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Surface Interactions in the System Re/γ-Al_2O_3

H. C. YAO AND M. SHELEF

Research Staff, Ford Motor Company, Dearborn, Michigan 48121

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The study of the system Re/γ-Al_2O_3 by chemisorption, ESR, and temperature-programmed reduction showed the existence of two aggregation states of Re on the surface of γ-Al_2O_3: a dispersed, two-dimensional phase and three-dimensional crystallites. The dispersed phase of Re interacts strongly with the γ-Al_2O_3. As a result, it can be reduced to zero-valent state by H_2 only at >500°C. Even when reduced, it does not dissociatively chemisorb hydrogen at room temperature, and therefore surface Re cannot be estimated reliably by ambient H_2 chemisorption. The dispersed phase cannot be oxidized at 500°C to the heptavalent volatile Re^{7+} but only to Re^{4+}. The limiting coverage of γ-Al_2O_3 surface by dispersed Re^{4+} is $\sim$10%. The formation of the stable, nonvolatile, tetravalent, dispersed phase is responsible for the prevention of Re loss in the oxidative regeneration of Re-containing, γ-Al_2O_3-supported reforming catalysts or during other uses in an oxidizing environment.

The crystalline, three-dimensional phase can be oxidized to Re^{7+} and reduced to Re° by H_2 at 350°C. Dispersion of it into the two-dimensional phase is accomplished by oxidation followed by vacuum or inert gas treatment at >500°C. Such treatment creates anion vacancies on the surface which are electron traps and sites for hydrogen adsorption. The anion vacancies can be annealed by oxygen at 500°C. Under high-temperature reducing conditions, the zero-valent dispersed phase may slowly aggregate into three-dimensional metallic crystallites.

The interaction of oxygen with the reduced dispersed phase at 25°C produces at the surface nondissociated oxygen molecules-ions (O_2^{2-}) and Re^{2+} ions which gives an axially symmetrical EPR spectrum. The EPR spectrum of the dispersed Re^{4+}, obtained at 500°C, has a six-peak HFS.

INTRODUCTION

Rhenium-containing supported catalysts are used presently in the reforming of petroleum feedstocks (*1–3*). The most useful catalysts contain Pt and Re. Since dual catalysts are more active than single-component materials, strong mutual interactions, such as alloy formation, have been suspected. However, Pt and Re differ widely in oxidation behavior, the first being a noble metal and the second a base metal with several stable oxidation states. Thus, their respective interactions with the gas phase and the support may be expected to differ vastly and in turn influence their mutual relationship. The interaction of Re with the support is important in the regeneration of spent catalysts in oxygen-containing streams, where it is not lost from support under conditions which otherwise result in the formation of volatile Re_2O_7 (*1, 4*).

In another context, Re seems to exhibit "oxygen-storage" properties in automotive three-way catalysts which are intended to operate in an exhaust produced by nearly stoichiometric engine carburetion, for simultaneous removal of hydrocarbons, carbon monoxide, and nitric oxide (*5*). In this application the prevention of volatilization loss is of primary importance. Also, it is important for the assessment of the "oxygen-storage" capacity to examine the oxidation-state changes which are influenced by the Re-support interactions. In silica-supported Re catalysts, Re was found to be reduced by H_2 to the metal (*6*, *7*) while such reduction was reported to be unattainable in alumina-supported samples (*8*). Recently, however, this nonreducibility has been questioned (*9*). Concurrently, other investigators (*10*) have also reached the conclusion that the reduction of finely dispersed Re on alumina by hydrogen at 450–500°C results in zerovalent surface Re atoms. In dual Pt–Re catalysts, the presence of Pt was shown to enhance Re reducibility at room temperature (*11*) and at temperatures in the >150°C range (*12*).

It has been suggested by Freel (*13*) that the Re–alumina interaction leads to the formation of a two-dimensional layer, although no direct proof was given. The Re ions associated with such a layer will differ, by implication, in their volatility, reducibility, etc.

It is the object of this work to examine in detail the surface interaction of rhenium with an alumina support to clarify the contradictions enumerated above. To this end three experimental techniques are employed: conventional chemisorption of simple gases, programmed reduction, and electron paramagnetic resonance.

EXPERIMENTAL

A. Materials

Re powder (99.9%, from J. A. Samuel & Co., Inc.) was washed with diluted hydrochloric acid, water, and acetone before use. The ReO_3 was purchased from Ventron Corp. Alumina-supported Re catalysts were prepared by mixing Dispal-M colloidal γ-Al_2O_3 (Conoco Chem.) with a measured amount of perrhenic acid, evaporating and drying at 150°C. The resulting solid was ground, rewetted, and dried again at 300°C in air to achieve uniformity. Rhenium content was determined by X-ray fluorescence. The reducing treatment was performed in flowing H_2 at 500°C for 3 hr. The oxidizing treatment which led to the dispersion of Re (see below) was done in either flowing air or O_2 at 500°C followed by heating in N_2 for 16 hr or *in vacuo* for 5 hr. For the chemisorption measurements, the samples were further reduced in flowing H_2 at 500°C for more than 1 hr.

