Reduction Kinetics of Surface Rhodium Oxide by Hydrogen and Carbon Monoxide at Ambient Gas Pressures As Probed by Transient Surface-Enhanced Raman Spectroscopy

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The transient reduction kinetics of surface rhodium oxide (Rh_2O_3) by gaseous H₂ and CO have been probed in situ by surface-enhanced Raman spectroscopy (SERS). The Rh surfaces are ultrathin films electrodeposited onto SERS-active gold, enabling surface vibrational spectroscopic information to be obtained with high temporal resolution (≈ 1 s) at elevated temperatures (up to 500 °C) and under ambient-pressure flow-reactor conditions. Surface Rh_2O_3 is formed by heating Rh in flowing O_2 at 1 atm and fingerprinted by an intense 530 cm⁻¹ $\nu_{\rm Rh-O}$ feature. The reduction of such oxidized surfaces upon sudden exposure to either H₂ or CO over a range of partial pressures (1–760 Torr) was monitored from the decay kinetics of the $\nu_{\rm Rh-O}$ band intensity. Surface oxide is readily reduced by both reductants, although striking differences in the observed kinetic behavior indicate the occurrence of distinct reaction pathways. In the case of H_2 , at low partial pressures (≤7.6 Torr) below 200 °C a temperature-dependent induction period is observed prior to rapid first-order oxide reduction. Such "autocatalytic" behavior is indicative of a "nucleation/growth" mechanism, where H₂ dissociatively adsorbs to form reaction centers, followed by facile reaction between adsorbed (or lattice) oxygen and (possibly subsurface) hydrogen atoms. Immeasurably fast H₂-induced oxide reduction, however, occurs at higher temperatures (≥ 200 °C) and pressures (≥ 76 Torr). In contrast, CO-induced oxide reduction was found to be substantially (at least 10-fold) slower than with H_2 at similar pressures and temperatures, yet no induction period was detected. At lower temperatures (≤ 250 °C), the oxide reduction kinetics by CO exhibit fast initial removal followed by a much more sluggish zero-order response. Such "autoinhibited" kinetic behavior, along with the lack of an appreciable CO pressure dependence, suggests that oxide removal is hindered by the extensive formation of adsorbed CO, which is observed to develop rapidly under these conditions from the characteristic Rh-CO and C-O stretching vibrations. This mechanism is further supported by the first-order kinetic response observed throughout oxide removal at temperatures (\geq 300 °C) where buildup of adsorbed CO is not detected. The transient kinetics for CO-induced oxide reduction are linked to the well-known poisoning effect that Rh surface oxidation exerts on catalytic CO oxidation by O_2 . Comparisons are also made between the present results and those recently obtained for methanol-induced oxide removal in order to elucidate which chemisorbed alcohol fragment(s) constitute the reactive oxygen "scavenger".

Introduction

Monitoring the chemical state of a metal surface during heterogeneous processes involving either gas- or solution-phase species constitutes a basic requirement in forging a molecular-level understanding of reaction kinetics and mechanisms in catalytic chemistry. The acquisition of such interfacial chemical information, especially in situ under technologically relevant conditions, such as high gas pressures, represents a substantial challenge and hence remains a key issue in heterogeneous catalysis. As a consequence, most molecular-level information on the nature and reactivity of adsorbates in gas-phase heterogeneous catalysis, in particular, has been extracted (or implied) from "surface-science" studies at much lower pressures, down to ultrahigh vacuum (UHV). The need to extrapolate between such widely differing gas-phase conditions has often been referred to as the "pressure-gap" problem.¹ Recently, there has

been increasing success at applying and adapting some surface spectroscopic and microscopic characterization methods to situations featuring even ambient-pressure gas or liquid (especially electrochemical) systems.^{1,2} Important examples in this regard include examinations of spatial atomic and molecular surface arrangements by means of scanning tunneling microscopy (STM)³ and vibrational spectra for adsorbed molecules obtained from infrared—visible sum-frequency generation (SFG).^{2,3}

With these objectives in mind, we have been exploring the utility of surface-enhanced Raman spectroscopy (SERS) as an in situ vibrational spectral probe on metals in gas-phase as well as electrochemical environments, especially catalytic systems. Some time ago, we found that the technique could be extended to transition-metal surfaces by electrodeposition of thin films onto SERS-active gold substrates.⁴ Significantly, several of these films (such as Rh, Pt, Pd, and Ru) display excellent thermal stability and SERS activity (at least up to 500 °C), enabling their surface chemistry to be scrutinized while acting as model catalysts in ambient-pressure gas-flow reactor systems. Such an arrangement enables the formation and reactivity of interfacial

