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Authors
Watson, P.R.
Somorjai, G. A.

Publication Date
1981-12-01
Submitted to the Journal of Physical Chemistry

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December 1981

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Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48
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THE INTERACTION OF CO, CO₂, AND D₂ WITH RHODIUM OXIDE (Rh₂O₃.5H₂O): ITS REDUCTION AND CATALYTIC STABILITY

P.R. Watson and G.A. Somorjai

Materials and Molecular Research Division, Lawrence Berkeley Laboratory and Department of Chemistry, University of California, Berkeley, CA 94720

Abstract

We have investigated the adsorption and interaction of CO, CO₂, and D₂ with Rh₂O₃.5H₂O by thermal desorption spectroscopy (TDS). Both CO and D₂ react strongly with the oxide lattice inducing decomposition during the desorption process to yield CO₂ and D₂O. Adsorbed CO₂ desorbs essentially intact. These results are compared with those found on rhodium metal formed by reducing the oxide to the metallic state. On this metallic surface CO₂ dissociates while CO and D₂ desorb without significant reaction. Pore diffusion effects are shown to have an influence on the kinetics of CO₂ formation. The use of CO₂ to maintain an oxidized metal surface in a reducing atmosphere during a catalytic reaction is discussed.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the U.S. Department of Energy under Contract W-7405-ENG-48.
1. Introduction

The oxides of the heavier Group VIII transition metals, Pt, Pd, Rh, and Ir in general and rhodium in particular, are little studied and poorly understood systems; they have relatively poor thermodynamic stability as their oxygen dissociation pressures reach $10^{-6}$ torr below 1000 K [1,2]. The most common and relatively stable oxide of rhodium is the sesquioxide which is known in three anhydrous forms as well as the hydrated form $\text{Rh}_2\text{O}_3\cdot5\text{H}_2\text{O}$. It is a yellow amorphous solid prepared by alkali precipitation from aqueous solution and may be more accurately represented by $\text{Rh(OH)}_3\cdot\text{xH}_2\text{O}$ [1-3].

In this laboratory we have made an extensive study of the surface properties of rhodium metal including the chemisorption of oxygen and the formation of ordered surface oxides [4]. Most recently we have explored the use of rhodium catalysts for the hydrogenation of CO using both metallic rhodium [5,6] and bulk rhodium oxides [7,8]. The latter study has shown that both anhydrous $\text{RhO}_2$ and $\text{Rh}_2\text{O}_3$ are readily reduced to the metal upon heating in vacuo or in an $\text{H}_2/\text{CO}$ mixture. However, the hydrated sesquioxide, $\text{Rh}_2\text{O}_3\cdot5\text{H}_2\text{O}$, which had been dried at 450°C for an hour, proved to be relatively stable upon heating in both vacuum and a reaction mixture of $\text{H}_2/\text{CO}$. Furthermore, this oxide proved to have the unusual catalytic ability to produce oxygenated products during the CO hydrogenation reaction rather than methane and small concentrations of ethylene and propylene typically formed over the Rh metal catalyst [5,6].

The chemisorption of CO and $\text{H}_2$ and their interaction with the lattice must be important processes during the hydrogenation of CO that also affect the stability of this oxide as a catalyst. In this paper we describe the chemisorption and reactions of CO, CO$_2$, and D$_2$ on such an oxide surface that
was investigated by means of thermal desorption spectroscopy (TDS) under UHV conditions.

The adsorption and reaction of these gases on metal oxides has long been an area of active interest, particularly with regard to the H$_2$ and CO oxidation and methanol synthesis reactions [8,9]. Relatively few of these studies, however, have been carried out on carefully characterized substrates under UHV conditions as were used here. While studies of the H$_2$-O$_2$ and CO-O$_2$ reactions over the platinum group metals abound [10-15], little if any such effort has been directed toward their oxides, although occasional mention of the effect of surface oxides is found [12,13]. There is mounting evidence of the importance of oxidized metal species for the catalytic activity of nominally reduced oxide-supported metal catalysts [7,16,17].