Research grade Ar, N_2, CO, and O_2 were used without further purification. Hydrogen was purified by passing over Engelhard Deoxo Pd catalyst and 4A molecular sieve at 78°K.

B. Apparatus

The volumetric adsorption measurements were performed in a conventional constant volume apparatus equipped with a quartz spiral Bourdon gauge (Texas Instrument).

The EPR spectra were taken with a Varian E-3 spectrometer equipped with a E-4531 multipurpose cavity operating at 9.5 GHz.

The temperature-programmed reduction and the CO uptake measurements were made in a flow system similar to that described by Gruber (*14a*) and Dalla Betta (*14b*). In measuring the CO uptake, a stream of H_2 was passed through a small volume injection valve containing CO, the catalyst sample, and a high sensitivity thermal conductivity detector. Before the measurement of CO uptake, the rhenium oxide on γ-Al_2O_3 was dispersed by flowing N_2 through the heated catalyst at 500°C for 16 hr. The catalyst was then reduced by the hydrogen carrier gas stream at 500°C for 1 hr and cooled down to room temperature. A small dose of CO was injected into the hydrogen carrier gas stream. As the CO passed over the catalyst, the Re metal preferentially adsorbed the CO. Measurement of the remaining CO and comparison

TABLE 1

Room Temperature Adsorption of Simple Gases on Metallic Rhenium

Adsorbate gas	Form of Re	Method of study	Total uptake $\times 10^{-15}$ atoms[a]/cm^2	Reference
H	Powder	Medium-pressure chemisorption	0.70	*15a*
H	Powder	Medium pressure chemisorption	0.48	*15b*
H	Filament	Flash-filament desorption	0.61	*16*
H	Filament	Low-pressure chemisorption	0.69	*17*
CO	Filament	Low-pressure chemisorption	1.1 (total)	*18*
CO	Filament	Low-pressure chemisorption	0.62 (β-CO only)	*19*
CO	Ribbon	Programmed desorption	0.57 (total)	*20*
O	Filament	Low-pressure chemisorption	0.86	*21*

[a] Molecules/cm^2 in the case of CO.

with the detector response upon injection of a similar dose over an empty cell permitted calculation of the amount of the adsorbed CO. In temperature-programmed reduction of the catalyst, a H_2 (15%)–Ar (85%) gas mixture was used. Measurement of the H_2 gas taken up by the sample during the reduction at the programmed temperature and comparison with the detector response upon injection of a comparable dose over the same sample at room temperature permitted the calculation of the rate and the amount of reduction. During the reduction, the temperature rise of the catalyst was controlled by a programmer at a constant rate of ~10°C per minute.

RESULTS

1. *Chemisorption Measurement*

A. *Chemisorption of H_2, CO, and O_2 at 25°C on Re metal.* In order to characterize the supported samples, a series of experiments were performed to establish the adsorption stoichiometry on a pure metal powder under our conditions. It is worth mentioning that such measurements were made on Re powder by Kubicka (*15*). In addition, a series of uptake measurements of simple gases were also reported in the literature on Re filaments and Re ribbons. These are summarized in Table 1. Since a surface roughness of unity was assumed for the filament and ribbon data, it is likely that in these cases the uptake values per unit of area are somewhat overestimated. In general, there is 1:1 correspondence between the uptake of CO molecules and H atoms. Although supporting evidence can be gathered from LEED experiments on various faces of single crystals of Re (*22*), these results are not easily translatable into uptake figures. Suffice it to say that the difference in exposed crystalline faces may account for at least a part of the differences in the values of Table 1.

Our measurements of H_2, CO, and O_2 chemisorption were made on reduced metallic Re powder with a surface area of 0.74 m^2 (BET)/g at 25°C. The results are given in Fig. 1. The curves labeled (A) give the uptake on a reduced and evacuated sample and are the total uptake at 25°C. The sample was then evacuated at 25°C

TABLE 2

H, CO, and O Uptake on Re Powder at 100 Torr and 25°C

Adsorbate	Total uptake		Irreversible uptake	
	Per m^2 (BET) $\times 10^{-18}$	Per $Re_{(s)}$ atom[a]	Per m^2 (BET) $\times 10^{-18}$	Per $Re_{(s)}$ atom[a]
H	6.19	0.56	4.03	0.37
CO	5.70	0.52	4.85	0.44
O (O_2)	13.24 (6.62)	1.20 (0.60)	12.6 (6.3)	1.14 (0.57)

[a] The value of 11 × 10^{18} atoms/m^2 is used as the average $Re_{(s)}$ concentration (*12b*).

