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The Effect of Drying Temperature on the Temperature-Programmed Reduction Profile of a Platinum/Rhenium/Alumina Catalyst

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Temperature-programmed reduction (TPR) has been used to examine the effects of drying on the reduction of Pt/Re/Al_2O_3 catalysts. The results obtained support the previous contention that water influences the mobility of Re_2O_7. The results further suggest a variety of possible degrees of hydration of Re_2O_7 which result in varying mobilities. The mobility of Re_2O_7 thus depends on both the drying temperature, which determines the degree of hydration, and the TPR temperature. At none of the drying temperatures investigated is the TPR of the Pt/Re/Al_2O_3 catalyst equal to the sum of the monometallics. It is concluded that, for drying temperatures of 500°C or less, a substantial fraction of the Re_2O_7 is at least partially hydrated and able to migrate to Pt reduction centers.

INTRODUCTION

Pt/Re/Al_2O_3 catalysts were first introduced in 1968 (*1*). Commercial experience with these catalysts has shown that, although their initial activity is similar to the once standard Pt/Al_2O_3 catalysts, their rate of deactivation is much lower (*2*). The superiority of the Pt/Re/Al_2O_3 and other bimetallic catalysts is such that by 1978, over 60% of the reforming capacity in the United States utilized bimetallic catalysts (*3*).

Despite their wide use, the role of Re in enhancing the stability of the Pt/Re/Al_2O_3 catalyst is not clear. The literature on Pt/Re/Al_2O_3 indicates that a variety of catalyst pretreatments have been utilized and suggests that catalyst pretreatment has a significant effect on the resulting Pt/Re/Al_2O_3 catalyst (*4–7*). We felt that the seemingly inconsistent results obtained by various authors regarding the role of Re may be due, in part, to an inadequate understanding of the effects of pretreatment on the Pt/Re/Al_2O_3 catalyst.

This paper concerns the effects of catalyst pretreatment on Pt/Al_2O_3, Re/Al_2O_3, and Pt/Re/Al_2O_3 reforming catalysts. The steps involved in the preparation of a reforming catalyst are shown in Table 1. Steps 2 through 5, drying through reduction, are commonly referred to as the catalyst pretreatment. As is generally the case, the catalysts used in this study were calcined by the manufacturer and were then stored, during which time they adsorbed water from the atmosphere. We therefore paid primary attention to the pretreatment steps of drying, prior to reduction, and reduction. Herein, the effects of drying on the reduction of the catalysts are described.

EXPERIMENTAL

The technique of temperature-programmed reduction (TPR) was utilized to characterize the reduction process. The necessary equipment for TPR measurements has been described previously (*8, 9*). In this study, a catalyst sample weighing about 1 g was reduced with 4.7% H_2 in Ar (Matheson) at a flowrate of 10 ml (STP)/min and a total pressure of 1 atm. The catalysts were dried in Ar at about 50 ml/min for 3 hr. All the gases utilized were of ultra high purity and were further purified by passage through an O_2 trap (Alltech), followed by a 13× molecular sieve (*10*). The gas emerging from the reactor was also dried over a 13× molecular sieve prior to entering the TC cell. The temperature was generally pro-

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TABLE 1

Preparation of Reforming Catalysts

1. Incorporation of metal onto support
2. Drying
3. Calcination
4. Drying
5. Reduction

grammed from room temperature to 720°C at 6°C/min.

The metal and chloride loadings of the three catalysts used in this work are shown in Table 2. The metals were supported on γ-Al_2O_3 with a BET surface area of about 200 m^2/g. The catalysts were supplied as cylindrical pellets about $\frac{1}{16}$ in. in diameter and $\frac{1}{4}$ in. long. The pellets were ground and sieved; a 60–120 mesh cut was used for most runs. No other information regarding the preparation of the catalysts was available, except that they had been calcined.

RESULTS

The TPR profiles of Pt/Al_2O_3, dried at 100 and 500°C prior to reduction, are presented in Fig. 1. The TPR of monometallic Pt/Al_2O_3 is a single peak with a maximum rate of reduction at about 300°C and complete reduction by 530°C. The temperature corresponding to the maximum reduction rate of Pt/Al_2O_3 is only slightly dependent on drying temperature, 285 and 300°C for 100 and 500°C drying, respectively. The shape of the TPR curve does change somewhat with drying temperature; 500°C drying results in a broader peak than 100°C drying.

