of First TPR Measurements on Fresh Pt–Re/Cl/Al_2O_3 Catalysts[a]

Fresh oxidic catalyst			Reduction		
Pt (wt%)	Re (wt%)	Re/Pt atomic ratio	Re reduced[b] wt% (abs)	Re/Pt atomic ratio of reduced species	Peak temperature (°C)
0.38	—	—	—	—	240
0.35	0.1	0.30	0.10	0.30	250
0.38	0.2	0.55	0.20	0.55	255
0.35	0.3	0.89	0.26	0.79	270
0.38	0.4	1.1	0.32	0.89	270
0.35	0.6	1.8	0.43	1.3	255

[a] Pretreatment: 1 hr drying at 180°C. Temperature-programmed reduction with 5 H_2/95 N_2 (vol%).

[b] In standard TPR measurement from −50 to +500°C (5°C/min) and a short period of isothermal operation at 500°C.

Our finding that low-load Pt–Re/Al_2O_3 catalysts are completely reducible confirms results reported by McNicol (*9*) for low metal loadings and supports those reported by Webb (*10*), Bolivar *et al.* (*11a*) and Yao and Shelef (*12*) for high metal loadings. No evidence was obtained to support the conclusion of Johnson and LeRoy (*13*) that rhenium can only be reduced to the tetravalent state in alumina-borne systems. Although at high water partial pressures thermodynamics will favor rhenium oxide over metallic rhenium (*14*), the very low

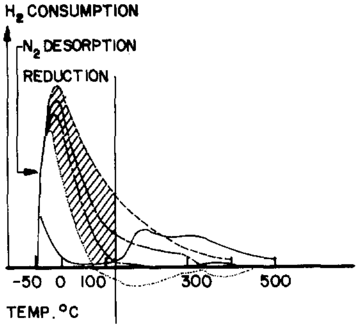

FIG. 4. TPR profiles after oxidation at 100°C: ——— Re/Al_2O_3, equivalent to 0.22 wt% Re; ...... 0.35 wt% Pt/Al_2O_3; – — – 0.35 wt% Pt/0.1 wt% Re/Al_2O_3; — — — — 0.35 wt% Pt/0.26 wt% Re/Al_2O_3; - - - - - 0.35 wt% Pt/0.43 wt% Re/Al_2O_3. All compositions refer to amounts of zerovalent metal after first TPR measurement (see also Table 1).

water partial pressure during actual catalytic reforming (0–50 ppmv) is closer to that used in the present experiments. Our experiments even show that a little water assists in the reduction of rhenium oxide on alumina (see below). We therefore conclude that during actual reforming both Pt and Re in Pt–Re/Al_2O_3 catalysts are in the metallic state.

The observed catalysis of rhenium oxide reduction by platinum suggests, but does not prove, that the reduced Pt and Re atoms are in intimate contact. More direct evidence was obtained by mildly reoxidizing (100°C) the reduced catalysts and measuring the subsequent TPR profiles (Fig. 4). These differ considerably from what would be expected from superimposing the separate profiles for Pt/Al_2O_3 and Re/Al_2O_3. Free rhenium is present only to a small extent in the Pt–Re catalysts. The rest reduces at low temperatures in the same region as platinum, indicating that this fraction of the Re is present in close contact with Pt, which points to a bimetallic interaction between Pt and Re atoms in the reduced state.

The area under the broad peak in Fig. 4 increases with increasing Re content which indicates that the platinum is more diluted in the bimetallic clusters at the higher than at the lower Re/Pt ratio. The hatched area in Fig. 4 represents the minimum estimate of the interaction or average bimetallic cluster composition, since deductions cannot be made from the parts of the TPR profile which overlap with the peaks normally found for Pt/Al_2O_3 and Re/Al_2O_3. For the 0.35 wt% Pt–2 wt% Re catalyst, which according to hydrogen consumption during the first TPR has a composition of 0.35 wt% metallic Pt and 1.98 wt% metallic Re, the "interaction" peak in the second TPR is very broad with its maximum at 95°C (Fig. 5), a considerable shift compared with the low-Re-load catalysts. Apparently the high dilution of Pt in Re makes the bimetallic clusters less easily reducible.

