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Surface Area Measurement of Platinum/Rhenium/Alumina

I. Stoichiometry of Hydrogen–Oxygen Chemisorptions and Titrations

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The stoichiometry of H_2 and O_2 adsorption by Pt/Al_2O_3, Re/Al_2O_3, and $Pt/Re/Al_2O_3$ has been studied. The gas uptakes of the monometallic catalysts were used to predict the expected uptakes by the $Pt/Re/Al_2O_3$ catalyst assuming no interaction between the two metals. A significant decrease in H_2 chemisorption and an increase in titratable O_2 in the bimetallic, compared to that expected for no metal interaction, suggest alloy formation in the $Pt/Re/Al_2O_3$ catalyst. A stoichiometry for H_2 and O_2 chemisorption and titration by $Pt/Re/Al_2O_3$ consistent with these observations is proposed.

INTRODUCTION

Metal surface area measurement by selective gas chemisorption is commonly utilized for characterization of reforming catalysts. In order to use selective gas chemisorption for metal surface area measurement, the stoichiometry of the surface reactions must be determined to relate the experimentally measured gas uptakes to the quantity of surface metal.

The uptake of H_2 and O_2 by $Pt/Re/Al_2O_3$ catalysts was first examined by Freel (*1*), who did not suggest a stoichiometry to relate his measured uptakes to surface metal. A method for separate determination of Pt and Re in the bimetallic catalyst was proposed by Menon *et al.* (*2*). These authors did not determine a stoichiometry for adsorption by Re and later stated that they were not able to determine a reliable chemisorption value for Re (*3*). Bolivar *et al.* (*4*, *5*) have also measured the uptake of H_2 and O_2 by $Pt/Re/Al_2O_3$ catalysts and proposed a stoichiometry to relate their measured uptakes to the quantity of surface metal.

The uptake of H_2 and O_2 by $Pt/Re/Al_2O_3$ catalysts has been examined by several research groups; one group has proposed a stoichiometry for surface area measurement. There are, however, significant differences in the results of these various groups, particularly with respect to H_2 chemisorption by Pt and titration of O_2 chemisorbed on Re. In this paper, we present further results on the uptake of H_2 and O_2 by $Pt/Re/Al_2O_3$ catalysts and suggest a stoichiometry for utilizing the measured gas uptakes for surface area measurement.

EXPERIMENTAL

The pulse flow surface area apparatus used in this study is similar to that described by Freel (*1*). All gases, argon, hydrogen, oxygen, 20% hydrogen in argon, and 15% oxygen in argon, were of ultrahigh purity (Matheson). The argon, hydrogen, and hydrogen in argon were further purified by passage through a fresh oxygen trap (Alltech), followed by a fresh 13× molecular sieve (Matheson). The concentration of oxygen in the carrier gas, argon, at the catalyst was less than 0.1 ppm (*6*).

The catalysts contained about 0.3 wt% Pt and/or 0.3 wt% Re supported on γ-Al_2O_3, obtained from Chevron Research Company. They were calcined by the manufacturer, probably at about 500°C (*7*). During storage, the catalysts adsorbed water (*7*). Thus, the first step of the pretreatment was to dry the catalyst, in this case at 500°C for 3 h in flowing argon, 50 ml/min. The tem-

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TABLE 1

Stoichiometry and Dispersion of Pt/Al_2O_3

Stoichiometry	Dispersion
H_2 Chemisorption $Pt_s + \frac{1}{2}H_2 \rightarrow Pt_sH$	0.54
O_2 Chemisorption $Pt_s + \frac{1}{2}O_2 \rightarrow Pt_sO$	0.43
1st O_2 Titration $Pt_sH + \frac{3}{4}O_2 \rightarrow Pt_sO + \frac{1}{2}H_2O$	0.47
H_2 Titration $Pt_sO + \frac{3}{2}H_2 \rightarrow Pt_sH + H_2O$	0.44
2nd O_2 Titration $Pt_sH + \frac{3}{4}O_2 \rightarrow Pt_sO + \frac{1}{2}H_2O$	0.48

perature was then lowered to about 100°C, at which time the gas flow was switched to hydrogen. After raising the temperature, at 6°C/min, to 500°C, the catalyst was reduced for 15 h. The catalyst was then purged with argon at 500°C for 1 h, then cooled to room temperature, which took about 1 h.