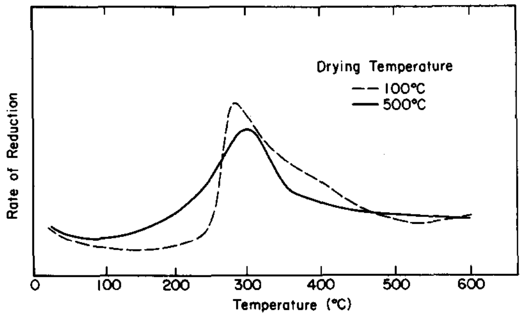

FIG. 1. TPR of Pt/Al_2O_3.

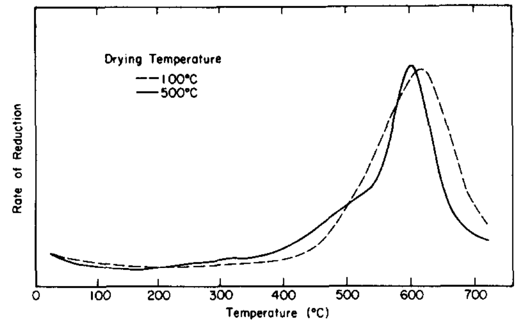

FIG. 2. TPR of Re/Al_2O_3.

The TPR profiles of Re/Al_2O_3 are shown in Fig. 2. Like Pt/Al_2O_3, Re/Al_2O_3 reduces in a single TPR peak. Re/Al_2O_3, however, is much more difficult to reduce than Pt/Al_2O_3 with a maximum rate of reduction at about 600°C; the reduction of Re/Al_2O_3 is not complete at 720°C. As in the case of Pt/Al_2O_3. Depending on the drying temperaature corresponding to the maximum reduction rate of Re/Al_2O_3, 617 and 603°C for 100 and 500°C drying, respectively.

The TPR profiles of the bimetallic $Pt/Re/Al_2O_3$ catalysts dried at various temperatures between 100 and 500°C are shown in Fig. 3. These results indicate that drying greatly influences the TPR profile of $Pt/Re/Al_2O_3$. Depending on the drying temperature, $Pt/Re/Al_2O_3$ reduces with one or two TPR peaks; the temperatures of the peak maxima vary from about 300 to 600°C. A summary of the number of TPR peaks and the temperatures of the peak maxima for the $Pt/Re/Al_2O_3$ catalyst, as a function of drying temperature, is presented in Table 3.

A $Pt/Re/Al_2O_3$ catalyst was dried at 500°C

TABLE 2[a]

Catalyst	Wt% Pt	Wt% Re	Wt% Cl
Pt/Al_2O_3	0.34	—	0.59
Re/Al_2O_3	—	0.33	0.64
$Pt/Re/Al_2O_3$	0.29	0.29	0.62

[a] Data supplied by Chevron Research Company.

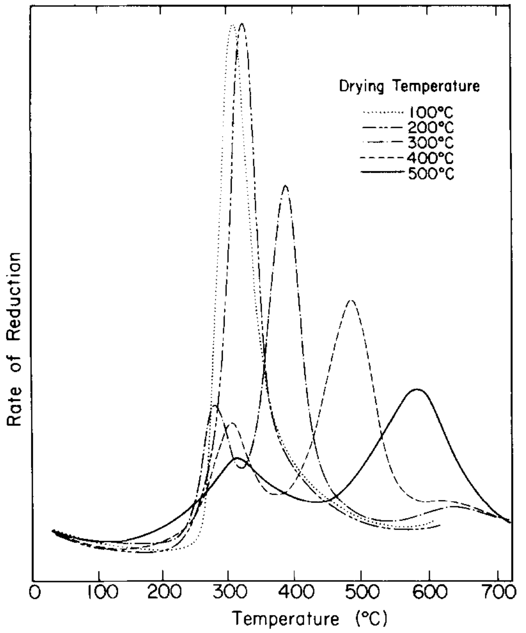

FIG. 3. TPR of Pt/Re/Al_2O_3.

for 3 hr, cooled to room temperature, and then wetted with saturated H_2O/He for 1 hr. The TPR of this dried and then wetted catalyst is similar to that of an undried Pt/Re/Al_2O_3 catalyst, as shown in Fig. 4. The undried catalyst was not heated at all prior to reduction. It was instead purged for 3 hr in Ar at room temperature. Wetting the catalyst in saturated H_2O/He at room temperature prior to purging did not affect the TPR of the undried catalyst.

