

Surface Area Measurement of Platinum/Rhenium/Alumina

II. Effects of Catalyst Pretreatment

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Surface area measurement has been used to examine the effects of catalyst pretreatment on reduced Pt/Re/Al₂O₃ catalysts. The results indicate significant alloy formation in reduced Pt/Re/Al₂O₃ for all drying temperatures of 500°C or less. While the surface amount of alloyed Pt-Re is insensitive to the drying temperature, the surface amount of unalloyed Re varies significantly with the drying temperature. Reduction of the Pt/Re/Al₂O₃ catalyst dried at 100°C, which contains no unalloyed Re, is complete after 1 h of 500°C H₂ reduction. Reduction of the Pt/Re/Al₂O₃ catalyst dried at 500°C, which does contain unalloyed Re, is not complete until after 15 h of 500°C H₂ reduction. For both drying temperature, alloy formation is complete after 1 h of 500°C H₂ reduction.

INTRODUCTION

Temperature-programmed reduction (TPR) results (1, 2) have shown a significant effect of drying temperature on the rate of reduction of Pt/Re/Al₂O₃. The results (2) further suggested alloy¹ formation in the Pt/Re/Al₂O₃ catalyst for all drying temperatures of 500°C or less. As the reduced form of a reforming catalyst is the active state, we would now like to examine the effects of drying temperature on the structure of reduced Pt/Re/Al₂O₃ catalysts. Direct examination of the reduced state is of particular importance as it has been shown (1) that two different TPR profiles can lead to the same reduced catalyst. One technique for characterizing reduced catalysts is metal surface area measurement, utilizing selective gas chemisorption.

We have previously (3) proposed a stoichiometry for surface area measurement of Pt/Re/Al₂O₃ catalysts that allows determination of (Pt_s + Re_s), (Pt_s + Re_s alloyed), Re_s unalloyed, and Pt_s^R/Pt, the fraction of

the total Pt which chemisorbs H₂. This work presented strong evidence of alloy formation in a Pt/Re/Al₂O₃ catalyst dried at 500°C.

The purpose of this paper is to examine the effects of varying drying temperature on the structure of a reduced Pt/Re/Al₂O₃ catalyst as characterized by metal surface area measurement. Charcosset *et al.* (4) have previously examined the effects of two greatly differing pretreatments on the surface structure of a reduced Pt/Re/Al₂O₃ catalyst. These authors compared a catalyst which was dried at 110°C and then directly reduced in H₂ at 500°C to a catalyst which was calcined in O₂ at 500°C, evacuated at 500°C and then reduced in H₂ at 500°C, which they referred to as being redispersed. They found a large difference in the extent of alloy formation and total Re dispersion between the directly reduced and redispersed Pt/Re/Al₂O₃ catalysts.

EXPERIMENTAL

The catalysts used in this work contained about 0.3 wt% Pt and/or 0.3 wt% Re (2). The experimental apparatus and procedures are identical to those described previ-

¹ Although some readers may prefer the term bimetallic cluster, alloy is used here for the sake of brevity.

ously (3), except that the drying temperature was varied and, in some cases, the length of reduction was varied.

RESULTS AND DISCUSSION

As shown in Table 1, the measured dispersions of the monometallic Pt/Al₂O₃ catalyst dried at 100 and 500°C are identical. Apparently, drying temperatures below 500°C do not affect the dispersion of Pt/Al₂O₃. This result is consistent with our observation (2) that the rate of reduction of Pt/Al₂O₃ is only slightly influenced by the drying temperature. It is also consistent with the observations of Mills *et al.* (5) that treatment of a Pt/Al₂O₃ catalyst with water vapor prior to reduction does not affect the resulting catalyst. It has been shown (6), however, that large differences in Pt/Al₂O₃ water content, prior to reduction, do affect the resulting Pt dispersion.