for 1 hr and a second isotherm (B) determined. Curves (B) correspond to the reversible adsorption and the differences, the irreversible adsorptions, are given by curves (C). Table 2 summarizes the chemisorption stoichiometry derived from the data of Fig. 1. The values for H and CO total uptake per $Re_{(s)}$ atom are close to or slightly lower than the average values in Table 1. But the value of oxygen atom total uptake per Re atom is higher than that in Table 1. The fact that the ratio of O/Re is higher than 1 may indicate the possibility of a nondissociative chemisorption of O_2 at 25°C. If this is the case, then the chemisorption ratio of O_2/Re becomes 0.61 which is close to H/Re (0.56) and CO/Re (0.52) values found on the same Re powder. Further evidence for nondissociative adsorption of oxygen at room temperature will be discussed below. It should be pointed out that the reversible (weak) part of the adsorption increases on the Re powder from oxygen to carbon monoxide to hydrogen. This difference is further enhanced on the supported samples.

B. *Chemisorption of H_2, CO, and O_2 at 25°C on Re/γ-Al_2O_3 catalysts.* Chemisorption isotherms for a representative supported sample (2.61% Re on γ-Al_2O_3) are shown in Fig. 2. Curves 1-A and 1-B are the total and reversible chemisorptions, respectively, on the sample reduced by flowing H_2 at 350°C for 16 hr and then at 500°C for 1 hr followed by outgassing at 500°C for another hour *without* a dispersion treatment. Curves 2-A and 2-B are the total and reversible chemisorptions, respectively, on the sample reduced in the same way as above *after* a dispersion treatment, i.e., an evacuation at 500°C for more than 5 hr. The differences between curves A and B are the irreversible chemisorptions indicated by arrows, $(I)_1$ and $(I)_2$. Table 3 summarizes the chemisorption data on supported Re/γ-Al_2O_3, for three samples

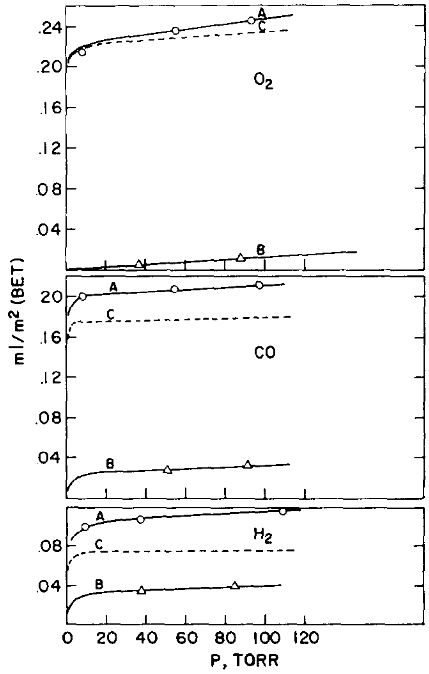

FIG. 1. Oxygen, carbon monoxide, and hydrogen chemisorption at 25°C on Re powder (Surface Area = 0.74 m^2/g). A = total chemisorption, B = reversible part, and C = irreversible part.

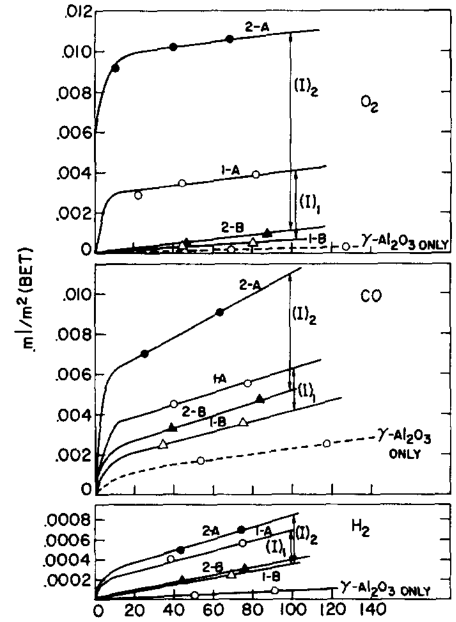

FIG. 2. Oxygen, carbon monoxide, and hydrogen chemisorption at 25°C on 2.61% Re/γ-Al_2O_3 catalyst. 1A and 2A are the total chemisorption before and after the dispersion treatment, respectively. 1B and 2B are the reversible part, before and after the dispersion treatment, respectively.

of different Re concentrations, in numerical form.

The results of Fig. 2 and Table 3 show firstly that the dispersion enhances the chemisorption of all adsorbents. O_2 and CO chemisorptions are enhanced more than that of H_2. Similar enhancement of chemisorption due to dispersion was noted also previously on CO or Ni supported on zirconia (*20, 21*). Secondly, the chemisorption of hydrogen on the supported samples is small compared with CO and O_2 chemisorptions. Thus, the H/CO chemisorption ratio decreases from about unity on powdered Re to ~0.2 on nondispersed, supported Re/γ-Al_2O_3 and then to ~0.1 on the same samples after dispersion. Thirdly, the differences between the reversibility of chemisorption noted for the different adsorbates on powdered Re are still more accentuated on the supported samples. In the powdered Re, the value of the ratio $(O_2/CO)_{irr.}$ after room temperature chemisorption, was 1.3; the values on the supported samples (from Table 3) fall in the 1.5 to 4.4 range.

