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The Number of Active Sites for the Disproportionation of Ethylene on Supported Rhenium Oxide Catalysts

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The adsorption and disproportionation of deuterated ethylene on an alumina-supported rhenium oxide catalyst has been studied. The average heat of adsorption of ethylene was found to be 6.02 kcal/mole and the adsorption entropy corresponded to that consistent with a mobile adsorbate. The activation energy for the surface reaction was found to be 9.45 kcal/mole, and, based on the available surface area, the preexponential factor was estimated to be 5×10^{-11} cm^2/molec-sec. Based on these kinetic and thermodynamic parameters, models for a pairwise and nonpairwise chain reaction with both a mobile and an immobile transition state have been considered. Although the disproportionation of ethylene is not sufficiently intricate enough to distinguish between a four-centered pairwise exchange and a nonpairwise sequence with a carbene chain carrier, the results suggest that, for either case, the reaction proceeds through an immobile transition state with an active site concentration on the order of 7×10^{11} sites/cm^2. For a mobile transition state, the calculated preexponential factor was at least six orders of magnitude greater than that observed experimentally.

INTRODUCTION

We have recently reported the results of a study of the adsorption and disproportionation of light and monodeuterated ethylene on an alumina-supported rhenium oxide catalyst (*1*, *2*). By measuring independently the extent of adsorption of light ethylene and the conversion of the monodeuterated isotope to the dideuterated olefin, we were able to demonstrate that the metathesis reaction is second order in the adsorbate concentration. To the extent that we could neglect the isotope effect, we were also able to measure the rate constant for the surface phase reaction and found a value of 9.45 kcal/mole for the activation energy. We wish to discuss here some observations with respect to the preexponential factor as it relates to the number of active surface sites for the disproportionation reaction on the supported rhenium oxide catalyst.

METHODS

The supported rhenium oxide catalysts were prepared following established procedures (*3*) and both the adsorption and kinetic studies were performed in a Pyrex glass system, using a two-stage mercury diffusion pump, liquid nitrogen traps, and greaseless stopcocks or Teflon glass valves. The details of the experimental procedure can be found in our previous paper (*2*). The BET surface area of the activated alumina-supported catalyst was found to be 104 m^2/g. The X-ray diffraction pattern of this catalyst (after H_2 reduction) contained lines characteristic of the Al_2O_3 support and a very weak, broad line centered at about $d = 2.39$ Å. By contrast,

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the X-ray pattern of a silica-supported rhenium oxide catalyst, which was found to be inactive for the disproportionation reaction (*2*), gave diffraction lines at 2.38, 2.23, and 2.11 Å, all characteristic of metallic rhenium. The metal particle size as estimated by the linewidths was about 75 Å.

RESULTS

The adsorption and disproportionation reaction was studied on both alumina- and silica-supported rhenium oxide catalysts (*1*, *2*). The silica-supported catalyst was found to discolor when the olefin was introduced and there was no detectable disproportionation activity. The X-ray diffraction results would suggest that the reactant olefin rapidly reduced most of the oxide to the zero-valent metallic state. By contrast, the alumina-supported catalyst was considerably more resistant toward reduction and remained highly dispersed on the support. As reported earlier (*1*), a 10% Re_2O_7/Al_2O_3 developed sites that adsorbed ethylene irreversibly (at room temperature) after reduction in hydrogen. The amount of irreversible ethylene, which we have associated with anion vacancies in the oxide structure, was found to be 5 ml (STP)/g. This would correspond to a ratio of ethylene molecules to *total* rhenium atoms of about 0.5. Adsorption of ethylene on the unreduced catalyst was found to be reversible with an average isosteric heat of adsorption of 6.02 kcal/mole and a corresponding adsorption entropy of −21.1 e.u. The isotherms could be best represented by the Freundlich equation, but the Langmuir isotherm with a monolayer volumes (STP) of 4.88 ml/g at 75°C and 5.01 ml/g at 95°C could also be used with a slightly smaller degree of reproducibility as measured by a least-squares deviation.