Also shown in Table 1, the dispersions of monometallic Re/Al₂O₃ dried at 300 and 500°C are essentially identical and about 23% higher than the dispersion resulting from 100°C drying. High temperature drying, 300°C or above, appears to redisperse the Re/Al₂O₃ catalyst. This result is very similar to that of Yao and Shelef (7) who found a 28% increase in the dispersion of a 2.61% Re/Al₂O₃ catalyst following a 500°C inert treatment. Our results further indicate that redispersion of Re/Al₂O₃ does not require drying temperatures as high as 500°C

since drying at 300°C results in essentially the same dispersion.

We have shown previously (3) that adsorption of H₂ and O₂ by a physical mixture of Pt/Al₂O₃ and Re/Al₂O₃, dried at 500°C, is very similar to that expected for the sum of the monometallics. This indicated no interaction of the two metals of the physical mixture. The same is true for physical mixtures of Pt/Al₂O₃ and Re/Al₂O₃ dried at 100°C. For example, the experimentally measured OT₂/OT₁ ratio of the physical mixture dried at 100°C was 0.72 as compared to OT₂/OT₁ = 0.70 predicted from the sum of the monometallics. Our results suggest no interaction of the two metals of a physical mixture of Pt/Al₂O₃ and Re/Al₂O₃, regardless of the drying temperature.

The effect of varying the length of drying of the Pt/Re/Al₂O₃ catalyst, between 1 and 6 h, is shown in Fig. 1, for 100°C drying, and Fig. 2, for 500°C drying. For both drying temperatures, the surface composition of the Pt/Re/Al₂O₃ catalyst is independent of drying time, for times greater than 1 h. Comparison of these two figures does indicate a dependence of the surface composition on the drying temperature, however. Previous results (2) demonstrated a similarity between the effects of drying temperature on the reduction of Pt/Re/Al₂O₃ and on the hydration of γ -Al₂O₃. It is worth noting that Peri (8) has shown that the degree of hydration of γ -Al₂O₃ is primarily set by the

TABLE I
The Effects of Drying Temperature on the Dispersion of Pt/Al₂O₃ and Re/Al₂O₃

Catalyst	Drying temperature (°C)	Dispersion				
		H ₂ Chemisorption	O ₂ Chemisorption	1st O ₂ Titration	H ₂ Titration	2nd O ₂ Titration
Pt/Al ₂ O ₃	100	0.53	0.42	0.45	0.43	0.45
	500	0.54	0.43	0.47	0.44	0.48
Re/Al ₂ O ₃	100	No reaction	0.27		No reaction	No reaction
	300		0.33			
	500		0.34			

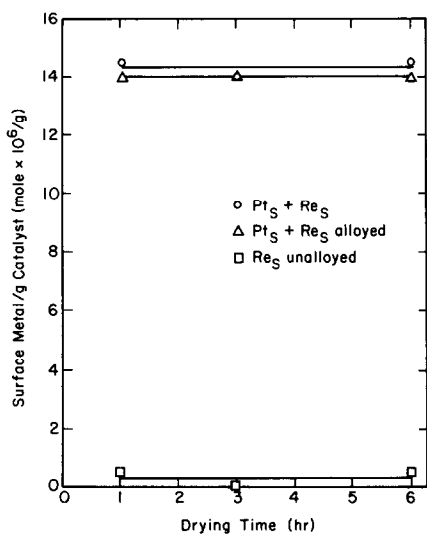


FIG. 1. Effect of 100°C drying time on Pt/Re/Al₂O₃.

drying temperature, with drying times in excess of 1 h having little additional effect. Once again, similarities between the effects of drying on Pt/Re/Al₂O₃ and γ -Al₂O₃ are suggested.