The surface area measurements were made at room temperature with argon as a carrier gas, 50 ml/min. Sixty microliter pulses of hydrogen, oxygen, 20% hydrogen in argon, or 15% oxygen in argon were utilized for catalyst samples weighing about 1 g.

RESULTS AND DISCUSSION

The surface area measurements were made in the order: H_2 chemisorption, O_2 titration, H_2 titration, and second O_2 titration. H_A designates H_2 taken up in the H_2 chemisorption. OT_1 is O_2 taken up in the first O_2 titration, HT is H_2 in the H_2 titration, and OT_2 is O_2 taken up in the second O_2 titration. O_A, the atoms of O_2 chemisorbed, was calculated from the expression: $O_A = OT_1 - \frac{1}{2} H_A$ (*1*). H_A, OT_1, HT, OT_2, and O_A are all expressed in units of atoms.

Platinum–Alumina Catalyst

The stoichiometry generally accepted for H_2 and O_2 chemisorptions and titrations on Pt/Al_2O_3 is shown in Table 1 (*8*). Monometallic Pt dissociatively chemisorbs both H_2 and O_2 and each gas will titrate the other. Also found in Table 1 is the dispersion, defined as atoms surface metal/atoms total metal (Pt_s/Pt), of the Pt catalyst calculated according to each of the stoichiometric equations. The dispersion values, other than the one determined by H_2 chemisorption, are in good agreement; the average is about 0.46 with an average percentage deviation of about 4%. The dispersion determined by H_2 chemisorption is higher at 0.54. Similar results have been obtained previously: our ratio of (dispersion from H_2 titration/dispersion from H_2 chemisorption) = 0.82 is in very good agreement with the value of 0.81 found by Kobayishi *et al.* (*9*) for a Pt/Al_2O_3 catalyst having a similar dispersion. Similarly, our value of $(O_A/H_A) = 0.80$ is also in agreement with the results summarized by Freel (*10*).

The dispersion of the Pt catalyst, as determined by H_2 chemisorption, was also measured in a static volumetric apparatus (*11*). The dispersion, in this case, was found to be 0.57, about 6% higher than that found in our pulse flow apparatus.

Rhenium–Alumina Catalyst

The stoichiometry for H_2 and O_2 chemisorptions and titrations on Re/Al_2O_3 is not well established. Yates and Sinfelt (*12*) found good agreement between crystallite size as measured by X-ray line broadening and H_2 chemisorption, assuming $H_A/Re_s = 1$, for a 10% Re/SiO_2 catalyst. In contrast, Kubicka (*13*) found that metallic Re only adsorbs approximately 0.5 atoms H/atom Re_s. Using this stoichiometry, she found good agreement between H_2 chemisorption and X-ray line broadening measurements for 1% Re/SiO_2; however, the agreement was less satisfactory if the Re was supported on γ-Al_2O_3. For a 1.33% Re/γ-Al_2O_3 catalyst, Freel (*1*) found that the amount of chemisorbed H_2 increased with increasing chemisorption temperature and that only a trace amount was chemisorbed at room temperature. He also found that his catalyst

TABLE 2

Stoichiometry for Re/Al_2O_3

H_2 Chemisorption:	No reaction
O_2 Chemisorption:	$Re_s + \frac{1}{2}O_2 \rightarrow Re_sO$
1st O_2 Titration:	$Re_s + \frac{1}{2}O_2 \rightarrow Re_sO$ (i.e., is actually an O_2 chemisorption)
H_2 Titration:	No reaction
2nd O_2 Titration:	No reaction

would chemisorb O_2 and that the chemisorbed O_2 could not be titrated with H_2. His ratio of O_A/Re was about 0.35 to 0.5 depending on the length of reduction. Yao and Shelef *(14)* found that 1.21% Re/γ-Al_2O_3 chemisorbs 0.33 molecules CO/atom Re, which they took to be descriptive of the catalyst dispersion. They found O_A/Re ratios larger than 1, which led them to suggest that O_2 chemisorption on Re may not be dissociative. These authors also found evidence of little H_2 chemisorption by Re: their ratio of (H atoms adsorbed/CO molecules adsorbed) was only about 0.1 to 0.2. Bolivar *et al.* (*4*) assumed that the chemisorption and titration stoichiometry for a 2% Re/γ-Al_2O_3 catalyst was the same as that for Pt/Al_2O_3. They found good agreement between their chemisorption values and particle size measured by electron microscopy if the H_2 chemisorption and H_2 titration were done at elevated temperature. If the chemisorption and titration were run at room temperature, the H_2 uptakes were much lower. They found dispersion values of about 0.21 to 0.25. Thus, the literature suggests that the chemisorption stoichiometry of supported Re varies with the support, the metal weight loading, and the chemisorption temperature.