The disproportionation rate of monodeuterated ethylene, R, expressed in molecules per second per gram of catalyst, was found to correlate with the extent of adsorption of the olefin, n_s, expressed in molecules per gram by

$$R = 8.12 \times 10^{-23}(n_s)^{1.95} \tag{1a}$$

at $T = 75°\mathrm{C}$ and

$$R = 17.07 \times 10^{-23}(n_s)^{2.03} \tag{1b}$$

at $T = 95°\mathrm{C}$, which would correspond to an activation for the bimolecular surface reaction of 9.45 kcal/mole and a preexponential factor of 7.03×10^{-7} g/molec-sec.

DISCUSSION

Before it is possible to present any theoretical discussion of the significance of the preexponential factor, it will be necessary to determine the surface area available to the adsorbate. An upper bound to the surface area is provided by the BET isotherm which gave a value of 104 m^2/g for the alumina-supported rhenium oxide catalyst. If the Langmuir isotherm is used to represent the reversible adsorption of ethylene on the unreduced sample, the average monolayer coverage is about 5 ml/g. Assuming that the area per molecule is given by (*4*)

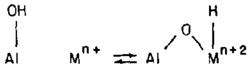
$$a = 1.091\left(\frac{M}{N_0\rho}\right)^{\frac{2}{3}}, \tag{2}$$

where ρ is the adsorbate density $(=0.57\ g/cm^3$ for ethylene), the area per ethylene molecule would be 20.5 $Å^2$, and a monolayer volume of 5 ml/g would correspond to about 30 m^2/g. In addition the X-ray diffraction pattern of this catalyst did not reveal any pronounced peaks due to rhenium or its oxides and the ratio of irreversible ethylene adsorption on the reduced catalyst loading of 10% Re_2O_7 would be sufficient to give a monolayer coverage of the oxide on the alumina support, and the calculations presented above would indicate that the oxide dispersion is high. Olsthoorn and Boelhouwer (*5*) have recently reported the results of an ir study of Re_2O_7 dispersed on Al_2O_3 where it was concluded that the Re_2O_7 exists as a monolayer. This conclusion was based primarily on the observation that the hydroxyl bands characteristic of the Al_2O_3 support were completely suppressed for Re_2O_7 concentrations in excess of 20 wt%. Their Al_2O_3 support was in the form of an aerogel structure and a catalyst containing 26 wt% Re_2O_7 had a BET surface area of 195 m^2/g. Thus their surface density would be essentially the same as that for the 10 wt% catalyst that we used. If it is assumed that the surface area is bound by 30 and 100 m^2/g and the disproportionation rate is expressed as

$$r = k_0 e^{-E/RT}(n_s')^2, \tag{3}$$

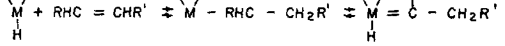
where n_s' now corresponds to the surface coverage in molecules per square centimeter, the value of k_0 is between 2×10^{-11} and 7×10^{-11} cm²/molec-sec. In the discussion that follows, we shall assume an average value of 5×10^{-11} cm²/molec-sec.

There have been a number of proposals with respect to the sequence of elementary steps and the nature of the intermediates for the disproportionation reaction (*6*). In general, they may be classified as pairwise chain reaction, involving a four-centered intermediate or a metallocyclic complex, and a nonpairwise chain reaction proceeding through a carbene intermediate. Grubbs (*7*) has recently reviewed the arguments supporting a carbene chain-carrying sequence for homogeneous and nonsupported heterogeneous metathesis catalysts. Comparable studies identifying the carbene as the pertinent intermediate for a supported catalyst have not been presented, but Laverty *et al.* (*8*) have advanced arguments that suggest that a carbene intermediate may be formed on a supported catalyst through an interaction of the olefin with a metal hydride. They propose that the metal hydride may be formed by the reaction of a coordinatively unsaturated metal ion in a low or intermediate oxidation state with a surface hydroxyl group. The overall process on Al_2O_3 may be represented by



$$\underset{Al}{\overset{OH}{|}} \quad M^{n+} \rightleftarrows Al{-}O{-}\overset{H}{\underset{M^{n+2}}{|}}$$