2. Experimental

The experiments were carried out in a stainless steel ultrahigh vacuum chamber equipped with retarding field electron optics which were used to regularly monitor the cleanliness of the sample surface by Auger electron spectroscopy. A quadrupole mass spectrometer (UTI 100 C) was used to detect gases desorbing from the surface which was heated with a linear temperature ramp of about 20 K/sec. The rhodium oxide (Rh$_2$O$_{3.5}$H$_{2}$O, 99.9%, Pfaltz and Bauer) was deposited from a methanol slurry onto a gold foil which provided both a physical backing for the powder sample and a means of heating. The foil was heated resistively, the temperature being measured by an alumel-chromel thermocouple attached to the foil.

The oxide sample was heated to 450°C for 15 minutes to remove water of crystallization. Auger spectra taken after this treatment showed that only
partial reduction of the oxide occurs [7]. The surface area of the oxide, before desorption, was estimated at 10 m²/gm by the B.E.T. method.

The CO (Matheson 99.95%) was passed through a dry-ice/acetone bath to remove carbonyls; the D₂ (Liquid Carbonic) was used without further purification. D₂ was employed for the TDS experiments to avoid the complication of residual H₂ in the vacuum chamber. The mass spectrometer reading were corrected where necessary for differences in ionization efficiency, electron multiplier gain, and relative transmission.

3. Results and Discussion

TDS spectra for various exposures of D₂ to the oxide surface at room temperature are shown in Fig.1. The temperature of the peak maxima is listed in Table I together with relevant data from desorption from rhodium metal [20-25].

The major desorbing species is D₂O which desorbs over a rather broad temperature range centered at about 270°C. A small amount of D₂ desorbs at 115°C. As the desorption temperature of D₂ does not seem to correlate with D₂O desorption and the cracking fraction of D₂ from D₂O in the mass spectrometer is very small, less than 1%, the D₂ desorption peak represents D₂ desorbing from the surface.

We can relate the areas under the O₂ and O₂O TDS peaks, A_D₂ and A_D₂O to the relative number of desorbed molecules N_D₂ and N_D₂O by [29]

\[
\frac{N_{D_2}}{N_{D_2O}} = C \cdot \left( \frac{S_{D_2}}{S_{D_2O}} \right) \cdot \left( \frac{A_{D_2}}{A_{D_2O}} \right)
\]

where \( S_{D_2} \) and \( S_{D_2O} \) are the relative pumping speeds for the two molecules. The ratio \( \left( \frac{S_{D_2}}{S_{D_2O}} \right) \) has been measured to be about 13.5 [29]. The proportionality
constant C describes the relative sensitivity of the mass spectrometer to the two species and was measured to be close to 0.7. From the above equation and the desorption data of Fig.1, we readily obtain the result that ~ 40% of the D$_2$ adsorbed reacts to form D$_2$O.

The shape of the D$_2$ desorption peak and the constant peak temperature, as the coverage is changed, suggest second order kinetics that do not involve lateral interactions. As shown in Table I, the desorption temperature of D$_2$ is very high compared to that desorbed from rhodium metal [20,21]. It is not likely, therefore, that this desorption arises from a small metallic component of the surface.

Presumably, deuterium adsorbs dissociatively to form hydroxyl species, as is observed by infrared spectroscopy on many oxide system [27]. On heating, the majority of the hydroxyl groups react to form D$_2$O, resulting in a reduction of the surface while a small fraction reform D$_2$.

The very different shapes of the desorption curves for D$_2$ and D$_2$O suggest that the D$_2$ arises from a small number of favored sites that allow for easy dissociation of O-H bonds. When D$_2$ desorption has been completed, D$_2$O desorption has only just begun, and the broad nature of its desorption curve extending over a range of 300°C suggests that transport of the reacting species, rather than reaction or desorption kinetics, is the rate limiting factor.

In Fig. 2 we present TDS spectra for CO adsorption with peak temperatures again listed in Table I. In this case, CO is detected desorbing at about 225°C at low exposures with a second peak which grows in with increasing exposure at ~ 160°. CO$_2$ desorbs in a single peak which has a maximum at about 190°C at low coverages which shifts to about 245°C at higher exposures.

We can estimate the amount of CO that reacts to form CO$_2$ by an analog of
Eq.1. In the case of CO/CO₂, we are helped considerably by the fact that the relative sensitivities (C) and the ratio of pumping speeds are both close to unity. Allowing for about 6% cracking of CO₂ to CO in the ionizer of the mass spectrometer, we find that about 75% of the adsorbed CO reacts to form CO₂.