The large disparities between the uptakes of the various adsorbents on the supported samples necessarily force the question as to which uptake represents better the surface density of Re atoms on γ-Al_2O_3. From the low values of hydrogen uptake with respect to CO, and previous experience of still lower chemisorptions (*10*), it has to

TABLE 3

The H_2, CO, and O_2 Chemisorption on Re/γ-Al_2O_3[a]

Catalyst		H_2		CO		O_2	
		μmol/m²	H/Re	μmol/m²	CO/Re	μmol/m²	O/Re(O_2/Re)
1.21% Re/γ-Al_2O_3	A[b]	—	—	—	—	—	—
(0.342 μmol/m²)	B[c]	0.0116	0.068	0.11	0.33	0.17	0.99 (0.50)
2.61% Re/γ-Al_2O_3	A	0.014	0.038	0.09	0.13	0.33	0.90 (0.45)
(0.73 μmol/m²)	B	0.021	0.058	0.26	0.29	0.42	1.15 (0.58)
5.51% Re/γ-Al_2O_3	A	0.022	0.028	0.08	0.05	0.17	0.22 (0.11)
(1.557 μmol/m²)	B	0.049	0.063	0.33	0.21	0.65	0.84 (0.42)

[a] The amount of adsorbate uptake is measured by the irreversible portion at 100 Torr and 25°C (see Fig. 2).

[b] A without the dispersion treatment.

[c] B, after the dispersion treatment.

be deduced that this adsorbent is unsuitable for the measurement of Re dispersion on γ-Al_2O_3. This is most probably the result of the relative inability of γ-Al_2O_3-supported and dispersed Re to dissociate the H_2 molecule. The remarkable change in this ability observed in supported samples as compared to metallic Re is the outcome either of the diminished amount of surface Re–Re pairs necessary for H_2 dissociation or some interaction with the support. We shall return subsequently to this question.

On the other hand, CO does not adsorb dissociatively and therefore its chemisorption is more representative of surface dispersion of Re supported on γ-Al_2O_3. It is so only in the relative sense, when compared with hydrogen chemisorption. As an absolute measure many issues remain unresolved such as the extent of bridge-bonding, which in itself is dependent on the dispersion and, perhaps, also the possibility of multiple CO adsorption on isolated Re sites. With these reservations in mind, CO chemisorption can be used as a measure, although not absolute, of Re dispersion and is so employed by us, subsequently, for a specific purpose. The stoichiometry of oxygen adsorption on supported and dispersed samples is again difficult to derive directly from chemisorption data. Here the complications are the possibility of both dissociative (O^{2-} ion formation) and nondissociative (O_2^{2-} ion formation) interaction at room temperature. Other uncertainties involve bulk oxidation and the number of charges transferred for each surface Re atom upon exposure to oxygen at room temperature. In the recent work of Milova *et al.* (*10*), a constant room temperature surface stoichiometry between oxygen and surface Re ($O/Re = 0.63$) is claimed both for powdered Re and supported dilute samples. The surface stoichiometry observed by these authors for the powder is considerably smaller than observed here; it is also smaller for the powdered samples. Perhaps, the differences are associated with the difficulties of surface titrations by oxygen in a dynamic flow system used in ref. (*10*) where extreme precautions are required to exclude oxygen from the sample after reduction in the process of purging and cooling.

The experiments described in the latter part of the paper were designed to clarify some of these ambiguities by the use of physical methods.

C. *The limits of Re dispersion on γ-Al_2O_3.* Since CO chemisorption on supported Re catalysts is a fairly good relative measure of the accessibility to surface Re in both nondispersed and dispersed samples, it was used to measure the limits of dispersion upon the increase of Re loading on the γ-Al_2O_3 support. Such work, performed previously with cobalt ions on zirconia (*23*, *24*), showed that the dispersed state of aggregation, two-dimensional patches or isolated ions, reaches saturation when a certain proportion of the support has been covered with it. In logarithmic plots of chemisorptions of NO and CO vs cobalt loading, a proportional increase of chemisorption of NO and CO with loading was observed until the additions of the cobalt ions can no longer be dispersed and therefore do not cause additional uptake increments. In the present work, the irreversible part of CO chemisorption was measured by a flow system in which H_2 was used as carrier gas. In this experiment the impregnated rhenium oxide catalysts were dispersed by heating at 500°C under flowing N_2 for 16 hr and then reduced by flowing H_2 at 500°C for 2 hr. The logarithmic plot of these results is given in Fig. 3. The saturation concentration of the dispersed Re phase is indicated by the intersection of the two lines and corresponds to about 2 μmol or 1.2×10^{18} Re atoms per m^2 of the alumina support. Since, as a rule of thumb, there are $\sim 10^{19}$ surface atoms on 1 m^2 of the surface, the upper bound of the part of the support occupied by the dispersed phase is around 10% of