This oxidative addition reaction may be promoted by donor ligands, such as an olefin in the coordination sphere of the metal ion. It is proposed that the metal carbene is formed by a β-H addition of the metal hydride to the olefin followed by an α-H elimination:



$$\underset{H}{M} + RHC = CHR' \rightleftarrows M - RHC - CH_2R' \rightleftarrows \underset{H}{M} = \overset{R}{C} - CH_2R'$$

The adsorption and kinetic studies of ethylene on supported Re_2O_7 suggest that the adsorbate is mobile (*2*) and that the reaction is second order in the adsorbate concentration. If it is assumed that the sequence involves the formation of a four-centered mobile transition state, then the reaction can be characterized by

$$O_a + O_a \rightleftarrows (O\text{–}O)_a^{\neq}, \tag{4}$$

where O_a represents the mobile adsorbed olefin molecule forming the transition state $(O\text{–}O)_a^{\neq}$. The preexponential factor, k_0, would be related to the corresponding partition functions by

$$k_0 = \frac{kT}{h}\frac{F_{oo}^{\neq}}{(F_o)^2}. \tag{5}$$

The partition function for the adsorbed species can be expressed as $F = F_t^2 F_{int}$, where F_{int} corresponds to the contribution from the internal degrees of freedom and F_t is the translational contribution per degree of freedom and, for free translation, would be given by (*9*)

$$F_t = \left[\frac{2\pi mkT}{h^2}\right]^{\frac{1}{2}}. \tag{6}$$

For ethylene at 350°K, $F_t = 5.7 \times 10^8$ cm⁻¹, and for the transition complex it would be a factor $\sqrt{2}$ greater. Thus

$$k_0 = 2\frac{kT}{h}\frac{1}{F_t^2}\frac{(F_{oo}{}^t)_{\text{int}}}{(F_o)_{\text{int}}{}^2}. \tag{7}$$

The partition function for the internal degrees of freedom are on the order of 1–10 and their ratios would be expected to be on the order of magnitude of unity. Given these assumptions, the calculated preexponential would be 4.5×10^{-5} cm²/molec-sec. Clark *(10)* has proposed a method for calculating the translational partition function for restricted translation characterized by a surface diffusion barrier of height V_0. The maximum possible value of V_0 would correspond approximately to the heat of adsorption, which in the present case was found to be on the order of 6 kcal/mole. Using this value for V_0, the translational partition function per degree of freedom would be reduced to 3.1×10^7 cm^{-1} and the calculated preexponential factor would be 1.5×10^{-2} cm²/molec-sec. Thus the calculated value, assuming both a mobile adsorbate and a transition state at least six orders of magnitude greater than the experimental value.

If it is assumed that, although the reactant is mobile, the reaction occurs on specific surface sites, then Eq. (4) is still applicable, but the transition state would be considered immobile. The rate would be given by

$$r = (n_{\Sigma_2})\frac{kT}{h}\frac{F_{oo}{}^{\neq}}{(F_o)^2}e^{-E/RT}(n_s')^2, \tag{8}$$

where n_{Σ_2} is the number of adjacent free sites per unit area, which for the Bragg–Williams approximation would correspond to *(11)*

$$n_{\Sigma_2} = \frac{1}{2}\frac{s(n_\Sigma)^2}{B_i}, \tag{9}$$

where s is the number of nearest neighbors (e.g., 4), n_Σ is the number of free sites and B_i is the total number of active sites. Since $n_\Sigma \approx B_i$ and if $s = 4$, the preexponential factor would be given by:

$$k_0 = 2\frac{kT}{h}B_i\frac{(F_{oo}{}^{\neq})_{\text{int}}}{(F_o)_t{}^4(F_o)_{\text{int}}{}^2}. \tag{10}$$

If it is assumed that the transition complex corresponds to two olefin molecules adsorbed on one site, then $n_{\Sigma_2} = B_i/2$, and k_0 is a factor 4 less than that given by Eq. (10). An order of magnitude estimate of the number of active sites can be obtained if the experimental value of k_0 is used and it is again assumed that the ratio of the internal contributions to the partition function is unity. The calculations suggest that

$$B_i \approx 7 \times 10^{11} \text{ sites/cm}^2.$$

Based on a total surface density of 10^{15} sites/cm² this corresponds to an active site concentration of 0.1% or less.