TABLE 3

Temperature Corresponding to Peak Maximum for Pt/Re/Al_2O_3

Drying temperature (°C)	Number of peaks	Temperature of peak maximum	
		1	2
100	1	311	—
200	1	324	—
300	2	283	383
400	2	307	487
500	2	319	584

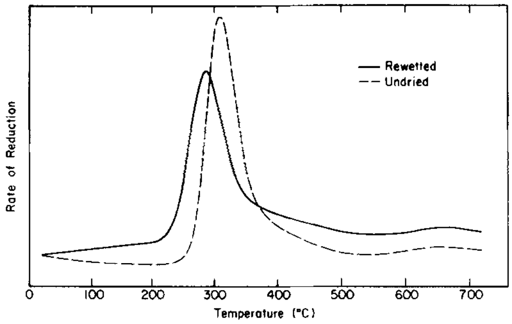

FIG. 4. Effect of rewetting on the TPR of Pt/Re/Al_2O_3.

A Pt/Re/Al_2O_3 catalyst was dried at 100°C, reduced in a TPR up to 600°C, and then reoxidized in O_2 at 500°C for 1 hr. After cooling the catalyst in Ar to room temperature, a second TPR was run. The resulting TPR (Fig. 5) had two peaks, one with a maximum at 120°C and one with a maximum at 485°C.

The chloride content of a Pt/Re/Al_2O_3 catalyst was reduced to 0.07 wt% by stripping it with saturated H_2O/He for 24 hr at 372°C. The stripped catalyst was then dried at 100°C. The resulting TPR is very similar to that of the normal chloride containing Pt/Re/Al_2O_3 catalyst dried at 100°C, as shown in Fig. 6.

Physical mixtures of Pt/Al_2O_3 and Re/Al_2O_3 were made by gently mixing together measured amounts of the monometallic catalysts. The quantities of each catalyst were similar to those used in the TPR runs with the monometallic catalysts. The TPR curves of the physical mixtures of Pt/Al_2O_3 and Re/Al_2O_3 are shown in Fig. 7 for 100°C drying and Fig. 8 for 500°C drying. Also

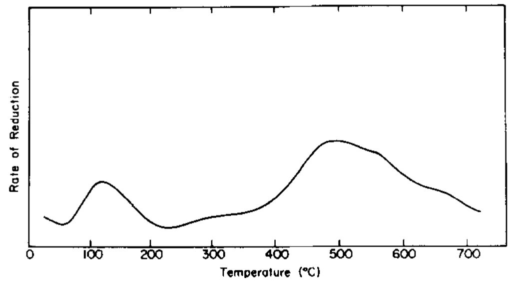

FIG. 5. TPR of Pt/Re/Al_2O_3 after 500°C reoxidation.

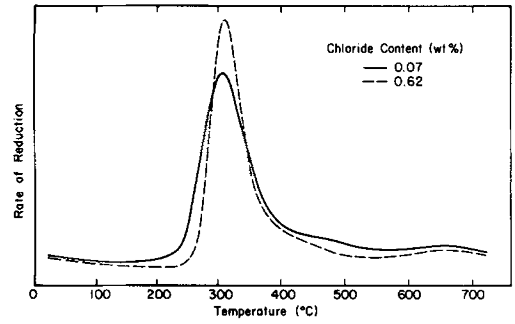

FIG. 6. Effect of chloride on the TPR of Pt/Re/Al_2O_3.

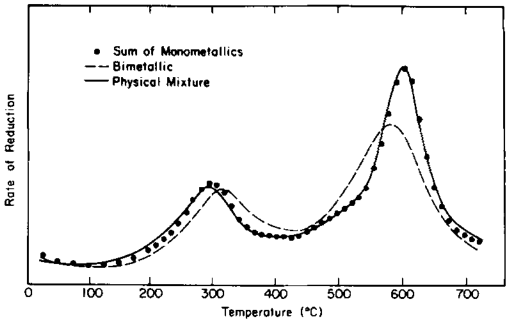

FIG. 8. TPR of various combinations of Pt and Re after 500°C drying.

shown for each drying temperature are the sum of the monometallic catalysts, obtained by graphically adding the TPR profiles of Fig. 1 and Fig. 2, and the TPR of the bimetallic catalyst. The TPR profile of the physical mixture dried at 100°C is not at all similar to that of the bimetallic Pt/Re/Al_2O_3 catalyst dried at 100°C, but is instead similar to the sum of the monometallics, dried at 100°C. After 500°C drying, the TPR profiles of the physical mixture and the sum of the monometallics are identical. For neither drying temperature is the TPR profile of the Pt/Re/Al_2O_3 catalyst equal to the sum of the monometallics.