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species to be examined in situ under transient as well as steadystate (or equilibrium) conditions, involving, for example, the acquisition of temporal spectral sequences (≥ 1 s time scales) following rapid alterations in gas-phase composition and/or catalyst temperature.⁵ Moreover, the anticipated relationships between surface speciation and reactivity with the overall catalytic rates can be addressed by means of simultaneous mass spectrometric (MS) detection of the gas-phase products.⁶

One interesting issue that we have been exploring recently by means of these "flow-reactor SERS" tactics involves the role of surface oxides in catalytic oxidations. The sensitive detection of low-frequency vibrations, such as oxide-lattice modes, afforded by SERS makes this technique a propitious choice for such in situ kinetic studies. These oxides, formed on transition metals at elevated temperatures with ambient-pressure oxidants such as O₂ and NO, are typically found to inhibit catalytic activity and/or alter reaction pathways. For example, the differing roles of surface oxides in the methanol oxidation reaction on rhodium and palladium catalysts, evident from temperature-dependent kinetic data,^{5b-d} are highlighted by a notable dissimilarity in the reactivity of these oxides toward methanol: rhodium oxide is capable of oxidizing methanol above 150 °C,5b-d while palladium oxide is entirely unreactive even at 500 °C.5d

We have been motivated to explore such processes on rhodium in view of the effectiveness of Rh-based catalysts for a variety of gas-phase reactions, together with the likely importance of surface oxidation given the high affinity of this metal toward oxygen. For example, the presence of rhodium oxide inhibits CO oxidation,⁷ while dramatically increasing the activity for alkane hydrogenolysis.⁸ However, while the reaction of *adsorbed* oxygen on Rh with various gas-phase species (e.g., CO,^{7,9} H₂,¹⁰ NO^{7,11}) has been examined in detail, surprisingly little is known about the reactivity of rhodium *oxide*, even though this surface species readily forms at moderate O₂ partial pressures (>0.01 Torr) and elevated temperatures (≥ 200 °C),^{12–14} conditions which are commonly encountered in oxidative catalysis.

Described here is a SERS study of the reaction kinetics of surface rhodium oxide with hydrogen and carbon monoxide under transient flow-reactor conditions. This selection of gaseous reductants was made mindful of comparisons with the corresponding reaction involving methanol, since H and CO are two likely oxide-scavenging fragments formed upon methanol dissociative adsorption on Rh.¹⁵ Striking dissimilarities are evident in the time-dependent oxide removal kinetics with H₂ and CO, which together with other vibrational spectral information indicates the occurrence of notably different reaction pathways. The results highlight the utility of our in situ transient SERS approach to probe surface reaction mechanisms under catalytically relevant conditions.

Experimental Section

The SERS-active rhodium films were prepared by utilizing 6 mm diameter disks cut out of 0.1 mm thick gold foil (99.95% pure, Johnson Matthey) and polished using 0.3 μ m alumina powder. They were then placed into an electrode holder that exposed ca. 0.07 cm² of the surface and subjected to oxidation–reduction cycling (ORC) in 0.1 M KCl to produce the surface roughness necessary for Raman enhancement.^{4a} The surface was rinsed thoroughly with deionized water and subsequently transferred to another cell for electrochemical deposition of the Rh overlayers, which utilized a 0.3 mM solution of RhCl₃ in 0.1 M HClO₄ at 0.1 V vs SCE. The cathodic charge was

monitored in order to limit the deposition to the desired film thickness, usually 2–6 equivalent monolayers.^{4b,c} The surfaces were pretreated by heating to 150 °C in 100 cm³ min⁻¹ of H₂ for about 5–10 min. This procedure resulted in a flat SERS background in the 200–1000 cm⁻¹ range, even though weak features remained in the 1300–1600 cm⁻¹ region due to surface carbonaceous residues.

Details of the reactor and sample holder utilized for the SERS experiments have been provided previously.^{5c,6d} The (room temperature) gaseous reactants are introduced into the reactor through a manifold that allows mixing of up to four inlet gases; flow rates are measured with a bubble flow meter. Recent reactor modifications allow for sudden introduction of such reaction mixtures close to the sample, providing efficient mixing characteristics required for transient spectral response experiments, of central interest here. The gas-phase composition was monitored by leaking the reactor gas into a quadrupole mass spectrometer (Stanford Research Instruments RGA200). The reactants utilized were 99.99% pure CO from an aluminum cylinder (Matheson) (see footnote 18), 99.994% pure O₂ (Airco), 99.9% pure H₂ (Airco), and 99.9% pure Ar (Airco). Laser excitation at 647.1 nm is provided by a Kr⁺ laser (Spectra Physics), and scattered light from the sample is collected by a three-stage spectrometer (SPEX Triplemate), equipped with a liquid nitrogen-cooled CCD detector (Photometrics).