For a nonpairwise chain reaction proceeding through a carbene chain carrier, the rate equation would be given by

$$r = k_0e^{-E/RT}(n'_s)(n_c'), \tag{11}$$

where n_c' is the carbene surface concentration and the preexponential factor; k_0 would be given by

$$k_0 = \frac{kT}{h}\frac{F^{\neq}}{(F_o)(F_c)}. \tag{12}$$

For the disproportionation of ethylene there will exist an equilibrium between the mobile adsorbed olefin and the metal carbene, and, if it is assumed that there are B_c carbene-forming sites, then

$$n_c' = B_c\frac{\dfrac{F_c}{F_o}n_s'e^{-\Delta H_c/RT}}{1 + \dfrac{F_c}{F_o}n_s'e^{-\Delta H_c/RT}}. \tag{13}$$

If the equilibrium constant for the formation of the carbene is sufficiently small, the rate would be given by

$$r = \frac{kT}{h} B_c \frac{F^{\neq}}{(F_o)^2} e^{-(E+\Delta H_c)/RT} (n_s')^2, \quad (14)$$

which is second order in the olefin concentration as observed experimentally. Since the preexponential factor obtained from Eq. (14) is the same to within a factor of 2 as that from Eq. 10,

$$B_c \approx B_i,$$

where B_c now corresponds to the number of sites available for carbene formation. The observed surface activation energy would now, however, correspond to a linear combination of the heat of formation of the metal carbene and the true activation energy. Thus the most likely sequence of elementary steps involves a reaction on specific surface sites, and for the case of either a pairwise or a nonpairwise chain reaction the active site concentration is relatively small.

Using ir techniques, Olsthoorn and Boelhouwer (*12*) have investigated the catalytic properties of the Re_2O_7/Al_2O_3 disproportionation catalyst. In particular, they found that metathesis activity is associated with a partially reduced oxide surface. By studying the adsorption of NO, which is a poison for the disproportionation reaction, they established the presence of bands characteristic of the adsorption of NO on partially oxidized Re ions. The extent of adsorption was too small to be determined accurately, but they estimate an amount less than 0.3% ot the total Re content which is consistent with the value reported above.

Maatman (*13*) has recently reviewed the question of active site concentration and concluded that a significant number of reactions can be characterized by active site concentrations less than 10^{11} sites/cm^2. The disproportionation of propylene on WO_3 (*14*) was found to give an anomalous mass transfer effect even though the rate per unit surface area was not anomalously large. It has been proposed that catalyst surface contains a small number of highly active sites leading to the phenomena of "site localized diffusion" (*15*). In the present case, the turnover number at 368°K based on a total surface density of 10^{15} sites/cm^2 and a monolayer ethylene coverage would be about 10^{-2} sec^{-1}. This value is comparable to those for other hydrocarbon reactions (*16*). However, if based on the number of active sites, the turnover number would be more like 10 sec^{-1}, and depending upon the disposition of these sites on the surface, one could indeed anticipate a relatively large localized activity and the attendant mass transfer limitations.