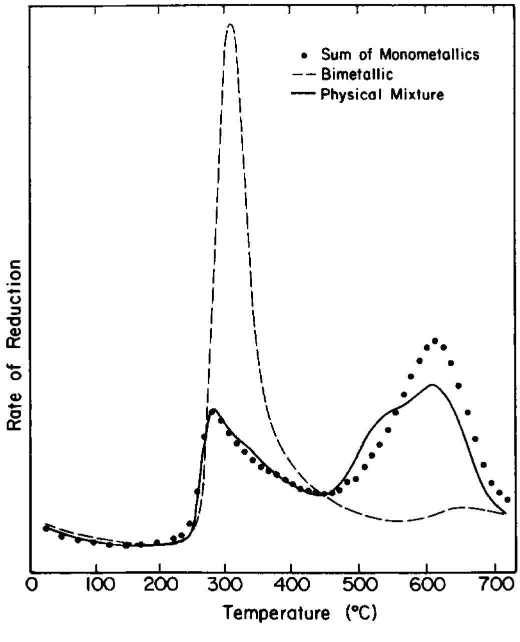

FIG. 7. TPR of various combinations of Pt and Re after 100°C drying.

With suitable calibration, the total amount of H_2 consumed during the reduction of the various catalysts can be calculated from the area under the TPR curves. The amount of H_2 consumed during the reduction of the Pt/Al_2O_3, Re/Al_2O_3, and Pt/Re/Al_2O_3 catalysts, dried at 100 and 500°C, is presented in Table 4. For comparison, the quantity of H_2 which would be consumed due to the reduction of Pt from the +4 to +0 and Re from the +7 to +0 oxidation states is also presented.

DISCUSSION

The temperatures corresponding to the maximum reduction rates of our monometallic catalysts, Pt/Al_2O_3 and Re/Al_2O_3, are in reasonable agreement with the literature, as shown in Table 5. In general, our TPR peak temperatures are slightly higher than

TABLE 4

H_2 Uptake during TPR

Catalyst	Drying temperature (°C)	H_2 uptake (μmol)	
		Experimental	Calculated
Pt/Al_2O_3	100	31	30
	500	28	30
Re/Al_2O_3	100	55	54
	500	51	54
Pt/Re/Al_2O_3	100	84	84
	500	80	84

TABLE 5

Effect of Oxidation Temperature on TPR of Pt/Al_2O_3 and Re/Al_2O_3

Catalyst	Oxidation temperature (°C)	Temperature corresponding to maximum reduction rate (°C)	Reference
Pt/Al_2O_3	?	300	This work
	525	280	(*5*)
	525	250	(*6*)
	300	100	(*6*)
	110	160	(*4*)
Re/Al_2O_3	?	600	This work
	525	550	(*5*)
	525	525	(*6*)
	500	550	(*20*)
	300	360	(*6*)
	300	360	(*20*)
	110	330	(*4*)

those found previously. This is due to our use of lower H_2 concentrations for reduction than other workers; the reduction rates of Pt/Al_2O_3 and Re/Al_2O_3 are positive in H_2 pressure (*4*).

Also evident from Table 5 is the strong dependence of the TPR peak temperature on the oxidation temperature of the catalyst. In general, Pt/Al_2O_3 and Re/Al_2O_3, oxidized at 500 to 550°C, reduce with a TPR peak at about 275 and about 550°C, respectively. After oxidation at 300°C or less, the TPR peaks for Pt/Al_2O_3 and Re/Al_2O_3 drop to about 150 and 350°C, respectively. This suggests that higher oxidation temperatures enhance interaction of the metal oxides with the Al_2O_3 support. It is clear that, although unstated by the manufacturer, the present catalysts were calcined at 500 to 550°C. This is consistent with our observation that a catalyst oxidized at 500°C and then dried at 500°C had an identical TPR to that of a catalyst which was just dried at 500°C.