The CO TDS spectra of Fig.2 resemble those reported for CO desorption from metallic rhodium foils [5,18] and crystals [19-24]. In these studies, CO was shown to desorb at ~ 230°C at low coverages and close to 200°C at higher exposures. At very high exposures, a second peak appears below 100°C [20,21]. The resemblance of the data we have obtained for CO desorption from rhodium oxide to the published data for the metal leads us to believe that much of the CO is desorbing from patches of metallic rhodium.

In Fig. 3 we show TDS spectra for CO and CO₂ that has been adsorbed on an oxide reduced to the metallic state by heating at 800°C, in vacuum, for 30 minutes. This reduction was observed visually and by Auger electron spectroscopy. As shown in this Figure and Table I, CO desorbs intact at about 200°C, in good agreement with results obtained by other workers for metallic rhodium [5,18-24]; a small CO desorption peak centered around 300°C may be due to residual surface oxygen. On the other hand, on this reduced surface, CO₂ is completely dissociated, desorbing solely as CO, again in good agreement with other reports [22].

Fig. 4 displays the TDS spectra for CO₂ adsorbed on a rhodium oxide sample. In contrast to the data of Fig.3, CO₂ desorbs intact at 170°C in a quite symmetric peak with a small shoulder at 280-305°C. The small amount of CO that also desorbs is due to the dissociation of CO₂ on the rhodium metal present in the oxide and is equivalent to about 15% of the total desorbed species.
Thus adsorbing CO on the rhodium oxide leads to the oxidation of the majority of the molecules to CO$_2$ (~75%) on heating, while the adsorption of CO$_2$ leads to mainly desorption of CO$_2$ with some 15% being dissociated to CO. This is due to the metallic content of the surface as rhodium metal dissociates CO$_2$ and associatively adsorbs CO while the oxide adsorbs CO$_2$ and oxidizes CO. Thus we suggest that CO or CO$_2$ adsorption could be used to titrate the degree of reduction of the oxide surface. Indeed, if many CO adsorption experiments are performed, the surface becomes progressively reduced as shown by a steady increase in the ratio of CO to CO$_2$ produced on desorption.

The CO$_2$ TDS spectrum from CO adsorption (Fig. 2 and Table I) has a very different shape and coverage dependence from the CO$_2$ TDS spectrum from CO$_2$ adsorption of Fig. 4. Thus the peak temperature in the CO$_2$/CO$_2$ case is independent of exposure at 165°C, while the peak of the CO$_2$/CO TDS spectrum varies from 190°C to higher temperatures as the exposure is increased. This implies that the rate determining step in the formation of CO$_2$ from CO is not desorption of CO$_2$ from the surface as adsorbed CO$_2$ desorbs below the temperature of CO$_2$ production from CO at all exposures.

The use of oxides as catalysts for the oxidation of CO is well known [8] as is the reduction of oxides by CO [25]. Using the enthalpy of formation of Rh$_2$O$_3$ as a guide (-70.1 kcal mol$^{-1}$) [26], then we can calculate the heat of the CO reduction reaction

$$\text{Rh}_2\text{O}_3 + 3\text{CO} \rightarrow 3\text{CO}_2 + 2\text{Rh} \quad \Delta H = -134.8 \text{ kcal/mole}$$

This highly exothermic value shows that we can expect this reaction to be facile.

The adsorption of CO on oxides has been interpreted to proceed through both adsorbed carboxylate [25] entities, and carbonate species formed through a reaction with lattice oxygen [8]. Both species have been detected by IR
spectroscopy depending upon the oxide and the conditions of adsorption [8,27].