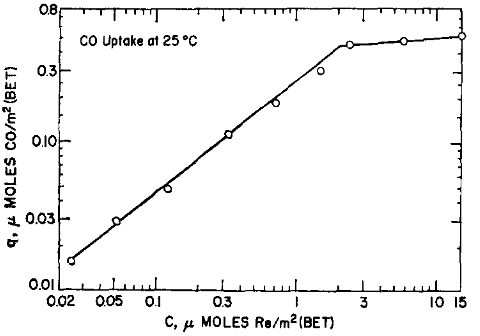

FIG. 3. Carbon monoxide chemisorption as function of Re loading.

the total support surface. This value is considerably less than the saturation concentration of dispersed Co ions on zirconia which is ~7 μmol/m²(BET) (*24*). We may regard the "dispersion limit" as an upper bound solely since not all incremental additions of Re, even in the dispersion region (i.e., below the intersection point of Fig. 3), may have been exposed on the surface. Indeed, as shown in Table 4 the ratio CO/Re total is not constant, but increases with dilution. Again, the changes in the surface stoichiometry of irreversibly adsorbed CO with dispersion make it impossible to establish the absolute limit of dispersion.

It is worth noting that the dynamic measurements of CO chemisorption of Table 3 are in fair agreement with the static measurements of Table 2.

D. *High temperature oxidation of the* *γ-Al_2O_3 supported Re catalysts.* One of our main objectives was to provide background for the use of Re in automotive catalyst formulation as an "oxygen storage" component. In this context it was of interest to determine the oxygen uptake in the temperature range of the intended use of such catalysts in both dispersed and nondispersed states. It is widely known, and we have previously established that small unsupported Re particles undergo under such conditions complete bulk oxidation to the heptavalent volatile Re_2O_7.

In these experiments, the γ-Al_2O_3 supported Re catalysts were reduced first at 500°C by flowing H_2 for 1 hr and outgassed for another hour. This was followed by measuring the O_2 uptake volumetrically at 500°C. After the oxidation, the catalyst was outgassed at 500°C *in vacuo* for more than 5 hr. After this dispersion treatment, the same sample was again reduced, outgassed, and the O_2 uptake was measured at 500°C.

The data of these experiments are presented in a stick diagram on Fig. 4, plotting on the ordinate the ratio of the oxygen atoms uptake at 500°C to the total rhenium atoms in the sample. In all cases, the dispersion of rhenium on the support diminishes the amount of oxygen taken up at high temperature indicating that the dispersed part is oxidized to an oxidation level which is lower than heptavalent.

The samples with 1.2 and 5.5% Re appear to be completely dispersed after the dispersion treatment and take up at 500°C only two oxygen atoms per Re atom. We assume that at this temperature the interaction produces two doubly charged oxygen ions and a tetravalent rhenium ion, as opposed to the ion-molecule formed in the O_2 chemisorption at 25°C. Before the dispersion treatment, the nondispersed Re could be oxidized to a higher oxidation

TABLE 4

CO Uptake on Dispersed Re/γ-Al_2O_3 Catalysts[a]

Wt.% Re	Re concn (μmol/m²) (BET)	CO uptake (μmol/m²) (BET)	CO/Re
0.094	0.027	0.017	0.63
0.22	0.062	0.032	0.51
0.46	0.13	0.053	0.40
1.21	0.34	0.118	0.34
2.60	0.74	0.184	0.26
5.51	1.52	0.237	0.16
8.8	2.49	0.453	0.18
15.5	4.38	0.421	0.10

[a] Data used also in Fig. 3.

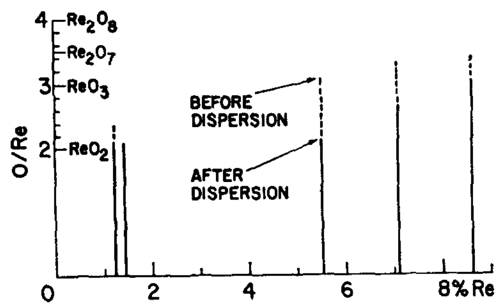

FIG. 4. Oxygen uptake at 500°C on reduced Re/γ-Al_2O_3 samples before and after the dispersion treatment.