Figures 1 and 2 demonstrate that the temperatures corresponding to the maximum reduction rates of Pt/Al_2O_3 and Re/Al_2O_3 are only very weakly dependent on the drying temperature. The TPR behavior of the monometallic catalysts is thus primarily determined by the oxidation temperature, the drying temperature having only a secondary effect.

In contrast to the monometallic catalysts, drying significantly effects the TPR profile of the $Pt/Re/Al_2O_3$ catalyst. As shown in Fig. 3 and Table 3, both the number and position of the peaks depend on the drying temperature.

The TPR profile of the $Pt/Re/Al_2O_3$ catalyst dried at 100 or 200°C consists of a single peak with a peak maximum temperature similar to that of monometallic Pt/Al_2O_3. The size of this peak corresponds to the reduction of both the Pt and the Re, as shown in Table 4. Apparently, both metals reduce simultaneously. A single TPR peak for $Pt/Re/Al_2O_3$ catalysts dried at less than 200°C has been observed previously by Bolivar *et al.* (*4*) and Wagstaff and Prins (*6*).

At the other temperature extreme, 500°C, two TPR peaks are found, one at a temperature characteristic of monometallic Pt/Al_2O_3 and one at a temperature characteristic of monometallic Re/Al_2O_3. This is similar to the finding of McNicol (*5*), who observed a TPR profile for $Pt/Re/Al_2O_3$, dried at 400°C, identical to the sum of the monometallics, also dried at 400°C. Wagstaff and Prins (*6*) also observed two peaks in the TPR of a $Pt/Re/Al_2O_3$ catalyst dried at 500°C.

Three different suggestions have been made to explain this variation between the low temperature drying and 500°C drying TPRs for the $Pt/Re/Al_2O_3$ catalysts, all involving the effect of drying temperature on the amount of water on the catalyst:

(1) The degree of hydration influences the ease of reduction of a metal oxide.

(2) The degree of hydration influences the rate of H_2 spillover.

(3) The degree of hydration influences the mobility of Re_2O_7.

Our findings do not support this first idea since, as discussed earlier, we find that drying has little effect on the reduction of either monometallic Pt or Re oxides. The ease of reduction of the metal oxides is primarily set by the oxidation temperature, not the drying temperature. The effect of drying temperature must therefore involve interaction of the Pt and Re.

The second idea mentioned above involves H_2 spillover (*11*). In this case, the suggestion is that atomic H produced by dissociative adsorption of H_2 on the Pt can migrate by way of the Al_2O_3 support to the Re_2O_7, leading to its reduction. Water is known to be a necessary cocatalyst for hydrogen spillover. Therefore, the difference in the reducibility of Re in the bimetallic $Pt/Re/Al_2O_3$ catalyst, with drying temperature, could be due to varying amounts of water on the Al_2O_3 support effecting the rate of H_2 spillover. H_2 spillover on Pt/Al_2O_3 catalysts has recently been studied quantitatively (*12*). An order of magnitude calculation, based on these quantitative results, indicates that the amount of H_2 which could spillover in our system is at least two orders of magnitude too low to account for the observed results. The details of the calculation are in Appendix A.

The idea of water influencing the mobility of Re_2O_7 was first proposed by Bolivar *et al.* (*13*) and has been further discussed by Wagstaff and Prins (*6*), based on their results after 180 and 500°C drying. They suggested that the Pt and Re oxides exist separately on the support. The reduction of the oxides is initiated by the formation of some reduced Pt which then acts as a nucleus for further reduction, probably by supplying atomic hydrogen. Low-temperature drying, below 200°C, does not remove the water adsorbed by the catalyst during storage and the Re_2O_7 is still hydrated. The proposal is that this hydrated Re_2O_7 is mobile and is able to migrate to the Pt reduction centers. Thus, the reduction of the two metal oxides is essentially simultaneous, resulting in a single TPR peak, and an alloy is formed. In contrast, high-temperature drying, 500°C, dehydrates the Re_2O_7 which is no longer able to migrate to the Pt reduction centers. The Re_2O_7 therefore reduces at the temperature of monometallic Re/Al_2O_3, resulting in two TPR peaks, and, by implication, no alloy is formed.