Our Re catalyst was supported on γ-Al_2O_3, had a very low metal loading of 0.33 wt% and our chemisorption measurements were made at room temperature. All of these factors should result in little H_2 chemisorption or H_2 titration. Experimentally, we found no H_2 chemisorption or H_2 titration by our monometallic Re/Al_2O_3 catalyst. There was also no uptake in a second O_2 titration. The catalyst did chemisorb O_2, with an O_A/Re ratio of 0.34, which we take to be equal to the Re dispersion. A stoichiometry for Re/Al_2O_3 consistent with the experimental measurements is shown in Table 2.

Platinum–Rhenium–Alumina Catalyst

If it is assumed that there is no interaction of the two metals of the bimetallic catalyst, a stoichiometry for $Pt/Re/Al_2O_3$ can be obtained by merely adding the stoichiometries of the two monometallic catalysts. This stoichiometry is shown in Table 3. It suggests two possible strategies for determining the dispersion of the $Pt/Re/Al_2O_3$ catalyst:

1. Measure Pt_s from H_A; measure (Pt_s + Re_s) from O_A; calculate Re_s by difference.
2. Measure (Pt_s + Re_s) from O_A; measure Re_s from $OT_1 - OT_2$; calculate Pt_s by difference.

This second strategy is essentially that proposed by Menon *et al.* (*2*).

Gas uptakes for the bimetallic $Pt/Re/Al_2O_3$ catalyst were calculated from the experimentally measured uptakes of the monometallic catalysts assuming no interaction between the metals. These calculated values are compared with those experimentally determined for the $Pt/Re/Al_2O_3$ catalyst in Table 4. The terms O_R ($O_R = O_A - O_{NR}$) and O_{NR} ($O_{NR} = OT_1 - OT_2$) are descriptive of the ease of H_2

TABLE 3

Stoichiometry for $Pt/Re/Al_2O_3$ Assuming no Interaction of Metals

H_2 Chemisorption:	$Pt_s + \frac{1}{2}H_2 \rightarrow Pt_sH$
O_2 Chemisorption:	$Pt_s + \frac{1}{2}O_2 \rightarrow Pt_sO$
1st O_2 Titration:	$Pt_sH + \frac{3}{4}O_2 \rightarrow Pt_sO + \frac{1}{2}H_2O$ $Re_s + \frac{1}{2}O_2 \rightarrow Re_sO$
H_2 Titration:	$Pt_sO + \frac{3}{2}H_2 \rightarrow Pt_sH + H_2O$
2nd O_2 Titration:	$Pt_sH + \frac{3}{4}O_2 \rightarrow Pt_sO + \frac{1}{2}H_2O$

TABLE 4

Comparison of Gas Uptakes Calculated Assuming no Metal Interaction and Those Experimentally Determined for $Pt/Re/Al_2O_3$

Ratio	Calculated value	Experimental value
H_A/Pt	0.54	0.22
$O_A/(Pt + Re)$	0.38	0.57
O_R/Pt	0.43	0.72
O_{NR}/Re	0.34	0.43

titration. For monometallic Pt/Al_2O_3, $O_{NR} = O$ and $O_R = O_A$, and for monometallic Re/Al_2O_3, $O_{NR} = O_A$ and $O_R = O$. The poor agreement between the values calculated assuming no interaction and those obtained experimentally suggests an interaction between the two metals of the $Pt/Re/Al_2O_3$ catalyst.[1]

Of particular note is the large suppression of H_2 chemisorption in the bimetallic catalyst relative to the expected chemisorption assuming no interaction of the Pt and the Re. The quantity of H_2 actually adsorbed by the $Pt/Re/Al_2O_3$ catalyst is only about 40% of that which would be chemisorbed if no Re was present.