A further indication for the occurrence of bimetallic clusters is the absence of a negative TPR signal in the Pt–Re profiles. For Pt-only catalysts a negative signal is always observed due to desorption of adsorbed hydrogen at higher temperatures. Although this negative peak should at least partly be cancelled by the positive hydrogen consumption due to reduction of nonalloyed rhenium in this temperature region, its complete absence even at low Re contents demonstrates that hydrogen adsorption–desorption is suppressed in the bimetallic systems. Supported rhenium shows little tendency to adsorb hydrogen (*12*), so we should expect much the same behavior with the Pt–Re interaction, in

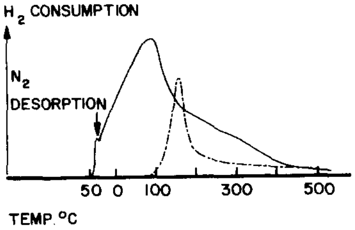

FIG. 5. TPR profiles after oxidation at 100°C: ——— 0.35 wt% Pt/1.98 wt% Re/Al_2O_3; – — – 1.5 wt% Re/Al_2O_3.

which few pairs of adjacent platinum atoms are present to adsorb hydrogen dissociatively.

The results also imply that oxygen chemisorption on platinum is stronger in the presence of rhenium, which again points to interaction between the reduced metals. The oxygen-to-metal ratio (O/Me) after the 100°C oxidation is unity in the case of Pt–Re/Al_2O_3 for all but the lowest Re contents (Table 2), but only about 0.35 for Pt/Al_2O_3. The low value for the Pt-only catalyst is probably due to part of the chemisorbed oxygen being titratable with hydrogen even at −50°C. Rapid hydrogen uptake at such low temperatures is not "seen" in our TPR experiments because the thermal conductivity cells have first to be balanced. In the case of Pt–Re/Al_2O_3, however, the full complement of adsorbed oxygen is observed by our method, which indicates a decreased titratability due to the presence of rhenium.

The evidence presented here for alloy formation in the reduced state supports the conclusions of Bolivar *et al.* (*11*), who also argued on the basis of infrared measurements on adsorbed CO (*11b*).

Pt–Re/Al_2O_3 in the Oxidized State

Whereas an oxidative treatment of the bimetallic clusters at 100°C apparently does not destroy the intimate contact of Pt and Re, oxidation at higher temperatures leads to segregation of the oxidic platinum and rhenium compounds. This is demonstrated in Fig. 6 which shows the TPR profiles of Pt–Re catalysts prereduced during a first TPR run and reoxidized at 200°C. After the oxidation at 100°C only a single broad reduction peak was observed between 0 and 100°C, but oxidation at 200°C led to a second peak around 250°C. In view of the results obtained for the Pt/Al_2O_3 and Re/Al_2O_3 catalysts, we assign the low-temperature peak to reduction of platinum-rich species and the high-temperature peak to reduction of rhenium-rich species. The marked increase in intensity of the high-temperature peak with increasing Re content of the catalyst (cf. Fig. 6 and Table 3) supports this.

TABLE 2

Hydrogen Consumptions from TPR Measurements after Reoxidation at 100°C

Composition of reduced catalyst (wt%) Pt–Re	H_2 consumption, N μl/g cat	
	Experiment	Theory for Pt^{2+}–Re^{2+}
0.35	140–170[a]	403
0.35–0.1	385	523
0.35–0.26	700	715
0.35–0.43	1050	920
0.35–1.98	2654	2790

[a] Low-intensity signal, difficult to measure accurately because of interference from N_2 surge peak.

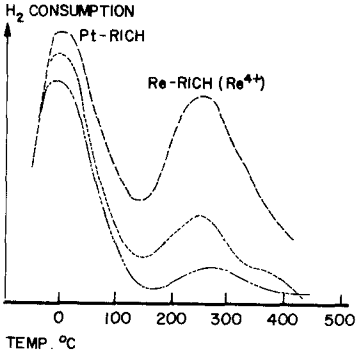

FIG. 6. TPR profiles after oxidation at 200°C: — — — 0.35 wt% Pt/0.1 wt% Re/Al_2O_3; ----- 0.35 wt% Pt/0.26 wt% Re/Al_2O_3; ——— 0.35 wt% Pt/0.43 wt% Re/Al_2O_3.