It has been established that in general the magnitude of the disproportionation activity is a sensitive function of the oxidation state of the metal promoter. As reported earlier (*2*), we found that when the rhenium oxide catalyst is reduced in hydrogen, its initial activity for the disproportionation of propylene is about five times that of the unreduced surface, but that the activity decays to that of the unreduced catalyst in a time comparable to that associated with the irreversible adsorption of ethylene that is characteristic of the reduced catalyst. We have tentatively identified the sites responsible for both the irreversible adsorption of the olefin and the enhanced activity with anion vacancies formed by a partial reduction of the rhenium oxide surface. Similar results for a reduced molybdena–alumina catalyst have been observed by Lo Jacono and Hall (*17*). For the isomerization and subsequent metathesis of cyclopropane there was an increase in the amount of irreversibly held hydrocarbon and disproportionation activity with increasing anion vacancy concentration. These experiments were performed in a microcatalytic pulse reactor, and, for a reduced surface, the disproportionation activity, as measured by the production of ethylene, was found to decrease with increasing pulse number. Olsthoorn and Boelhouwer (*12*) have also observed an enhanced activity for the partially reduced rhenium oxide surface and they present ir spectra which suggest that a partial reduction is initiated by propylene and butene at reaction conditions (i.e., 25°C). Reduction by ethylene was considerably slower and metathesis activity at room temperature was established only after exposing the surface to propylene. Our results would suggest that at moderately higher temperatures (i.e., 75–95°C), ethylene can act as a reducing agent and promote activity. It appears that at least a partial reduction, even by the reactant olefin, is a prerequisite to metathesis activity. Since the number of active sites may be a small fraction of the total available surface sites (see above), olefin adsorption as a whole may appear to be reversible (*1*). The break-in period observed for many heterogeneous metathesis catalysts may, in part, be related to a slow reduction of the surface. Luckner and Wills (*18*) have, however, demonstrated that the break-in regime for WO_3/SiO_2 still exists on a surface prereduced in H_2 or CO. Based on the proposal advanced by Laverty *et al.* (*8*), the break-in period may be associated with a slow carbene chain carrier initiation step subsequent to a lowering of the oxidation state of the metal promoter. The ir spectra of methylene groups have been observed after olefin reduction of rhenium oxide (12).

The reducibility (in H_2) of Al_2O_3-supported Re_2O_7 catalysts has been the center of considerable debate (*5*, *19–21*). It has, however, been clearly established that there is a relatively strong interaction between this support and the metal oxide, and, in contrast to bulk Re_2O_7, little, if any, rhenium is volatilized in an oxidizing environment (*22*). The SiO_2-supported oxide can be readily reduced by H_2 (*23*) but it now appears that the ease and degree of reduction, as well as the final oxidation state, for the Al_2O_3-supported oxide are a strong function of the catalyst pretreatment. Yao and Shelef (*21*) have shown that the oxide subjected only to a precalcination step can be completely reduced by H_2 at 350°C. In contrast, if the metal is reoxidized and then subjected to a prolonged evacuation or exposed to an inert gas atmosphere at elevated temperatures (i.e., 500°C), reduction is initiated only at temperatures in excess of 500°C. They propose that this procedure promotes the formation of a two-dimensional dispersed rhenium phase (dispersion cycle), and the maximum rhenium oxidation state is Re^{+4}. The majority of the rhenium is present in this dispersed phase up to a surface concentration of 1.2×10^{18} Re ions/m^2. For metal loadings in excess of this value, they propose the coexistence of a three-dimensional phase with a maximum oxidation number for the metal of +7. They also observe that H_2, CO, and O_2 are absorbed irreversibly on these surfaces and that the extent of adsorption correlates with the amount of the dispersed phase. In contrast, Olsthoorm and Boelhouwer (*5*) propose that the Re_2O_7 remains dispersed in a monolayer up to surface concentrations in excess of 3.3×10^{18} Re ions/m^2. They do however observe that the oxide cannot be completely reduced. Since their catalysts were evacuated for 1 hr at 550°C after oxidation, they were undoubtedly subjected to the dispersion cycle mentioned above. In a reduction–oxidation cycle, they observed that the O_2 uptake was only 80% of the value required for complete oxidation of the metal to Re^{+7}. If it is assumed that, after reduction both Re^{+4} and Re^0 coexist on the support, then the observed O_2 consumption would correspond to a surface where 35% of the rhenium exists as Re^{+4}. The total metal surface density was reported to be 3.3×10^{18} Re atoms/m^2; thus the Re^{+4} concentration matches that reported by Yao and Shelef (*21*) (i.e., 1.2×10^{18} Re ions/m^2).