Results

The surface oxidation of Rh films by O₂ at ambient pressures and elevated temperatures (25-300 °C) was examined previously in detail by Tolia et al.^{13b} by using SERS together with X-ray photoelectron spectroscopy (XPS). A broad Raman band centered around 530 cm⁻¹ was evident above 150 °C along with a second feature at 290 cm⁻¹. The former band was assigned to the metal-oxygen symmetric stretch (ν_{Rh-O}) of Rh₂O₃ based on comparisons with Raman spectra of bulk oxide and correlations with the parallel XPS data. More recent observation of the expected ca. 20 cm⁻¹ downshift upon substitution with ¹⁸O confirms that the species responsible for the 530 cm^{-1} feature is formed from O₂.^{6d} Assignment of the 290 cm⁻¹ band was more challenging (see footnote 19). However, in the experiments reported herein, this 290 cm⁻¹ feature was found to be less reproducible as well as typically much weaker than the dominant 530 cm⁻¹ band and is therefore not considered further here.19

The reactivity of rhodium oxide was probed by monitoring its removal in real time by means of SER spectral sequences acquired following sudden exposure of the surface to CO or H₂ at various partial pressures and surface temperatures (cf. ref 5c). Oxidized Rh surfaces were first formed by heating a sample to 350 °C in a 100 cm³ min⁻¹ flow of pure O₂ at 1 atm, yielding an intense broad 530 cm⁻¹ band associated with Rh₂O₃. Further heating in pure oxygen has little effect on the intensity of the 530 cm⁻¹ feature, indicating that the Rh film oxidation is essentially complete by 350 °C. The reactor was subsequently flushed out with argon and the surface temperature adjusted to the desired value. This procedure retains the oxide-covered surface, since the temperatures investigated (50-400 °C) are lower than those reported for thermal desorption of oxygen from Rh¹⁶ and decomposition of Rh₂O₃,^{12,16} ca. 800 and 550 °C, respectively. The reactive gas (consisting of various partial pressures of H₂ or CO in Ar at 1 atm) was then suddenly introduced at 2400 cm³ min⁻¹ while simultaneously monitoring the SER spectra. Each spectrum in a sequence spanning the desired overall time scale was acquired within periods as short



Figure 1. Real-time SER spectral sequence acquired upon sudden exposure of an initially oxide-covered Rh surface at 100 °C to a 2400 cm³ min⁻¹ flow of 1% H₂ in Ar at 1 atm. The surface was previously heated in 100 cm³ min⁻¹ of pure O₂ to 350 °C, followed by flushing of the reactor with argon and cooling to the temperature of interest before H₂ addition. The spectral acquisition time was 0.5 s.

as 0.5 s. (This lower limit is constrained by our CCD camera.) The chosen flow rate is sufficient to change entirely the composition in the reactor chamber within ca. 3 s (i.e., 4 residence times).

The transient reactivity of surface Rh₂O₃ toward H₂ over a wide range of temperatures (50-400 °C) and reactant partial pressures (1-760 Torr) is considered first. Utilizing mixtures containing 100% (760 Torr) or 10% (76 Torr) H₂ resulted in immeasurably rapid (<0.5 s) removal of oxide, even at 50 °C. However, lowering the H₂ composition another 10-fold, to 1% (7.6 Torr), resulted in measurable oxide removal rates below 200 °C. Interestingly, an induction period is observed after H_2 addition during which no measurable (by SERS) reaction occurs, yet followed by rapid and complete oxide removal. Figure 1 shows typical time-dependent SER spectra acquired during reaction of oxide with a 1% H₂ mixture at 100 °C. The intensity of the 530 $\rm cm^{-1}$ oxide band remains unchanged until about 4 s after H₂ addition, whereafter it is removed rapidly (within the following 5 s or so). Similar kinetic characteristics were obtained at 50 and 150 °C, the responses at higher temperatures $(\geq 200 \text{ °C})$ being immeasurably fast.