A suppression of H_2 chemisorption of similar magnitude to that shown in Table 4 was first observed by Freel (*1*) who suggested that this finding was consistent with alloy formation. Various other authors (*7, 15, 16*) have also suggested that during reduction of a $Pt/Re/Al_2O_3$ catalyst an alloy is formed. An alloy of Pt and Re would be expected to have fewer contiguous Pt atoms than a normal Pt crystallite; i.e., one would expect fewer Pt pairs in a Pt–Re alloy than in pure Pt. Monometallic Re does not chemisorb H_2 while monometallic Pt dissociatively chemisorbs H_2 which requires a pair of Pt atoms. Our observation of the suppression of H_2 chemisorption is further evidence of the reduction of the number of pairs of Pt atoms necessary for dissociative H_2 chemisorption and alloy formation.

TPR studies (*15*) have also shown a suppression of H_2 adsorption–desorption in the $Pt/Re/Al_2O_3$ catalyst which was attributed to fewer Pt pairs due to alloy formation. An IR study (*4*) of CO chemisorption on $Pt/Re/Al_2O_3$ has shown that the intensity of bridged CO decreases much more rapidly than the intensity of linear CO as the % Re increases. This finding was also attributed to a lowering of Pt pairs. Biloen *et al.* (*17*) also found a suppression of dissociative chemisorption, relative to nondissociative chemisorption, in $Pt/Re/SiO_2$ catalysts which they attributed to alloy formation. Bolivar *et al.* (*4*), however, assumed no suppression of H_2 chemisorption by Pt due to the presence of Re, based on their TPD studies (*18*). Menon *et al.* (*2*) also assumed no suppression of H_2 chemisorption on $Pt/Re/Al_2O_3$ catalysts.

It is also shown in Table 4 that the ratio O_R/Pt experimentally measured for the $Pt/Re/Al_2O_3$ catalyst is almost twice as large as what would be predicted assuming no metal interaction. O_R is indicative of the amount of chemisorbed O_2 atoms which can be titrated by H_2. Since monometallic ReO is not titratable by H_2, this enhancement of titratable O_2 also suggests alloy formation in the $Pt/Re/Al_2O_3$ catalyst. Probably, alloyed Pt supplies atomic H which is capable of titrating ReO in the alloy even though molecular H_2 is not. Freel (*1*) also found an increase in titratable O_2 over what would be expected with no metal interaction. He, in fact, found titratable O_2 to total Pt ratios for his $Pt/Re/Al_2O_3$ catalysts as high as 1.64. Bolivar *et al.* (*4*) also found an increase in titratable O_2 in their $Pt/Re/Al_2O_3$ catalysts which they attributed to alloy formation. Menon *et al.* (*2*), however, assumed that the titration of the ReO of the $Pt/Re/Al_2O_3$ catalyst was not affected by the presence of Pt.

Since both monometallic Pt and Re are

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[1] We shall refer to this interaction as alloy formation for convenience, the exact nature of the interaction is not known. The term bimetallic cluster may be preferred by some readers.

TABLE 5

Proposed Stoichiometry for Chemisorption and Titration by $Pt/Re/Al_2O_3$

H_2 Chemisorption:	$Pt_s^R + \frac{1}{2}H_2 \rightarrow Pt_s^RH$
O_2 Chemisorption:	$Pt_s^R + \frac{1}{2}O_2 \rightarrow Pt_s^RO$
	$Pt_s^{NR} + \frac{1}{2}O_2 \rightarrow Pt_s^{NR}O$
	Re_s alloyed $+ \frac{1}{2}O_2 \rightarrow Re_s$ alloyed O
	Re_s unalloyed $+ \frac{1}{2}O_2 \rightarrow Re_s$ unalloyed O
1st O_2 Titration:	$Pt_s^RH + \frac{3}{4}O_2 \rightarrow Pt_s^RO + \frac{1}{2}H_2O$
	$Pt_s^{NR} + \frac{1}{2}O_2 \rightarrow Pt_s^{NR}O$
	Re_s alloyed $+ \frac{1}{2}O_2 \rightarrow Re_s$ alloyed O
	Re_s unalloyed $+ \frac{1}{2}O_2 \rightarrow Re_s$ unalloyed O
H_2 Titration:	$Pt_s^RO + \frac{3}{2}H_2 \rightarrow Pt_s^RH + H_2O$
	$Pt_s^{NR}O + H_2 \rightarrow Pt_s^{NR} + H_2O$
	Re_s alloyed O $+ H_2 \rightarrow Re_s$ alloyed $+ H_2O$
2nd O_2 Titration:	$Pt_s^RH + \frac{3}{4}O_2 \rightarrow Pt_s^RO + \frac{1}{2}H_2O$
	$Pt_s^{NR} + \frac{1}{2}O_2 \rightarrow Pt_s^{NR}O$
	Re_s alloyed $+ \frac{1}{2}O_2 \rightarrow Re_s$ alloyed O