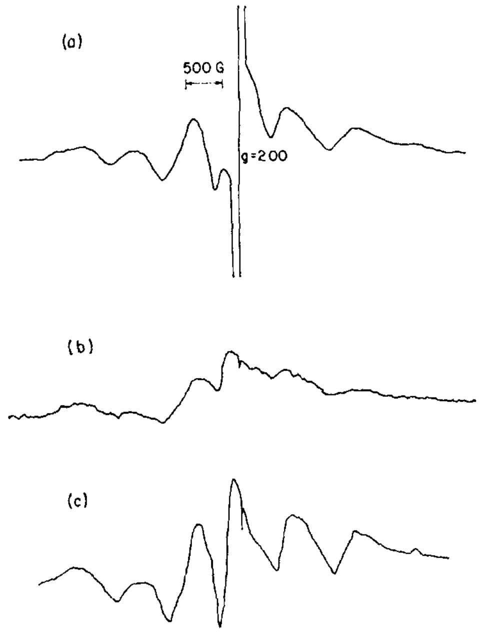

FIG. 5. Room temperature EPR spectra at 1.21% Re/γ-Al_2O_3 sample (a) degassed in vacuum at 500°C for 5 hr; (b) reexposed to air at 500°C for 10 min; (c) degassed again in vacuum at 500°C for 3 hr.

state (probably +7). For samples with Re concentrations beyond the saturation limit of 2 μmol/m^2, even after dispersion treatment, only a portion of the Re atoms will be oxidized to Re^{4+} and the remainder will be oxidized to about +7 at 500°C (the oxidation state +8 is also possible but is less stable under these conditions) (*25*). Depending on the loading, the partial dispersion brings down the average oxidation state to somewhere between +7 and +4.

Thus, we conclude that the equilibrium high-temperature oxidation state of the dispersed phase of Re is +4 and of the nondispersed phase is +7 at 500°C. As will be discussed below, this fact is of utmost importance both in the stabilization of Re against volatilization and in its potential role as "oxygen storage" component in automotive catalysts designed to operate under narrow carburetion control.

E. *EPR studies.* The literature reports EPR signals originating from different oxidation states of Re in various environments. Spectra of Re^{4+} ($5d^3$) in single cubic crystals were recorded by Low and Llewellyn (*26*), Rahn and Dorain (*27*), and Griffiths *et al.* (*28*). In ref. (*8*), a signal originating from supported Re^{4+} ions was obtained. Spectra originating from Re^{6+} ($5d^1$) in oxy-anions have been noted also (*29-31*). On the other hand, solid ReO_3 does not give an EPR signal even at temperatures down to 14°K and is considered diamagnetic (*28*). No EPR signals associated with other Re oxidation states have been reported, especially not with Re^{2+} ($5d^5$).

In order to support the results on the oxidation states of the dispersed and nondispersed Re on γ-Al_2O_3, both at 500°C and at room temperature, by independent

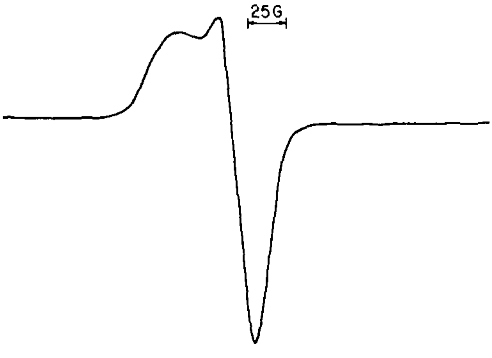

FIG. 6. Room temperature EPR spectrum of a 1.21% Re/γ-Al_2O_3 after reduction in H_2 at 500°C, and air exposure and outgassing at 25°C.

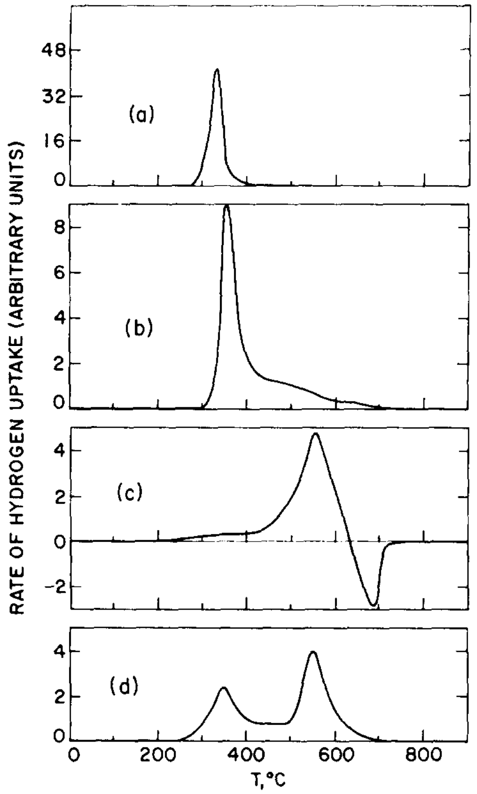

FIG. 7. Temperature-programmed reduction: (a) nonsupported ReO_3; (b) 1.21% Re/γ-Al_2O_3, before dispersion; (c) 1.21% Re/γ-Al_2O_3 after dispersion at 500°C in flowing N_2 for 16 hr; (d) 1.21% Re/γ-Al_2O_3 after dispersion and reexposure to air at 500°C for 1 hr.

physical evidence, we have carried out the EPR studies presented in Figs. 5 and 6.