Such band intensity-time $(I_{ox}-t)$ data can be utilized to provide at least an approximate measure of the temporal decay of the surface oxide concentration as it reacts with the added H₂. We will assume here that the integrated band intensity is proportional to the oxide "relative coverage," θ_{ox} . (A rough proportionality between these quantities has been noted for several metal-adsorbate SERS bands.¹⁷) Figure 2 shows the relative oxide band intensity plotted versus time during reactive removal by 1% H₂ at 150, 100, and 50 °C. While numerous experiments were performed at each temperature, the data sets shown are those typical of the observed behavior. The induction time following H₂ addition is seen to decrease by at least 10fold from 50 to 150 °C (Figure 2). The ensuing oxide removal kinetics are roughly first order in coverage. Surprisingly, however, the latter $I_{ox}-t$ behavior exhibits only a weak



Figure 2. Plot of the relative integrated ν_{Rh-O} oxide band intensity as a function of time at 150 (circles), 100 (squares), and 50 °C (triangles) following the sudden addition of a 2400 cm³ min⁻¹ flow of 1% H₂ in Ar at 1 atm. Band intensities, as deduced from time-dependent SER spectra as in Figure 1, are normalized to the maximum (i.e., initial) values.

temperature dependence. Approximate pseudo-first-order rate constants, k_1 , were extracted via semilogarithmic plots of the relative band intensity versus ($t-t_{ind}$), where t_{ind} is the (induction) time following H₂ addition at which the oxide band begins to attenuate. The temperature-dependent k_1 data yield an Arrhenius activation energy of 3 ± 1 kcal mol⁻¹ and a preexponential factor equal to 30 s^{-1} . As discussed below, such intriguing "biphasic" $I_{ox}-t$ behavior is suggestive of a "nucleation-growth" mechanism for H₂ reduction of the oxide. Given the large differences observed in the results for 10% and 1% H₂ mixtures, the effect of lowering the reactant partial pressure further was investigated. Surprisingly, however, the kinetic responses for 0.1% H₂ were observed to be nearly identical to those described above for the 1% H₂ case.

Finally, the effects of increasing the average Rh film thickness on the oxide removal process were investigated. For these experiments, rhodium films were deposited with 50% more Coulombic charge, so to yield about six equivalent Rh monolayers. Thermal oxidation of such films in flowing oxygen to 350 °C resulted in Raman spectral features identical to those described above (cf. Figure 1, bottom spectrum). These "thicker" oxide films were readily reduced by hydrogen over the range of partial pressures examined. While utilizing 100% and 10% H₂ again yielded kinetics that were faster than our temporal resolution, significant differences were observed for the two types of Rh films with the 1% mixture. In addition to slightly longer induction times, the oxide removal kinetics were significantly (2-5-fold) slower than observed for the thinner films at the lowest temperatures. Nevertheless, the overall "biphasic behavior" noted above was consistently observed for both types of Rh films examined here.

Strikingly different kinetic behavior was obtained for reduction of surface rhodium oxide by gaseous CO in place of H₂. While the former reductant was able to completely remove surface oxide at all partial pressures (8–760 Torr) and temperatures (150–400 °C) investigated, the process was substantially slower than observed with H₂ under similar conditions. No induction period prior to oxide removal was discerned under any of the conditions examined. Two distinct types of kinetic behavior were nonetheless observed, depending on the surface temperature.

Figure 3 shows a typical SER spectral sequence obtained upon sudden exposure of an oxidized Rh surface held at 300 $^{\circ}$ C to 1



Figure 3. Real-time SER spectral sequence acquired upon sudden exposure of an initially oxide-covered Rh surface at 300 $^{\circ}$ C to a 2400 cm³ min⁻¹ flow of 100% CO at 1 atm. Other details as in Figure 1 caption.



Figure 4. Plot of the relative integrated intensities of ν_{Rh-O} (open circles) and ν_{Rh-CO} (closed circles) bands for oxide and adsorbed CO, respectively, as a function of time at 300 °C following the sudden addition of a 2400 cm³ min⁻¹ flow of 100% CO at 1 atm. Band intensities, as deduced from the time-dependent SER spectra as in Figure 3, were normalized to the maximum values in the experiment.