capable of chemisorbing O_2, the ratio O_A/(Pt + Re) should be indicative of the overall dispersion of the $Pt/Re/Al_2O_3$ catalyst (*1*, *19*). It appears that the overall dispersion of the $Pt/Re/Al_2O_3$ catalyst is significantly larger than would be expected with no metal interaction.

If alloyed ReO is titratable, the quantity O_{NR} which is related to the amount of nontitratable O_2, should be descriptive of the quantity of unalloyed Re_s. It appears that the amount of unalloyed surface Re in the $Pt/Re/Al_2O_3$ catalyst is similar to that in the monometallic Re/Al_2O_3 catalyst for this particular pretreatment.

Proposed Stoichiometry for a Supported Platinum–Rhenium Catalyst

The comparison shown in Table 4 between the actual gas uptake by a Pt/Re/Al_2O_3 catalyst and that expected assuming no interaction of the two metals suggests alloy formation in the reduced $Pt/Re/Al_2O_3$ catalyst. This information leads us to suggest the stoichiometry shown in Table 5 for $Pt/Re/Al_2O_3$ catalysts. Two types of surface Pt are found in the $Pt/Re/Al_2O_3$ catalyst, that which is able to chemisorb H_2, Pt_s^R, and that which is not, Pt_s^{NR}. Pt which chemisorbs H_2 may either be unalloyed, or be alloyed and have another Pt atom as a nearest neighbor. Thus, the quantity Pt_s^R is only a semiquantitative measure of the extent of alloying. Two types of Re are also found, alloyed and unalloyed.

The stoichiometry shown in Table 5 suggests the following procedure for determining the dispersion of the $Pt/Re/Al_2O_3$ catalyst:

1. Measure (Pt_s + Re_s) from O_A.
2. Measure Re_s unalloyed from OT_1 OT_2.
3. Calculate (Pt_s + Re_s alloyed) by difference.
4. Measure Pt_s^R from H_A.

According to the proposed stoichiometry, it is not possible to separate the quantity (Pt_s + Re_s alloyed) since only a percentage of the Pt_s can be measured by H_2 chemisorption and Re_s alloyed O is titrated identically to $Pt_s^{NR}O$. Thus, a totally separate dispersion value for each metal cannot be obtained by this method.

The proposed stoichiometry differs from that suggested by Bolivar *et al.* (*4*, *5*) primarily in its description of H_2 chemisorption by the Pt of the $Pt/Re/Al_2O_3$ catalyst. Bolivar *et al.* assume normal H_2 chemisorption. For confirmation of their proposed stoichiometry, Bolivar *et al.* showed good agreement between their experimentally measured ratio HT/OT_1 and that predicted by their stoichiometry, $HT/OT_1 = 0.125$ g/g. It should be noted that our proposed stoichiometry also predicts that $HT/OT_1 = 0.125$ g/g; this ratio is independent of the amount of H_2 chemisorbed by Pt. In their most recent work (*20*), this research group also found evidence that "could reflect a somewhat lower hydrogen coverage of Pt_s in the platinum–rhenium alloys compared to Pt_s in pure platinum."

TPR studies (*7*, *15*) have shown that Pt and Re oxides are immiscible leading to segregation of alloyed Pt–Re upon oxidation. Bolivar *et al.* (*4*) found that the ratio OT_n/OT_1 continually decreased as *n*, the number of the titration, increased. They suggested that the room temperature O_2 titrations may themselves cause some segre-

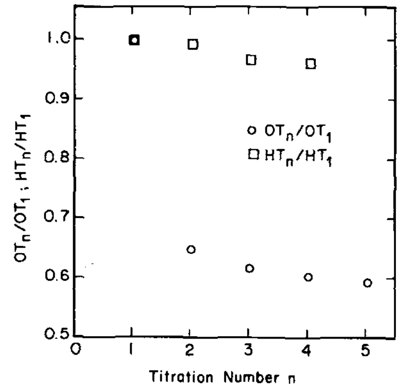

FIG. 1. Variation of gas uptake in successive titrations of $Pt/Re/Al_2O_3$.

gation of the alloyed Pt–Re. A similar suggestion has also been made for bimetallic Pt–Pd catalysts (*21*) based on IR studies.