Oxidation states found for the metals in Pt-only and Re-only catalysts after oxidation at 200°C are 2 and 4, respectively. The total H_2 consumption for the bimetallic catalysts (Table 3) indicates that these values are approximately retained at low Re loadings, but the average oxidation state of the metals increases at the higher Re loads.

As the oxidation temperature is increased the separation of Pt- and Re-oxidic species continues and the oxidation states are

TABLE 3

Hydrogen Consumptions from TPR Measurements after Reoxidation at 200°C

Composition of reduced catalyst, (wt%) Pt–Re	Experimental H_2 consumption (N μl/g cat)			Theoretical H_2 consumption (0.35 Pt^{2+} = 403 N μl/g cat, 0.10 Re^{2+} = 120 N μl/g cat)			
	Low-temp. peak	High-temp. peak	Total	Pt^{2+}–Re^{2+}	Pt^{2+}–Re^{4+}	Pt^{4+}–Re^{4+}	Pt^{4+}–Re^{7+}
0.35–0.1	560	155	715	523	643	1046	1226
0.35–0.26	660	420	1080	715	1027	1430	1898
0.35–0.43	875	950	1825	920	1436	1839	2613
0.35–1.98	1310	6366	7676	2790	5177	5580	9160

further increased. The results are summarized in Table 4, while a representative TPR profile is given in Fig. 7. The high-temperature peak (Re-rich) moves to progressively higher temperatures on increasing the oxidation temperature and develops a tail extending beyond 500°C. The hydrogen consumptions show that the oxidation state of rhenium changes from 4 to about 7 between oxidation temperatures of 200 and 350°C. After oxidation at 350 and 400°C, most if not all of the rhenium is accounted for by this high-temperature peak with its tail.[3] Consequently the low-temperature peak should consist of almost pure platinum. Calculated on the basis of pure Pt, the oxidation state of this Pt is about 3 to 3.5, in contrast to the valence state of 2 for Pt in Pt/Al_2O_3 after a similar pretreatment. This Pt oxidation state in the bimetallic catalysts is the same after oxidation at 350 or 400°C and is independent of the rhenium load (see Table 4, H_2 consumptions for the low-temperature peak).

The high valence state of Pt is not easy to explain but seems to be related to the presence of rhenium. After reoxidation at 350°C the low-temperature TPR peak indicates a Pt oxidation state approaching 4. Before and during this reoxidation the platinum was in contact with rhenium, which apparently acts as an oxidation catalyst for platinum. A similar catalyst (reduced during the first TPR up to 500°C, reoxidized at 350°C) was given a reductive treatment up to 250°C in a second TPR run. In this way only the low-temperature reducible Pt-rich species were reduced, whereas Re-rich species remained oxidic. The platinum, now completely segregated, was then reoxidized at 250°C and subjected to a third TPR measurement. The result showed that platinum had reverted to its "normal" oxidation state of 2. Thus, when there is no close contact between Pt and Re the oxidation at 250°C leads to the Pt^{2+} state.

The above results indicate that oxidation of bimetallic Pt–Re clusters leads to segre-

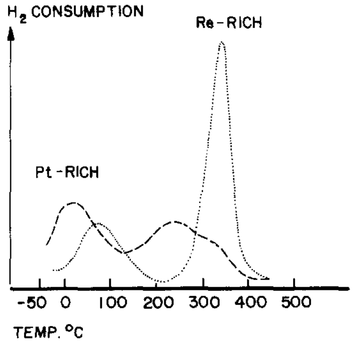

FIG. 7. TPR profiles after oxidation at 200°C (— — —) and 350°C (. . . . . .). Catalyst: 0.35 wt% Pt/0.43 wt% Re/Al_2O_3.

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[3] That the (average) oxidation state of rhenium species tends to remain a little less than 7 under these conditions is probably due to the presence of some Re^{4+} in the form of a two-dimensional, dispersed species bound strongly to the alumina, as demonstrated in the work of Yao and Shelef (*12*).