Firstly, no EPR signal was observed from the impregnated rhenium oxide on γ-Al_2O_3 before or after thorough reduction in H_2 at 500°C. This indicates that rhenium ions (or atoms) on γ-Al_2O_3 before or after reduction without the dispersion treatment are diamagnetic. After the dispersion treatment, i.e., evacuation at 500°C for 5 hr, the 1.21% Re on γ-Al_2O_3 sample yields a strong EPR signal (Fig. 5a). The spectrum shows two distinct features: a very strong sharp line at $g = 2.00$ and a weaker six-line signal with $g = 2.25$ and a splitting constant A of 780 gauss. The sharp line at $g = 2.00$ can be removed by exposing the sample to air at 500°C (Fig. 5b) and is not recreated after evacuation at 500°C (Fig. 5c). We assign this line to the free electrons trapped in vacant surface anion sites. The creation of the vacant surface anion sites in the dispersion treatment is not surprising. In an extensive series of publications, Teichner and his co-workers (*32*, *33*) have shown that prolonged heating at 500°C *in vacuo* can remove some oxygen anions from the amorphous γ-Al_2O_3 to form anion vacant sites on the surface. The EPR signal originated from the treated alumina itself is a weak one but can be enhanced by treatment with a moisture-free solution of tetracyanoethane. The sharpened signal is due to the charge transfer complex formed from the trapped electron and the TCNE molecule. On the rhenium oxide-γ-Al_2O_3 surface the change of oxidation state from +7 to +4 is necessarily associated with the removal of oxygen anions during the dispersion treatment. The removal of oxygen can leave behind free electrons which may be trapped in the vacant anion sites. The strong signal of Fig. 5a at $g = 2.00$ shows that this process is much more intense on Re_2O_7/γ-Al_2O_3 than on various forms of "reactive" alumina. The weaker six lines in Fig. 5a–c are presently assigned to the dispersed Re^{4+} ions. Although the reported g-value and splitting constant of the weak six lines from the Re^{4+} ions imbedded in cubic K_2PtCl_6 crystal are not the same ($g = 2.05$ and $A = 109$ Gauss) (*23*), the large difference may be attributed to the different environment in which the Re^{4+} ions are situated. In K_2PtCl_6 the Re^{4+} ions are in an octahedral coordination, while in the dispersed and supported Re^{4+} on γ-Al_2O_3 they may be in deformed tetrahedral sites.

Figure 6 shows the EPR signal of the same sample (1.21% Re on γ-Al_2O_3) after it was reduced by flowing H_2 at 500°C, exposed to air at 25°C, and outgassed at room temperature. The intense and relatively narrow signal is completely different from that observed after high temperature oxidation. Its shape is indicative of the axial symmetry in the environment of the paramagnetic source. We associate this signal with Re^{2+} formed upon nondissociative adsorption of ion-molecules, O_2^{2-}, on the surface, in accordance with the considerations given above. Thus, the EPR studies provide support for the nondissociative adsorption of oxygen at room temperature.

F. *Temperature-programmed reduction.* The results of the temperature programmed reduction are presented on Fig. 7. There are four hydrogen uptake diagrams. Figure 7a is the hydrogen uptake of particulate ReO_3, Fig. 7b is that of 1.21% Re/γ-Al_2O_3 prepared from impregnation and dried at 300°C without the dispersing treatment, Fig. 7c is the same γ-Al_2O_3 supported sample but with a dispersing treatment, and Fig. 7d is the same supported sample after a dispersing treatment and then exposed to air at 500°C for 1 hr.

Particulate ReO_3 and nondispersed supported rhenium oxide are reduced in the 350–375°C temperature range. The supported nondispersed sample has a hydrogen uptake tail extending into the higher temperature region. Dispersion treatment of the supported sample pushes the major portion of the hydrogen uptake to ~550°C with a small tail in the low temperature region. At temperatures above 600°C, the sample gives up part of the hydrogen back into the gas phase. Finally, reheating in air at 500°C gives a distinct double-humped uptake trace with maxima at 350 and 550°C, indicating some particle growth during this treatment.

TABLE 5

Extent of Dispersion Measured by Temperature-Programmed Reduction

Sample	Amount of Re (μmol)	Found H_2 uptake (μmol)	Calculated H_2 uptake (μmol)
ReO_3 particles	64.9	156.1	194.7
1.21% Re/γ-Al_2O_3 before dispersion	16.7	57.2	58.5[a]
1.21% Re/γ-Al_2O_3 after dispersion and oxidation	20.8	49.6	72.8[a]

[a] Based on complete reduction of Re_2O_7 to Re.