Our results support the proposal that water influences the mobility of Re_2O_7. However, they further suggest that the actual effect of water on the mobility of Re_2O_7 is more complex than previously suggested. TPRs for $Pt/Re/Al_2O_3$, dried at 300 and 400°C, are also shown in Fig. 3. In these cases, two TPR peaks are found. The low-temperature peaks are about the same size as monometallic Pt/Al_2O_3 and are at about the same temperature; they correspond to the reduction of Pt. The higher temperature peaks, which are about the same size as those of monometallic Re/Al_2O_3, have a maximum at temperatures not characteristic of either monometallic Pt/Al_2O_3 or Re/Al_2O_3, but intermediate between the two. These peaks probably correspond to the reduction of Re which is influenced by the reduced Pt. These peaks demonstrate that Re_2O_7 is not just hydrated and mobile or dehydrated and immobile, as previously suggested. If this were the case, only peaks at characteristic Pt/Al_2O_3 temperatures and characteristic Re/Al_2O_3 temperatures could exist. The sizes of the two peaks would vary according to how much Re_2O_7 was hydrated and thus able to migrate to the Pt reduction centers.

We suggest, instead, that a variety of degrees of hydration of Re_2O_7 can exist which result in varying mobilities of the oxide. We further suggest that the mobility of Re_2O_7 is also dependent on the TPR temperature. The degree of hydration of the Re_2O_7 is set by the drying temperature: the higher the drying temperature, the lower the degree of hydration and thus the lower the mobility of the Re_2O_7. As the TPR temperature increases, the mobility of the Re_2O_7 also increases. Thus, as the drying temperature is raised, the TPR temperature necessary for Re_2O_7 migration to the Pt reduction centers, which results in a TPR peak due to Re reduction, increases. At sufficiently high drying temperatures, the TPR temperature necessary for Re_2O_7 migration will be higher than that needed for monometallic Re/Al_2O_3 reduction and the Re_2O_7 of the bimetallic catalyst will reduce at the temperature of monometallic Re/Al_2O_3.

Comparison of the TPRs of the bimetallics and the monometallics, e.g., Fig. 7 and Fig. 8, demonstrates that at none of the drying temperatures investigated is the TPR of the bimetallic catalyst equal to the sum of the monometallics. In all cases, there is evidence of interaction between the Pt and the Re of the $Pt/Re/Al_2O_3$ catalyst during reduction. It appears that even after 500°C drying, there is still some hydration of the Re_2O_7, so that a TPR temperature can be reached at which Re_2O_7 has sufficient mobility to migrate to Pt reduction centers. Our TPR results suggest alloy formation, during reduction, for all drying temperatures of 500°C or less.

Our proposal regarding Re_2O_7 migration assumes that drying serves primarily to dictate the amount of water on the catalyst and otherwise does not significantly affect the catalyst structure. This assumption is substantiated by the TPR shown in Fig. 4 which demonstrates that a $Pt/Re/Al_2O_3$ catalyst dried at 500°C and then rewetted at room temperature has a TPR very similar to that of an undried catalyst; it is not at all similar to that of a 500°C dried $Pt/Re/Al_2O_3$ catalyst. The 500°C drying prior to rewetting apparently does not significantly alter the structure of the catalyst; of primary importance is the amount of water on the catalyst prior to reduction.

An explanation for the lack of alloying during drying is provided by the TPR shown in Fig. 5. This result, which has been previously discussed in detail (*6*), suggests that oxidation of an alloyed $Pt/Re/Al_2O_3$ catalyst segregates the alloyed metals; the metal oxides of the $Pt/Re/Al_2O_3$ catalyst are immiscible. Thus, even though the Re_2O_7 may be hydrated and therefore mobile during the drying process, no alloy is formed due to immiscibility of the oxides. The areas under these two peaks are not as large as those of the fresh calcined catalysts. This indicates that the 1 hr 500°C reoxidation is not sufficient to fully oxidize either the Pt or the Re. The temperatures corresponding to the peak maxima are also lower than those found with the calcined catalysts. This also suggests that the metals are not fully oxidized and that the interaction of the partially oxidized metals with the Al_2O_3 support is not as strong as the interaction in the fresh catalysts.