The effects of varying drying temperature on the surface composition of the Pt/Re/Al₂O₃ catalyst are shown more explicitly in Fig. 3. It is evident from these data

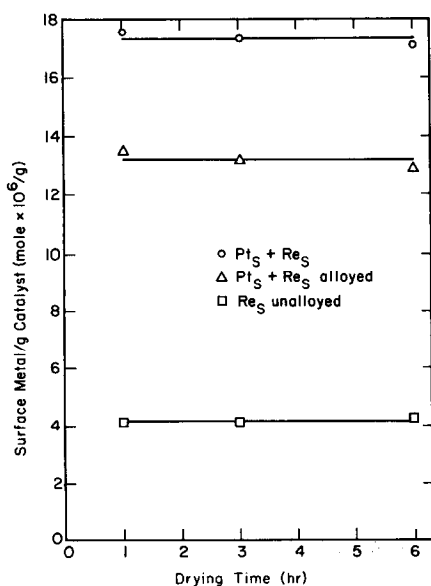


FIG. 2. Effect of 500°C drying time on Pt/Re/Al₂O₃.

that the surface structure of the active Pt/Re/Al₂O₃ catalyst is dependent on the catalyst pretreatment. As mentioned earlier, Charcosset *et al.* (4) observed differences in the structure of a reduced Pt/Re/Al₂O₃ catalyst which had been submitted to two different pretreatments. The pretreatment of their redispersed catalyst is similar to that of our catalysts dried at 500°C. All of our catalysts were calcined, so that we have no pretreatment directly comparable to that of Charcosset and co-worker's direct reduction; the 100°C drying pretreatment would be closest, however.

The overall dispersion of the Pt/Re/Al₂O₃ catalyst is about 0.46 after 100°C drying, rises to a maximum dispersion of 0.63 at about 300–375°C and then falls slightly to a dispersion of 0.57 after 500°C drying. This is consistent with Charcosset and co-worker's finding that their redispersed catalyst had a significantly higher overall dispersion than their directly reduced catalyst. It is of note that for all drying temperatures, the measured dispersion of the Pt/Re/Al₂O₃ catalyst is significantly larger than that predicted by the sum of the monometallics, 0.34 and 0.38 for 100 and 500°C drying, respectively.

As shown in Fig. 3, the increase in the overall dispersion of the Pt/Re/Al₂O₃ catalyst with increasing drying temperature is

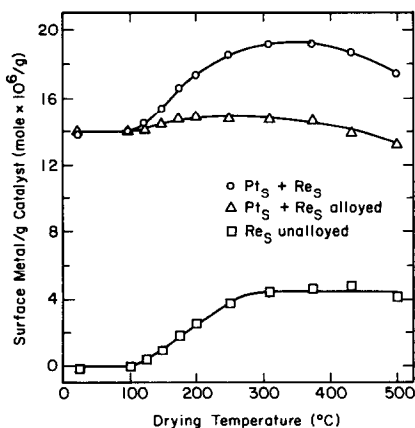


FIG. 3. Effect of drying temperature on Pt/Re/Al₂O₃.

primarily due to an increase in Re_s unalloyed, in agreement with previous work (4). After 100°C drying, the Pt/Re/Al₂O₃ catalyst contains essentially no unalloyed Re but is instead all Pt and alloyed Re. Charcosset *et al.* found a similar result for their directly reduced catalyst. As the drying temperature is increased from 100°C, the amount of Re_s unalloyed increases linearly up to about 300°C, above which it is approximately constant. This variation in Re_s unalloyed of the Pt/Re/Al₂O₃ catalyst with drying temperature is similar to the variation in Re_s of the Re/Al₂O₃ catalyst with drying temperature shown in Table 1. Both values do not differ significantly for drying temperature variations between 300 and 500°C while both are significantly larger after 300–500°C drying than after 100°C drying. The Re dispersion of the Pt/Re/Al₂O₃ catalyst, after 500°C drying, appears to be significantly smaller than the essentially total Re dispersion reported by Charcosset *et al.* for their redispersed catalyst.

The most significant differences between the present results and those of Charcosset *et al.* concern the quantity ($Pt_s + Re_s$ alloyed). Charcosset *et al.* found that ($Pt_s + Re_s$ alloyed) was much lower for their redispersed catalyst than for their directly reduced catalyst which they felt showed “a strong decrease in the Pt–Re interaction for the redispersed catalyst.” We instead find that ($Pt_s + Re_s$ alloyed) is relatively insensitive to the drying temperature, as shown in Fig. 3; the total variation in these ($Pt_s + Re_s$ alloyed) values is only 11%. As we expect little change in Pt_s with drying temperature, this result suggests that the amount of Re_s alloyed does not vary strongly with drying temperature. It further suggests that the extent of alloying of the Pt/Re/Al₂O₃ catalyst is only a weak function of the drying temperature.