As rhodium does not form a bulk carbonate and in the absence of detailed spectral information on this system we will postulate a mechanism proceeding through an adsorbed carboxylate species (CO₂ ads) which we will write as

\[ \text{CO} \rightleftharpoons \text{CO}_{\text{ads}} \]

\[ \text{CO}_{\text{ads}} + \text{O}_{\text{latt}} \rightarrow \text{CO}_{2}\text{ads} \]

\[ \text{CO}_{2}\text{ads} \rightarrow \text{CO}_2(\text{g}) \]

As discussed earlier, the TDS data of Figs. 2 and 4 imply that desorption of adsorbed CO₂ is not a rate determining step and that formation of CO₂ ads is probably rate determining. Hence we can write a rate equation:

\[ \text{Rate of CO}_2 \text{ production} = r_{\text{CO}_2} = k_1 [\text{CO}_{\text{ads}}][\text{O}_{\text{latt}}] \]  

(2)

If we assume the concentration of lattice oxygen atoms to be constant, probably a good approximation during the early stages of the reaction, then a plot of log (r CO₂) against log [CO ads] at constant temperature will yield a line whose slope is the order of the reaction, here assumed to be 1.

Such data can be obtained from the CO₂ TDS spectrum of Fig. 2 by measuring the intensity of the desorption signal at a given temperature for various exposures; this is proportional to the rate of production of CO₂. The amount of CO₂ remaining on the surface at that temperature, [CO ads], is found by integrating the area under the peak above that temperature at each exposure considered. When this is presented in a log-log plot as in Fig 5, the slope has a value of 0.74 ± 0.02 indicating a reaction order in CO close to 3/4.

This derived reaction order does appear to increase slightly with temperature from a value of slightly less than 0.70 at 100°C to about 0.76 at 175°C.
This unusual reaction order may be a manifestation of pore diffusion effects. The presence of significant diffusion effects in the oxide crystallites is a likely occurrence; such effects often manifest themselves by altering the apparent order of reaction [28]. Thus a zero-order reaction becomes an apparent 1/2 order reaction. Therefore it may be that, at least during the initial stages of desorption, the surface is effectively saturated in adsorbed CO, but significant diffusional barriers are present that hinder the adsorbate from finding an oxygen lattice site at which to react.

We can write the rate equation as:

\[ r_{CO_2} = \nu \gamma [CO_{ads}]^{0.75} [O_{latt}] \exp \left[ -\frac{E_r}{RT} \right] \]  

(3)

where \( E_r \) is the apparent activation energy and \( \nu \gamma \) is a pre-exponential factor which may depend upon the reactant concentrations and the temperature. We can transform this to:

\[
\log \left[ \frac{r_{CO_2}}{[CO_{ads}]^{0.75}} \right] = -\frac{E_r}{RT} + \log \nu \gamma + \log [O_{latt}]
\]

Assuming \([O_{latt}]\) is effectively temperature independent, we obtain the Arrhenius plot of Fig.6 which shows a temperature dependence of the activation energy. We can fit two lines to the low- and high-temperature portions of this curve to yield activation energies of 14.3 and 6.4 kcal mol\(^{-1}\), respectively. This type of behavior is typical of pore diffusion influenced reactions where the apparent activation energy observed varies with temperature [28]. At low temperatures, where the rate of reaction is controlling, the observed activation energy is that of the chemical reaction. When the rate of mass transfer is controlling at higher temperatures, the activation energy becomes characteristic
of the value for mass transfer which is very small. At intermediate temperatures, the measured energy activation is often given by the average of those for mass transfer and reaction which approximates to one-half of the chemical reaction activation energy. Thus we see a transition from $E_r=14.3$ kcal mol$^{-1}$ to $E_r=6.4$ kcal mol$^{-1}$ as the temperature is raised, a value close to one-half of the low temperature value, which may indicate a significant diffusion contribution to the rate of CO oxidation.

We note that the low temperature value of $14.3$ kcal mole$^{-1}$ for the CO oxidation on rhodium oxide obtained here is in good agreement with literature values for the reaction of carbon monoxide with oxygen on Pt(111) [12] and polycrystalline rhodium [14] below 500 K where values of $14$ kcal mole$^{-1}$ are reported.

4. **Implications for Catalysis**

We have shown elsewhere [7] that Rh$_2$O$_3$ prepared by drying the hydrated oxide is an effective catalyst for the conversion of mixtures of CO and H$_2$ to oxygenated hydrocarbons. However, under reaction conditions (6 atm 1:1 H$_2$/CO, 300°C) the oxide is metastable, eventually reducing to the metal after many hours of use. The present work shows that reduction by both CO and H$_2$ are likely pathways for this decomposition process.