Our catalysts were also subjected to a high-temperature evacuation for 1 hr and the discrepancy between the ethylene adsorption isotherms for the silica- and alumina-supported samplers implied only a partial reduction for the Re_2O_7/Al_2O_3 catalysts. Our rhenium surface density (10.95 wt% Re_2O_7; 104 m^2 BET) was 2.7×10^{18} Re atoms/m^2 and the extent of irreversible ethylene adsorption was found to be 1.3×10^{18} molec/m^2. In view of the irreversible adsorption of H_2, CO, and O_2 on the dispersed phase (*21*) if we identify the ethylene adsorption with the Re^{+4} ions our numbers are in good agreement with those presented above. It is, however, still possible that the sites adsorbing ethylene irreversibly are associated with anion vacancies. Free electron trapped in anion vacancies have been observed by ERP on the reduced rhenium oxide surface after a dispersion cycle (*21*), but the signal was removed by an additional oxidation–reduction cycle. Undoubtedly the ease of formation and stability of the dispersed phase are also a function of structure and pretreatment (i.e., dehydration temperature) of the alumina support. The decay in metathesis activity that we observed after reduction is attributed to the irreversible adsorption of the olefin on these sites, whatever their nature, at the relatively low reaction temperatures (i.e., 75–95°C). Unless the olefin–metal bond is unusually strong, this self-poisoning should be diminished at elevated temperatures.

The results obtained so far would indicate that, although the coupling between the rhenium ions and the support is relatively strong, there exists a distribution of bond energies as reflected in the varying levels of hydrogen-promoted reducibility. Whether the rhenium ions exist in a monolayer (*5*) or are distributed between a dispersed and three-dimensional phase (*21*) is still unclear. In addition, the dispersed or monolayer phase may correspond to an epitaxial layer similar to that proposed for MoO_3/Al_2O_3 (*24*) or to an actual displacement of Al cations for Re in the support surface. The latter process may be promoted by the high-temperature evacuation of the catalyst after oxidation. Presumably epitaxial growth would not require such a severe pretreatment. A comparison of the surface densities for MoO_3/Al_2O_3 and Re_2O_7/Al_2O_3 would suggest that the monolayer is not epitactic (*5*).

The question remains then as to the nature of the active sites and their relation to the oxidation state of the metal promoter. Following arguments originally advanced by Mango and Schachtschneider (*25*), Lo Jacono and Hall (*17*) have proposed that, for molybdenum, reduction produces the anion vacancies which are associated with Mo (IV) and that this d^2 ion has the proper orbital symmetry to facilitate the pairwise exchange proceeding through a four-centered intermediate. Alternatively, reduction or high-temperature evacuation is expected to produce coordinatively unsaturated ions in a lower oxidation state (i.e., Re^{+4}) which may in effect increase the number of carbene chain carriers (*8*). In a temperature-programmed reduction of a dispersed catalyst, Yao and Shelef (*21*) observed the reliberation of H_2 when the sample temperature exceeded 600°C. If the sample was reoxidized and the reduction was repeated, H_2 liberation was not observed. Similar results were observed for the EPR signal associated with trapped electrons in the anion vacancies (see above) and it was therefore assumed that this hydrogen was associated with anion vacancies in the surface layer. This metal–hydrogen bond is therefore quite stable (in the absence of O_2) and would probably be of a hydridic character and therefore a precursor to the metal carbene.

In conclusion, there exists a considerable amount of circumstantial evidence that supports the carbene chain carrier sequence for the metathesis reaction and in view of the results with homogeneous catalysts, this scheme seems entirely plausible for supported catalysts as well. However, more detailed studies similar to those presented by Grubbs (*7*) need to be performed before the distinction can be made unambiguously. Nevertheless, it appears that the presence of at least a partially reduced surface is a characteristic of the metathesis reaction and that the active site concentration is relatively low.

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