The ratio Pt_s^R/Pt is a semi-quantitative measure of the extent of alloying of the Pt/Re/Al₂O₃ catalyst (3); the lower the amount of Pt which chemisorbs H₂, the greater the extent of alloying and vice versa. Pt_s^R/Pt as

a function of the drying temperature, for both Pt/Re/Al₂O₃ and Pt/Al₂O₃, is shown in Fig. 4. For Pt/Al₂O₃, Pt_s^R/Pt is independent of the drying temperature and is equal to about 0.54. For Pt/Re/Al₂O₃, Pt_s^R/Pt is only weakly dependent on the drying temperature, varying from about 0.16 to about 0.22 over the drying temperature range of 100 to 500°C. We thus find that Pt_s^R/Pt for Pt/Re/Al₂O₃ is only about 30 to 40% of Pt_s^R/Pt for Pt/Al₂O₃ for all drying temperature. This strongly suggests significant alloy formation in the Pt/Re/Al₂O₃ catalyst for all drying temperatures of 500°C or less. The results of Fig. 4 not only suggest significant alloy formation, but a relatively constant extent of alloying, in the Pt/Re/Al₂O₃ catalyst, regardless of the drying temperature. It is worthy of mention that Charcosset and co-worker's ir data did not show any difference in $\nu(\text{CO})$ frequency for CO chemisorbed by Pt, for the two catalyst pretreatments, as they expected. This could indicate that the amount of Re interacting with the Pt of their two catalysts was similar, in agreement with our results.

Thus, both the ($Pt_s + Re_s$ alloyed) results of Fig. 3 and the Pt_s^R/Pt results of Fig. 4 suggest significant alloy formation in reduced Pt/Re/Al₂O₃ catalysts after drying at 500°C or below. The same conclusion was drawn previously from TPR results (2). They further suggest that the extent of alloy formation in Pt/Re/Al₂O₃ is not significantly

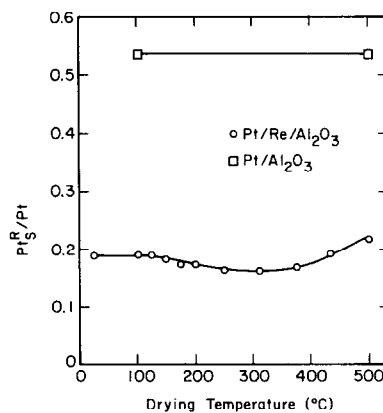


FIG. 4. Effect of drying temperature on Pt_s^R/Pt .

affected by the drying temperature. Instead, the major effect of the drying temperature is on the amount of Re_s unalloyed.

The surface composition of a Pt/Re/Al₂O₃ catalyst which was "dried" at 25°C, i.e., was purged in flowing Ar at room temperature, is also shown in Fig. 3. The Pt_s^R/Pt ratio for this "undried" catalyst is shown in Fig. 4. These results indicate that the surface structure of an "undried" Pt/Re/Al₂O₃ catalyst is identical to that of a catalyst dried at 100°C. This is consistent with the previously result (2) that the reduction profile of Pt/Re/Al₂O₃ is identical for 25 and 100°C drying. Once again, it is suggested that water on Pt/Re/Al₂O₃, prior to reduction, in excess of that which corresponds to a monolayer on γ -Al₂O₃ does not affect the catalyst.