It is probable that the active catalyst surface consists of patches of oxidized rhodium that are necessary for the production of oxygenates and reduced metal [7]. Our results for CO$_2$ adsorption indicate that if reaction to produce CO$_2$ is a chief mode of reduction of the oxide, then concomitant dissociation of CO$_2$ on metallic patches on the surface can serve to re-oxidize the surface. Therefore, CO$_2$ formed during the synthesis reaction, or added with the reactants as in the case for the methanol synthesis [9], may perform
a valuable function in keeping at least a portion of the catalyst surface oxidized and active for the synthesis of oxygenated products.

Conclusions

We have examined the adsorption and interaction of CO, CO₂, and D₂ with an Rh₂O₂.5H₂O sample that had been dried at 450°C. Our major findings are:

1. Approximately 40% of adsorbed D₂ reacts to form D₂O which desorbs over a broad temperature range centered at 270°C. The D₂ that desorbs does so at a temperature (115°C) that is too high to be due to adsorption on metallic patches on the surface.

2. Approximately 75% of adsorbed CO reacts to form CO₂ which desorbs between 190° and 245°C depending on coverage.

3. Both CO and D₂ desorb without significant reaction on an oxide sample that had been reduced to the metal in agreement with literature findings.

4. Adsorbed CO₂ desorbs intact at 170°C regardless of coverage.

5. Analysis of the temperature dependence and shape of the CO₂ desorption peak from adsorbed CO shows that pore diffusion effects have a pronounced effect on the kinetics of CO₂ formation and oxide reduction.

Acknowledgement

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U. S. Department of Energy under Contract W-7405-ENG-48.
References

29. S. Ferrer and G.A. Somorjai, Appl. of Surface Sci. to be published.
Figure Captions

1. Thermal desorption spectra (TDS) of D₂ and D₂O desorbed from dried Rh₂O₃·5H₂O after exposure (measured in Langmuirs) to D₂. The notation should be read desorbing gas/adsorbed gas/substrate in this and other diagrams. The mass spectrometer signal is in arbitrary units, but is consistent from one diagram to the next.

2. As the previous figure, but for CO and CO₂ desorbing after exposure to CO.

3. TDS spectra for CO (AMU 28) and CO₂ (AMU 44) desorbing from a reduced sample of rhodium oxide after exposure to 25 L of CO and CO₂.

4. As Fig. 2 but using CO₂ as adsorbate.

5. Plot of log of the rate of production of CO₂, rCO₂, against adsorbed CO remaining on the surface [CO ads] at various temperatures, after exposure to different quantities of CO. Data taken from Fig. 2 as described in the text.

6. Plot of log of rCO₂/[CO ads]⁰.⁷⁵ against 1/T taken from the data of Fig. 2. Each point is the average of the data from the five exposures shown in that Figure.
Fig. 1
The figure shows mass spectrometer signals as a function of temperature for two different conditions:

- **CO<sub>2</sub>/CO/oxide**
  - Amu 44

- **CO/CO/oxide**
  - Amu 28

The graphs represent CO exposure (L) and temperature (°C) with peaks indicating the mass spectrometer signal (arb. units) for different levels of exposure:

- Line labels: 250, 100, 50, 25, 10

The figure is labeled as Fig. 2.
Fig. 3
CO₂/CO₂/oxide
\[\text{Amu 44}\]

CO/CO₂/oxide
\[\text{Amu 28}\]

Fig. 4
Fig. 5
Fig. 6
Table I. The temperature of the maximum rate of desorption ($T_{max}$) for the desorption of various species after adsorbing $D_2$, CO, and $CO_2$ on rhodium oxide (fresh and reduced) compared with Rh(111).

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Exposure</th>
<th>$T_{max}$ (°C) ± 5°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$D_2$</td>
</tr>
<tr>
<td>Rhodium oxide</td>
<td>low</td>
<td>115</td>
</tr>
<tr>
<td></td>
<td>high</td>
<td>115</td>
</tr>
<tr>
<td>Reduced Rhodium Oxide</td>
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<td>&lt;60</td>
</tr>
<tr>
<td></td>
<td>high</td>
<td>&lt;50</td>
</tr>
<tr>
<td>Rh(111)</td>
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</tr>
<tr>
<td></td>
<td>high</td>
<td>40</td>
</tr>
</tbody>
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