We also find a continual decrease in OT_n/OT_1 as *n* increases, as shown in Fig. 1. Thus, it appears that the structure of the $Pt/Re/Al_2O_3$ catalyst is altered by the surface area measurement and that another reaction needs to be added to the stoichiometry presented in Table 5:

$$Re_s \text{ alloyed} \xrightarrow{O_2} Re_s \text{ unalloyed}$$

The extent of this reaction can be quantified by assuming that there is no Re_s unalloyed in the $Pt/Re/Al_2O_3$ catalyst after drying at 100°C (*22*).

Physical Mixture of Supported Platinum and Rhenium Catalysts

The experimentally determined gas uptakes of a physical mixture of Pt/Al_2O_3 and Re/Al_2O_3 are compared to those calculated from the sum of the monometallics in Table 6. Physical mixtures are of interest as it has been proposed (*23*) that physical mixtures of Pt and Re and bimetallic $Pt/Re/Al_2O_3$ have identical stability for reforming. The measured uptakes for the physical mixture are essentially identical to the sum of the monometallics, which suggests no metal interaction. The same result has been found previously by Freel (*1*). This result is also consistent with our TPR results (*7*). It is not, however, in agreement with the results of Bolivar *et al.* (*4*). They found that a physical mixture of Pt and Re has an OT_2/OT_1 ratio more than twice as large as that predicted by the sum of the monometallics, which suggests metal interaction. The experimental OT_2/OT_1 ratio for our physical mixture is .66, which is identical to the value predicted by the sum of the monometallics. As discussed previously (*7*), the findings of Bolivar *et al.* may be due to their use of uncalcined catalysts.

CONCLUSIONS

Surface area measurements indicate that the Pt/Al_2O_3 catalyst has a dispersion of approximately 0.5 and that the stoichiometry for H_2 and O_2 chemisorptions and titrations on this catalyst is in agreement with that commonly accepted. The Re/Al_2O_3 catalyst does not chemisorb H_2, it dissociatively chemisorbs O_2, but the chemisorbed O_2 cannot be titrated by H_2. This proposed stoichiometry is consistent with the available information on H_2 and O_2 uptake by supported Re catalysts. The O_2 chemisorption measurement indicates that the dispersion of the Re/Al_2O_3 catalyst is about 0.34.

Comparison of the gas uptakes expected based upon the sum of the monometallic catalysts with those experimentally found for the $Pt/Re/Al_2O_3$ catalyst suggests alloy formation in the reduced bimetallic catalyst. The $Pt/Re/Al_2O_3$ catalyst exhibits a suppression of H_2 chemisorption and an in-

TABLE 6

Comparison of Gas Uptakes Calculated Assuming no Metal Interaction and Those Experimentally Determined for Physical Mixture

Ratio	Calculated value	Experimental value
H_A/Pt	0.54	0.56
$O_A/(Pt + Re)$	0.38	0.43
O_R/Pt	0.43	0.48
O_{NR}/Re	0.34	0.39

crease in titratable O_2, both of which are consistent with alloy formation. The gas uptakes also suggest that the overall dispersion of the bimetallic catalyst is larger than one would expect with no metal interaction, while the quantity of unalloyed surface Re is about the same as in the Re/Al_2O_3 catalyst for this particular pretreatment. Unlike the $Pt/Re/Al_2O_3$ catalyst, a physical mixture of Pt/Al_2O_3 and Re/Al_2O_3 is found to behave as the sum of the monometallics.

A stoichiometry consistent with the experimental observations for H_2 and O_2 chemisorption and titration by $Pt/Re/Al_2O_3$ is suggested that allows the quantities (Pt_s + Re_s), (Pt_s + Re_s alloyed), Re_s unalloyed, and Pt_s^R to be calculated from the measured gas uptakes. Separate determination of the dispersion of the Pt and the Re of the $Pt/Re/Al_2O_3$ catalyst cannot be obtained with this method since Re_s alloyed and Pt_s^{NR} react identically.

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