The catalysts used in this work were reduced at 500°C in H₂, generally for 15 h. The effects of varying the length of reduction of the Pt/Re/Al₂O₃ catalyst are shown in Fig. 5, for 100°C drying, and Fig. 6 for 500°C drying. These results are of interest due to the known difficulty of reducing monometallic Re/Al₂O₃. For example, Webb (9) found that Re/Al₂O₃ calcined at 500°C required almost 70 h of 400°C H₂ for complete reduction. The data of Lin *et al.* (10) indicates that the reduction of their

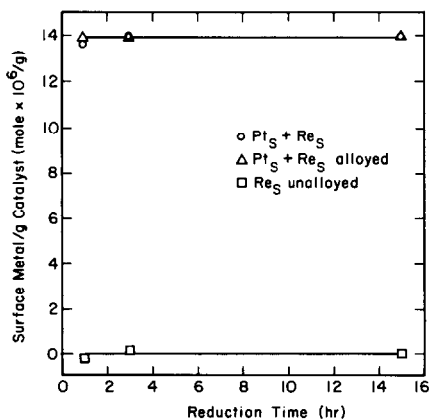


FIG. 5. Effect of reduction time on 100°C dried Pt/Re/Al₂O₃.

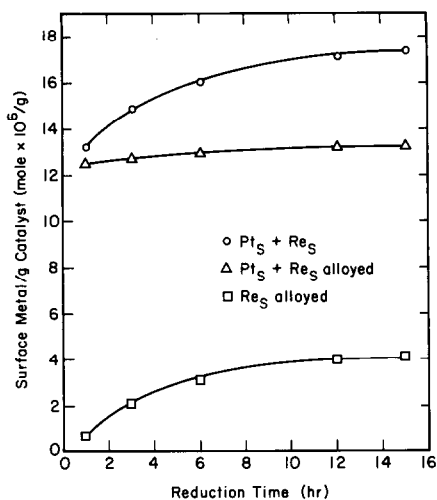


FIG. 6. Effect of reduction time on 500°C dried Pt/Re/Al₂O₃.

500°C calcined Re/Al₂O₃ catalyst was complete only after 15 h of 500°C H₂ reduction.

It is thus somewhat surprising that after 100°C drying, the surface structure of the Pt/Re/Al₂O₃ catalyst is independent of the reduction time for times greater than one hour, as shown in Fig. 5. Apparently, reduction of the 100°C dried catalyst is complete with 1 h of 500°C H₂ reduction. This result is consistent with previous TPR results (1, 2, 11) that demonstrated a strong catalysis of Re reduction in the Pt/Re/Al₂O₃ catalyst. This catalysis is probably due to Re₂O₇ migration to Pt reduction centers where alloy formation takes place. Accordingly, we would not expect that reduction of unalloyed Re in the Pt/Re/Al₂O₃ catalyst would differ from that of Re in Re/Al₂O₃. As the reduction of monometallic Re/Al₂O₃ is slow, this independence of the amount of Re_s unalloyed on the reduction time suggests that there is no unalloyed Re in the Pt/Re/Al₂O₃ catalyst after 100°C drying. Bolivar *et al.* (12) arrived at a similar conclusion regarding a directly reduced Pt/Re/Al₂O₃ catalyst based on their IR studies with CO as an adsorbate.

As shown in Fig. 6, reduction of the Pt/Re/Al₂O₃ catalyst dried at 500°C is not complete after 1 h of 500°C H₂ reduction. The

extent of reduction instead increases with increasing reduction time, reaching completion only after 15 h of 500°C reduction. As in the 100°C drying case, the reduction of (Pt_s + Re_s alloyed) is essentially complete after 1 h of 500°C reduction, suggesting once again that the reduction of Re which becomes alloyed is catalyzed by Pt. There does appear to be unalloyed Re in the Pt/Re/Al₂O₃ catalyst after 500°C drying. It is the unalloyed Re which requires 15 h of 500°C H₂ for complete reduction, in agreement with the results of Lin *et al.* (10) for monometallic Re/Al₂O₃.

After both 100 and 500°C drying (Pt_s + Re_s alloyed) is independent of 500°C reduction time. We would thus also expect Pt_s^R/Pt, for the Pt/Re/Al₂O₃ catalyst, to be independent of the reduction time after both 100°C and 500°C drying. This is indeed the case, as shown in Fig. 7. Thus, our Pt_s^R/Pt results also demonstrate that alloy formation in the Pt/Re/Al₂O₃ catalyst is complete after 1 h of 500°C reduction, regardless of the drying temperature.