Interpretation of the data in Fig. 7, with the exception of diagram (c), is relatively straightforward. The dispersed two-dimensional phase is reduced in the 550°C range and the particulate oxide in the 350°C range. The release of H_2 at high temperature takes place only in a freshly dispersed sample and is not a recurring phenomenon. Since the EPR signal associated with the trapped electron behaves likewise, we assign the hydrogen released at high temperature to the uptake on oxygen vacancies with trapped electrons. This hydrogen is held relatively strongly but can be desorbed at high temperatures. At present this assignment is tentative and more work is required to prove its correctness. The overall material balances in the reduction processes corresponding to diagrams (a), (b), and (d) of Fig. 7 are given in Table 5. Completeness of the reduction can be judged from the comparison of the hydrogen uptake found in the experiment and the calculated value for the complete reduction. For the particulate ReO_3, the found H_2 uptake is about 20% less than the calculated. We attribute this to the sublimation loss during the reduction. For the nondispersed supported sample, 97% of the Re_2O_7 is completely reduced to Re, indicating that Re_2O_7 on γ-Al_2O_3 can be reduced to Re at a temperature below 500°C. For the supported sample after dispersion and reoxidation, the found hydrogen uptake is only about 68% of the calculated value. However, complete reduction is achieved if, according to the evidence found in high temperature oxidation and EPR studies, one assumes that the dispersed Re ion is present in the tetravalent state. Assuming a complete reduction, it is found that the dispersed and reoxidized sample has about 75% of the

Re ions in the dispersed and tetravalent state which is in qualitative agreement with the double-humped shape of the programmed-reduction diagram (Fig. 7d).

DISCUSSION

The data obtained here by three different and complementary techniques showed the nature of the interaction of Re with γ-Al_2O_3. Thus, the existence of the dispersed two-dimensional phase was clearly demonstrated. At low Re concentrations on a support of a high surface area, this phase may account for the major part of the Re. The existence of such a state has, of course, been suggested before (*13*). It has also been suggested that such a state is related to the very important circumstance that rhenium is not lost from alumina under conditions when otherwise volatilization is expected. Indeed, a volatilized Re_2O_7 particle (or cluster) in highly porous γ-Al_2O_3 will interact, upon collision, with the surface leading to tetravalent and nonvolatile Re ions and release the excess oxygen into the gas phase. No volatilization is likely if there exists a tenfold or higher excess of γ-Al_2O_3 surface, to accommodate the incident volatile Re_2O_7. Even if γ-Al_2O_3 surface excess is lower than tenfold, such stabilization may be still effective to some extent. This permits oxidative regeneration of Re-containing reforming catalysts or prospective uses in automotive catalysis.

Obviously, the usefulness of the dispersed Re phase as an "oxygen-storage" component in automotive catalysts depends on the reducibility of the two-dimensional phase. There was considerable disagreement in the literature on this subject, as mentioned in the introduction. The formation of the two-dimensional phase itself is the outcome of a strong interaction with the γ-Al_2O_3, which manifests itself in deeply altered oxyreduction properties of the Re ions in this phase: limitation of the upper oxidation state to +4 and a slow reduction rate.

If room-temperature chemisorption of hydrogen is being used as a criterion of reducibility, the conclusion will be erroneous. It appears that the dispersed phase does not dissociate H_2 readily at room temperature. It begins to do so at ~200°C as noted by Freel (*13*). The slower reduction rate, at ~500°C, than the nondispersed phase, is also due to rather sluggish activation of H_2 by this phase. However sluggish, our data indicate that complete reduction can be obtained. Obviously, the presence of Pt can catalyze this process (*11, 12*). The relative inactivity of the dispersed phase in hydrogen activation may be due to the prohibitive M-M distances or/and to the strong interaction with the support. It should be pointed out that the rate of the oxyreduction process is important in practical catalytic applications and would preclude the full utilization of the dispersed phase as "oxygen-storage" under certain operating conditions.

Data on the stability of the dispersed phase in actual use are presently scarce. One would not anticipate however, that the oxyreduction processes will lead to loss of the "oxygen storage" capacity. Prolonged reduction periods might cause particle growth which upon oxidation will give Re_2O_7 particles, and subsequent dispersion. A cyclic process can be visualized as follows:

$$\begin{tikzcd}
Re^{\circ} \arrow[r, "\text{oxidation}"] & Re^{7+} \arrow[r, shift left, "\text{dispersion}"] & \overline{Re}^{4+} \arrow[l, shift left] \arrow[r, "\text{reduction}"] & \overline{Re}^{\circ} \arrow[lll, bend left, "\text{particle growth}"]
\end{tikzcd}$$

where $\overline{Re}$ denotes the dispersed, two-dimensional phase.

On the other hand, deactivation by poisons, such as sulfur to form rhenium sulfates under oxidizing conditions, cannot be ruled out. Further, the change, upon prolonged high-temperature exposure, of the support alumina from γ- to α-phase may diminish the chances of the formation of the dispersed Re phase and therefore enhance Re volatilization. These matters are worthy of further study.

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