It is well known (*14*) that combinations of Cl_2, air, and water can lead to redispersion of reforming catalysts, probably due to the formation of mobile metal oxy-chlorides. Since our catalysts contained significant quantities of chloride, we decided to examine the effect of removing this chloride. The stripping procedure used should not greatly affect either the surface area of the γ-Al_2O_3 (*15*) or the metals (*16*). As shown in Fig. 6, the removal of chloride from the $Pt/Re/Al_2O_3$ catalyst does not significantly affect the resulting TPR. The mobility of Re in the $Pt/Re/Al_2O_3$ catalyst does not appear to be due to Re oxy-chloride formation or depend on chloride on the Al_2O_3 support.

Drying at 100°C results in about one monolayer of water on γ-Al_2O_3 (*17*). The weight loss of our catalysts after extensive drying indicates that prior to drying they contain well in excess of a monolayer of water. Wetting the catalyst in saturated

H_2O/He at room temperature would certainly result in greater than a monolayer of water. A comparison of Fig. 4 and Fig. 6 demonstrates that the TPRs of a Pt/Re/Al_2O_3 catalyst which has been dried at 100°C and an undried catalyst are identical. Thus, quantities of water on the catalyst in excess of what corresponds to a monolayer on the support appear to have no additional effect on the reduction of the Re_2O_7. This suggests two possibilities. First, the Re_2O_7 may actually be interacting with water or hydroxyl groups on the Al_2O_3 surface during its migration. In excess of monolayer water coverage on the Al_2O_3 apparently would not affect the mobility of the Re_2O_7. Alternatively, the drying temperature may actually affect the hydration of the Re_2O_7 itself. In this case, the effect of drying temperature on the hydration of Re_2O_7 must be similar to that for γ-Al_2O_3 and water on the Re_2O_7 in excess of a monolayer must not influence its mobility. Thus, even though we have been referring to the degree of hydration of Re_2O_7, the important factor influencing the mobility of Re_2O_7 may be the degree of hydration, or hydroxylation, of the Al_2O_3 support.

In a recent paper (*18*), the behaviors of a bimetallic Pt/Re/Al_2O_3 catalyst and a physical mixture of Pt/Al_2O_3 and Re/Al_2O_3 were compared for reforming of a naphtha feed. The bimetallic catalyst and the physical mixture were found to have identical stability for reforming. This finding raises questions regarding the relative structures of the bimetallic catalyst and the physical mixture. Figure 7 demonstrates a large difference between the TPR, after 100°C drying, of the bimetallic Pt/Re/Al_2O_3 and the physical mixture of Pt/Al_2O_3 and Re/Al_2O_3; the TPR of the physical mixture is instead similar to the sum of the monometallics. The catalysis of Re reduction by Pt found with the bimetallic catalyst is largely missing with the physical mixture. This result is not in agreement with previous work (*4*), where little difference was found between the reduction behavior of a physical mixture of Pt/Al_2O_3 and Re/Al_2O_3, and bimetallic Pt/Re/Al_2O_3. Perhaps, this difference is due to the use of uncalcined catalysts in the previous work. Since high-temperature calcination enhances interaction of the metal oxides with the support, lack of calcination would encourage metal migration; evidence of substantial Re migration from particle to particle was found after reduction of an uncalcined physical mixture on α-Al_2O_3. Both the lack of calcination and the use of α-Al_2O_3, in the previous work, would encourage Re migration. Our own similar experiments on physical mixtures with different particle sizes, with high-temperature calcination and a γ-Al_2O_3 support, show no evidence of metal migration from particle to particle.

After 500°C drying, the TPR behavior of the physical mixture of Pt/Al_2O_3 and Re/Al_2O_3 is identical to the sum of the monometallics (Fig. 8). This suggests no interaction of the two metals of the physical mixture during reduction. In contrast, comparison of the TPR of the Pt/Re/Al_2O_3 and the sum of the monometallics does suggest some interaction of the Pt and the Re of the bimetallic catalyst. Thus, regardless of the drying temperature, physical mixtures of Pt/Al_2O_3 and Re/Al_2O_3 have TPR profiles much more similar to the sum of the monometallics than to the bimetallic Pt/Re/Al_2O_3 catalyst. The bimetallic catalyst consistently demonstrates more interaction of the two metals during reduction than the physical mixtures.

After high-temperature calcination, the oxidation states of Pt and Re are $+4$ and $+7$, respectively. As shown in Table 4, the amount of H_2 actually consumed by the catalysts during a TPR is in good agreement with the amount needed to reduce the metals to the $+0$ oxidation state. We thus find that both the Pt and the Re of our catalysts can be completely reduced to metal, in agreement with others (*4–6, 19, 20*). No evidence was found that alumina-supported Re can only be reduced to an intermediate oxidation state (*21, 22*).