Freel (13) has previously presented data regarding the length of 500°C reduction on Pt/Re/Al₂O₃ catalysts. It is not possible to compare his results directly to ours since Freel (13, 14) first reduced his catalysts for about an hour, ran a surface area measurement, and then rereduced them for about 15 h and ran another surface area measurement. He thus varied both the amount of water on his catalysts, prior to reduction,

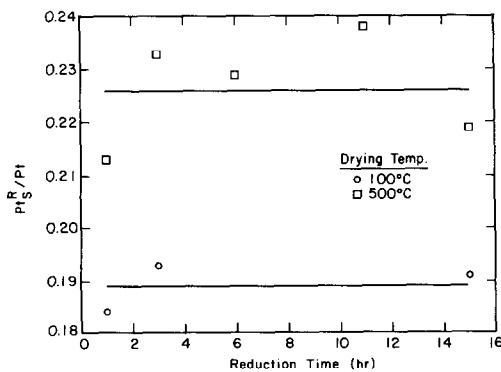


FIG. 7. Effect of reduction time on Pt_s^R/Pt.

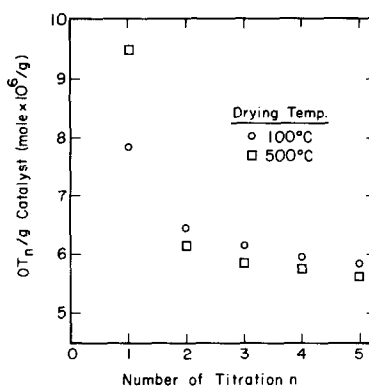
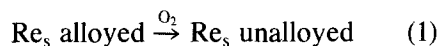


FIG. 8. Variation of oxygen uptake in successive titrations of Pt/Re/Al₂O₃.

and the reduction time. Nevertheless, Freel did find that his results corresponding to our Pt_s^R/Pt and (Pt_s + Re_s alloyed) values did not differ significantly between the two surface area measurements. This indicates that the alloyed portion of his Pt/Re/Al₂O₃ catalysts was insensitive to the reduction time and the drying temperature, in agreement with our results. He also found that his second reduction led to an increase in nonreactive oxygen, corresponding to our Re_s unalloyed, which is also consistent with our results.

We have shown previously (3) that the ratio OT_n/OT₁ continuously decreases as *n*, the number of the titration, increases for the Pt/Re/Al₂O₃ catalyst dried at 500°C. This suggested that the O₂ titrations themselves segregate the Pt-Re alloy after 500°C drying. As shown in Fig. 8, the value of OT_n also continuously decreases with increasing *n* for the Pt/Re/Al₂O₃ catalyst dried at 100°C. Thus, it appears that the reaction:



needs to be included in the surface area stoichiometry for Pt/Re/Al₂O₃, regardless of the drying temperature. Some quantification of this segregation is necessary in order to utilize the stoichiometry to relate measured gas uptakes to the quantity of surface metal in the Pt/Re/Al₂O₃ catalyst.

The metal surface area values reported in this paper, for Pt/Re/Al₂O₃, are based on the assumption that there is no Re_s unalloyed after 100°C drying, which allows quantification of reaction (1), and that the extent of reaction (1) is independent of the drying temperature. The absence of Re_s unalloyed in the Pt/Re/Al₂O₃ catalyst, dried at 100°C, is suggested by the independence of its surface structure on the reduction time, as discussed earlier.

As shown in Fig. 8, there is a large difference in the values of OT₁ after 100 and 500°C drying of the Pt/Re/Al₂O₃ catalyst, due to the presence of Re_s unalloyed after 500°C drying. There is, however, little differences between the OT_n values for $n > 1$, for the two drying temperatures. This suggests that the effect of the O₂ titrations on segregation of alloyed Re is similar for the two drying temperatures.