TABLE 4

TPR Data after Reoxidation at Various Temperatures

Composition of reduced catalyst (wt%) Pt–Re	Peak	H_2 consumptions in N µl/g cat and peak temperatures in (°C) after reoxidation at				
		100°C	200°C	250°C	350°C	400°C
0.35	Low temp.	155 (−25)			470 (55)	
0.35–0.1	Low temp.	385 (−10)	560 (15)	600 (32)	640 (70)	660 (78)
	High temp.		155 (270)	260 (290)	440[a] (379)	400[a] (410)
0.35–0.26	Low temp.	700 (−3)	660 (15)	620 (30)	630 (70)	660 (78)
	High temp.		420 (255)	670 (290)	830[a] (372)	890[a] (387)
0.35–0.43	Low temp.	1050 (0)	875 (20)	785 (42)	675 (70)	665 (82)
	High temp.		950 (257)	1380 (292)	1570[a] (355)	1710[a] (369)
0.35–1.98	Low temp.	2654 (95)	1310 (70)	957 (60)	624 (95)	
	High temp.		6366	7592	8166	

[a] These high-temperature peaks have a tail up to the highest measuring temperature, indicating that reduction was not complete.

gation of the oxides and lend support to the suggestion made by Bolivar *et al.* (*11b*) that the oxygen titration of a $Pt\text{-}Re/Al_2O_3$ catalyst at room temperature, as used in dispersion measurements, could cause some segregation of Pt and Re. The more severe the oxidation treatment the higher the oxidation states of the metal oxides and the more complete the segregation. Oxidation at 350°C for 1 hr alone causes practically complete segregation, as the platinum and rhenium oxides then reduce at approximately the same temperatures as found for Pt/Al_3O_3 and Re/Al_2O_3 after the same oxidative treatment. Comparison of Figs. 1 and 7, however, shows that the situation after calcination has not been reached yet. It is only at still higher reoxidation temperatures that the Pt^{4+} complex appears. Thus, after oxidation at 500°C two peaks are found for platinum, one around 100°C and the other around 250°C, due to reformation of the Pt(IV) oxide–alumina complex (Fig. 8). Prolonged oxidation at 500°C completely restores the $Pt\text{-}Re/Al_2O_3$ catalyst to the "calcined state."

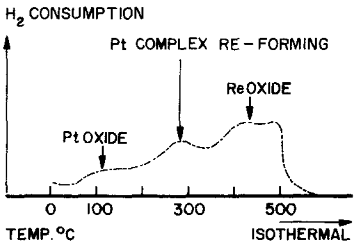

FIG. 8. TPR profile after oxidation at 500°C. Catalyst: 0.35 wt% Pt/0.43 wt% Re.

Mechanism of (Co)reduction and Cluster Formation

In the case of the calcined $Pt\text{-}Re/Al_2O_3$ catalysts described above, platinum catalyzes the reduction of rhenium oxide above ca. 220°C (Fig. 3) and bimetallic alloy clusters are formed. With the reoxidized systems, however, separate reduction peaks are observed, indicating that platinum is not able to catalyze the rhenium oxide reduction, which occurs at a temperature close to that in Re-only catalysts. Nevertheless, even under these circumstances, reduction of both metal oxides leads to the formation of bimetallic clusters. This was shown by an experiment in which the metal oxides were deliberately separated by oxidation at 350°C, reduced again (to

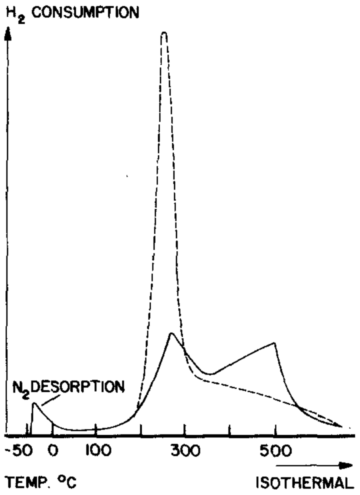

FIG. 9. First TPR of calcined 0.35 wt% Pt/0.6 wt% Re/Al_2O_3, after *in situ* drying at 180°C (- - - -) and 500°C (——).