CONCLUSIONS

The effect of drying on the reduction of $Pt/Re/Al_2O_3$ catalysts has been studied utilizing temperature-programmed reduction. Drying has little effect on the reduction of the monometallic catalysts Pt/Al_2O_3 and Re/Al_2O_3. In contrast, both the number of TPR peaks and the peak maximum temperatures of the $Pt/Re/Al_2O_3$ catalyst vary with drying temperature. The results suggest that water influences the rate of Re_2O_7 migration to Pt reduction centers. Apparently, the degree of hydration of Re_2O_7 is variable which results in varying degrees of mobility of the oxide. The mobility of Re_2O_7 is thus dependent on both the drying temperature, which determines the degree of hydration, and the TPR temperature.

At none of the drying temperatures investigated is the TPR profile of the bimetallic $Pt/Re/Al_2O_3$ catalyst equal to the sum of the monometallics. For drying temperatures up to 500°C, it is concluded that a substantial fraction of the Re_2O_7 is at least partially hydrated and able to migrate to Pt reduction centers.

The drying temperature determines the amount of water on the catalyst prior to reduction but does not otherwise significantly alter the structure of the catalyst. Pt and Re oxides appear to be immiscible resulting in no alloy formation during drying. The mobility of Re_2O_7 is not influenced by chloride on the catalyst or water in excess of that which corresponds to a monolayer on γ-Al_2O_3.

Physical mixtures of the monometallic catalysts have TPR profiles much more similar to the sum of the monometallics than to the bimetallic catalyst. Both the Pt and the Re of the catalysts examined can be reduced to metal.

APPENDIX A

H_2 spillover on Pt/Al_2O_3 catalysts has been studied quantitatively by Kramer and Andre (*12*). They showed that at short reduction times, where the spillover rate is highest, the amount of H_2 spillover can be described by a diffusion equation:

$$c = 4Nac_e(\pi Dt)^{1/2} \qquad (1)$$

where c = amount spillover/cm^2, N = number Pt crystallites/cm^2, a = crystallite radius, c_e = amount spillover at equilibrium/cm^2, D = diffusion coefficient, and t = time.

Assuming that it is equal to the overall metal dispersion, the Pt dispersion of the $Pt/Re/Al_2O_3$ catalyst is about 0.57 (*10*). Knowing the dispersion, a and N can be calculated if regular crystallites are assumed (*23*). The quantities c_e and D are given by Kramer and Andre for reduction at 400°C and 710 Torr H_2. For the time needed to program the catalyst temperature to 400°C, the result, calculated from Eq. (1), is $c = 4.2 \times 10^{10}$ atoms H/cm^2.

We would like to compare this value of H_2 spilled over to the quantity of H_2 consumed by Re reduction, up to 400°C, in the bimetallic catalyst after 200°C drying. Andre and Kramer, however, dried their catalysts at 550°C. The rate of H_2 spillover is dependent on the amount of water on the support, which is determined by the drying temperature. Thus, a correction needs to be made for the amount of water on the catalyst after 200°C drying rather than 550°C drying. It has been shown (*24*) that, for less than a monolayer of water on the support, the amount of H_2 spilled over, at any given time, is proportional to the amount of water on the support. After 200°C drying, there is about 80% of a monolayer of water on the surface; after 550°C drying there is about 25% of a monolayer (*17*). Thus, for our catalysts, after 200°C drying, we would predict that 2.7×10^{17} atoms H would spillover at 400°C and 710 Torr H_2 during the time necessary to program the temperature to 400°C. It should be noted that the actual H_2 partial pressure during the TPR was less than 36 Torr and the temperature was programmed up from room temperature to 400°C. Since the spillover rate is positive in both temperature and H_2 pressure (*12*), the calculated value of 2.7×10^{17} atoms H spillover is an upper limit of the possible spillover during the TPR.

The area under the curve, up to 400°C, of the TPR of the $Pt/Re/Al_2O_3$ catalyst dried at 200°C, indicates that 6.0×10^{19} atoms H are needed to reduce the Re_2O_7. The amount of H_2 which could spillover is at least two orders of magnitude lower than that needed to reduce the Re_2O_7.

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