The amount of Re_s unalloyed, in the Pt/Re/Al₂O₃ catalyst after 500°C drying, extrapolates to zero at zero time of 500°C reduction, as shown in Fig. 6. Thus, after both 100 and 500°C drying, the amount of Re_s unalloyed extrapolates to the same assumed zero value at zero time of 500°C reduction. Since we expect no Re_s unalloyed after zero time of 500°C reduction for either drying temperature, this result substantiates the suggestion that there is no Re_s unalloyed after 100°C drying. It further suggests that the extent of reaction (1) is independent of the drying temperature which is not surprising as the structure of the alloyed portion of the Pt/Re/Al₂O₃ catalyst is insensitive to the drying temperature.

We have assumed that at zero time of 500°C reduction there is no Re_s unalloyed in the Pt/Re/Al₂O₃ catalyst after 100 or 500°C drying. The 500°C reduction is, however, preceded by a H₂ treatment in which the catalyst temperature is raised to 500°C at 6°C/min. Obviously, some reduction of the Pt/Re/Al₂O₃ catalyst occurs during this temperature ramp. In fact, TPR results (2) indicate that about 10% of the Re in monometallic Re/Al₂O₃ is reduced by 500°C re-

duction for both 100 and 500°C drying. Surface area measurements also indicate that atoms of oxygen chemisorbed per total atoms of Re is about 10% for monometallic Re/Al₂O₃ after this temperature ramp, for both 100 and 500°C drying. Thus, it is possible that there could be Re_s unalloyed in the Pt/Re/Al₂O₃ catalyst at zero time of 500°C reduction. We, however, feel that a significant reduction of Re_s unalloyed during this temperature ramp is unlikely, considering that there is no additional formation of Re_s unalloyed during 15 h of 500°C reduction, for the Pt/Re/Al₂O₃ catalyst dried at 100°C. We instead prefer the alternate explanation that the Re in the Re/Al₂O₃ catalyst which is reduced during the temperature ramp has the least interaction with the Al₂O₃ support and that similar Re in the Pt/Re/Al₂O₃ catalyst would be the most likely Re to migrate to Pt reduction centers where it would become alloyed.

Thus, the results suggest that the surface area measurements themselves cause segregation of the Pt-Re alloy. The results further suggest, however, that the effect of this segregation on the surface area stoichiometry can be accounted for so that meaningful data on reduced Pt/Re/Al₂O₃ catalysts is obtainable. The data suggest that Pt/Re/Al₂O₃, dried at 100°C, contains no unalloyed Re and that the extent of segregation due to the surface area measurements is independent of the drying temperatures.

CONCLUSIONS

Surface area measurements indicate that drying temperature does not affect the dispersion of monometallic Pt/Al₂O₃ catalysts. High temperature drying, 300–500°C, does lead to redispersion of monometallic Re/Al₂O₃. Physical mixtures of the monometallic catalysts behave as the sum of the monometallics regardless of the drying temperature.

Although drying times greater than 1 h do not have any additional effect on the Pt/Re/Al₂O₃ catalysts, drying temperature does.

The effect of drying temperature is primarily on the quantity of Re_s unalloyed. Re_s unalloyed increases as the drying temperature is raised to about 300°C ; above 300°C , the amount of Re_s unalloyed is independent of the drying temperature. Alloy formation in the $\text{Pt/Re/Al}_2\text{O}_3$ catalyst is significant and of approximately equal magnitude for all drying temperatures of 500°C or less.

Reduction of the $\text{Pt/Re/Al}_2\text{O}_3$ catalyst dried at 100°C is complete after 1 h of 500°C reduction. This indicates that there is no unalloyed Re in this catalyst. The $\text{Pt/Re/Al}_2\text{O}_3$ catalyst dried at 500°C does contain Re_s unalloyed, and requires at least 15 h in H_2 at 500°C to reduce it. The alloyed portion of the $\text{Pt/Re/Al}_2\text{O}_3$ of catalysts dried at 100 and 500°C is reduced after 1 h of 500°C H_2 reduction.

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