500°C, second TPR), after which the catalyst was reoxidized at 100°C. The subsequent (third) TPR measurement showed the reduced state of the metals to be similar to that after direct reduction of a calcined catalyst, although the peak intensity was somewhat lower. Despite there having been no platinum-catalyzed reduction of rhenium oxide, bimetallic interaction clearly took place here, implying that rhenium (metallic or oxidic) has mobility on the Al_2O_3 surface at temperatures above ca. 250°C.

The formation of alloy clusters during reduction of segregated platinum and rhenium oxides is envisaged as involving the initial formation of reduced metal atoms or clusters which act as nuclei for further reduction (*15*). Surface-mobile species presumably migrate to these nuclei where they become reduced and alloyed. For the catalysts of the present study, this process leads to a (kinetically) stable dispersion of small clusters (no particles detectable by electron microscopy). The high surface area of the support, low metal loadings, moderate reduction temperature, and high state of dispersion and metal oxide–support interaction are probably important factors in maintaining a high dispersion in the reduced state.

Results in Fig. 9 illustrate a further, quite unexpected feature of the Pt–Re/Al_2O_3 system, namely, the effect of water on the reducibility of rhenium. TPR profiles are shown for Pt–Re/Al_2O_3 samples that had been calcined, stored for a few weeks, and then dried either at 180°C (our normal procedure) or more thoroughly at 500°C. The profile of the sample dried at 180°C is the normal one of a calcined Pt–Re catalyst, demonstrating simultaneous reduction of Pt and Re around 250°C. The other sample shows that after thorough drying rhenium is much more difficult to reduce, leading to separate Pt and Re peaks in the TPR spectrum. Thus, even though Pt is reduced around 250°C, Pt-catalyzed reduction of Re occurs only if water is present. Rewetting in damp O_2/He, followed by reoxidation, indeed restored the original profile during a TPR run. In our experience this effect of water is much more pronounced with rhenium than with other metals in Pt–Me/Al_2O_3 systems.

The most likely explanation of these phenomena is that water increases the mobility of rhenium oxide molecules on the carrier surface, enabling them to approach reduction nuclei. In the dehydrated state oxides of rhenium are highly dispersed and probably strongly bound to the surface. Hydration of the dispersed phase should occur readily (Re_2O_7 is highly hygroscopic) and the hydrated form is much more mobile on the surface, as the results of Yao and Shelef (*12*) imply. The observation that in a thoroughly dried, calcined catalyst rhenium oxide starts being reduced above 300°C, even though platinum oxide is reduced at the rather high temperature of 250°C, suggests that the mobility of rhenium oxide is the most important factor for the formation of bimetallic Pt–Re clusters on γ-alumina.

The effect of water is apparent at levels in the order of the normal loss of ignition for calcined catalysts after a short period of storage, that is from a few tenths of a percent to a few percent by weight. This is usually more than enough to hydrate the rhenium oxide present. The effect of thorough drying is strongest at the higher Re loadings where the ratio H_2O/Re_2O_7 is most critical. At low Re loadings enough water will be present even after drying at 500°C to hydrate the small amount of rhenium present.

That water may play a role in the reduction of rhenium in Pt–Re/Al_2O_3 catalysts has previously been suggested by McNicol (*9*). He observed separate, noncatalyzed, reduction of rhenium and speculated that this result, which was in conflict with observations by Bolivar *et al.* (*11*), might be due to the effect of water. McNicol indeed dried his samples more thoroughly than was done in our own work or that of Bolivar *et al.*

Metals Intimacy or Hydrogen Spillover?

Proponents of the "spillover" theory (*16*) might argue that the coreducibility of Pt and Re is caused not by intimacy of supported metal compounds but rather by hydrogen spillover. In particular, water has been cited as a cocatalyst aiding in the mobility of spilt-over hydrogen on the carrier. In such a case reduction of the rhenium oxide might be taking place remote from the platinum site of hydrogen adsorption, and the occurrence of a common reduction peak in a TPR profile would not necessarily imply bimetallic interaction. Although spillover may conceivably play a role in the reduction mechanism, in our opinion the TPR profiles furnish conclusive evidence for a bimetallic interaction between Pt and Re. If spillover were involved in all the work described, the occurrence of a single reduction peak in some cases and separate peaks in others could be explained only by assuming that water was acting as a cocatalyst in spillover phenomena. However, in a critical test we found that it made no difference to the second TPR spectrum (Fig. 4) of a catalyst that had been calcined, reduced up to 500°C (first TPR) and reoxidized at 100°C, whether or not we inserted a drying step in helium at 500°C prior to the oxidation at 100°C. Since these crucial experiments to demonstrate the alloy formation were not influenced by the wetness of the sample, and taking into account that in other cases (where the TPR data argued strongly for oxides segregation) a positive influence of water was found, the evidence for the existence of Pt–Re clusters seems well founded.

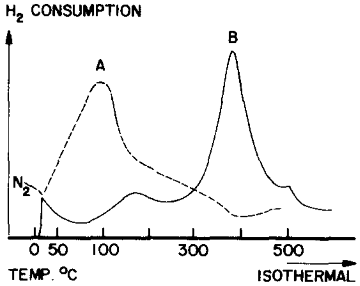

FIG. 10. TPR profiles of 0.35 wt% Pt/2.0 wt% Re/Al_2O_3 prereduced, reoxidized at 100°C, with (B) and without (A) a subsequent treatment in He at 450°C.

Mechanism of Oxidative Segregation

Segregation of metal oxides has been found to take place on oxidation above ca. 200°C, whereas oxidation at ca. 100°C is too mild to separate platinum and rhenium species. To investigate whether it is the act of oxidizing the metals or the thermal treatment above 200°C which leads to oxide segregation, we have given a sample that was reoxidized at 100°C a subsequent heat treatment up to 450°C in pure helium. The TPR profile recorded after this heat treatment is presented in Fig. 10 together with that of a sample which had only undergone a reoxidation at 100°C. It is evident that the heat treatment after 100°C oxidation has caused a drastic change, there being no longer a clearly identifiable "interaction" peak. Instead we see a high-temperature rhenium oxide peak and a smaller platinum reduction peak at about 170°C. The total hydrogen consumption is the same for both samples, as was to be expected since both were oxidized at 100°C. We conclude that separation of the metal oxides also occurs for samples oxidized at 100°C and heated up to high temperatures.

These observations are best explained by assuming that oxidation of metallic Pt–Re clusters gives rise to metal oxides which are intrinsically immiscible. Thus the intimacy of platinum and rhenium atoms in the metallic clusters is ended by an oxidative treatment. The strong interaction between the platinum and rhenium oxides and the Al_2O_3 support is a further factor which helps in segregating platinum and rhenium in the oxidic state. Obviously, the situation after an oxidative treatment of a reduced bimetallic catalyst will in general depend on the nature of the metals involved, in particular the miscibility characteristics of the bulk metal oxides, and on the strength of the interactions between metal oxides and support.

That intimacy is maintained after a mild oxygen treatment is probably due to a kinetic limitation at these low temperatures (ca. 100°C) or because the oxygen is only "loosely" chemisorbed, so that the metals retain much of their metallic electronic character. At higher temperatures, no matter whether or not oxygen is present in the gas phase, the kinetic limitation to segregation is overcome.

In the absence of adsorbed oxygen the zerovalent metal clusters appear to be thermally stable, because a heat treatment in helium to 450°C followed by oxidation at 100°C led to the same state as was reached without the heat treatment (Fig. 4).

CONCLUSIONS

In this study of temperature-programmed reduction of Pt–Re/Al_2O_3 catalysts with metal loadings comparable to those used in commercial reforming catalysts we have found that both Pt and Re are completely reduced to the metallic state by hydrogen at moderate temperatures. The reduction of Re was catalyzed by the presence of Pt and of water. That the metals in the reduced catalyst are present as bimetallic clusters was deduced from the following observations: (i) the reduction of rhenium oxide is catalyzed by Pt; (ii) a completely new TPR profile occurs after reoxidation of a reduced catalyst at 100°C; (iii) there is no negative TPR signal in Pt–Re profiles; and (iv) the strength of oxygen chemisorption on Pt is increased in the presence of Re. Oxidative treatments were found to segregate Pt and Re species, but under mild conditions (e.g., at ca. 100°C) the rate of segregation was found to be slow.

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