atm of flowing CO. A severe attenuation of the 530 cm⁻¹ oxide band is evident even within the first spectral acquisition time (0.5 s), along with the appearance of a band at 455 cm⁻¹. While the former feature is fully removed within the next 4 s, the latter remains largely unchanged thereafter (see footnote 18). The 455 cm⁻¹ band is similar to that observed previously during SERS studies of CO adsorption on Rh^{5c,6d} and is assigned to the metal–adsorbate stretch (ν_{Rh-CO}) of CO adsorbed on atop sites. An accompanying C–O stretch (ν_{C-O}) at 2030 cm⁻¹ is also observed, confirming the identity of the adsorbed species. Figure 4 shows the relative intensities of the ν_{Rh-O} and ν_{Rh-CO} bands (open, filled circles), extracted from the data in Figure 3, again plotted versus time. (The integrated intensities for ν_{Rh-CO} were normalized to the *final* asymptotic value.) The



Figure 5. Plot of the relative integrated ν_{Rh-O} oxide band band intensity as a function of time at 350 °C following the sudden addition of 2400 cm³ min⁻¹ of a 10% CO in Ar mixture at 1 atm (cf. Figure 4). The solid trace is a "best-fit" first-order decay curve.

Rh₂O₃ removal kinetics were found to be roughly first order under these conditions, although the rapidity of the decay hampers a quantitative analysis. The ν_{Rh-CO} band was not discerned during oxide removal for temperatures above 300 °C, consistent with the lack of spectrally detectable adsorbed CO even for oxide-free surfaces under these conditions. Lowering the CO partial pressure down to 76 Torr or below (i.e., ≤10%) yielded readily measurable oxide removal kinetics even at 350 °C. Figure 5 is a $I_{ox}-t$ plot obtained from temporal spectral data for oxide removal upon exposure to 76 Torr of CO at 350 °C. The kinetic profile is seen to be roughly consistent with first-order decay kinetics as shown by the "best-fit" solid curve.

Oxide removal by CO at lower temperatures (≤ 250 °C), however, exhibits a distinctly different kinetic fingerprint. Figure 6 shows a representative set of time-dependent SER spectra obtained for reduction of oxide at 200 °C by 10% CO (76 Torr). The intensity of the 530 cm^{-1} oxide band is seen to be attenuated by about 40% within the first 20 s and is accompanied by the appearance of a small amount of adsorbed CO, evident as a "shoulder" at ca. 455 cm⁻¹ on the overlapping stronger oxide feature. However, the subsequent diminution and growth of the ν_{Rh-O} and ν_{Rh-CO} bands, respectively, are markedly slower, taking several minutes to occur. Figure 7 is a plot of the relative integrated intensity of the v_{Rh-O} and v_{Rh-CO} bands (open, filled circles) versus time, extracted from data in Figure 6. The temporal decay of the oxide band intensity exhibits a distinctly "curvilinear" shape. The initial (≤ 20 s) oxide removal kinetics are very rapid before giving way to a much more sluggish and approximately zero-order behavior (i.e., a θ_{ox} -independent reduction rate) for the remainder of the process (\geq 75 s). Also noteworthy is that the v_{Rh-CO} band intensity increases initially very rapidly, in tandem with the oxide removal, exhibiting a similar (yet oppositely directed) curvilinear time response (Figure 7).

Rate constants, k_1 , for the initial stage of oxide reduction by CO (i.e., the first portion of the $I_{ox}-t$ decay) over the whole range of conditions investigated were extracted from the kinetic data. Figure 8 summarizes the rate data in the form of an Arrhenius plot. The entries shown with upward-pointing arrows are lower-bound estimates for oxide removal rates that were faster than the temporal resolution of our instrument. At lower temperatures (≤ 250 °C), k_1 is largely independent of CO partial



Figure 6. Real-time SER spectral sequence acquired upon sudden exposure of an initially oxide-covered Rh surface at 200 $^{\circ}$ C to a 2400 cm³ min⁻¹ flow of a 10% CO in argon mixture at 1 atm. Other details as in Figure 1 caption.



Figure 7. Plot of the relative integrated intensities of ν_{Rh-O} (open circles) and ν_{Rh-CO} (closed circles) bands for oxide and adsorbed CO, respectively, as a function of time at 200 °C following the sudden addition of a 2400 cm³ min⁻¹ flow of a 10% CO in Ar mixture at 1 atm (cf. Figure 4). Data extracted from time-dependent SER spectra as in Figure 6.

pressure, exhibiting an Arrhenius activation energy of 7.5 ± 1 kcal mol⁻¹ with a preexponential factor of 200 s^{-1} . While this trend in k_1 continues up to 350 °C for the two lowest CO partial pressures, a distinct "knee" is observed in the case of 100% CO (Figure 8). At 300 °C the rate constant for this reactant composition is almost 10-fold higher than those for the two lower pressures. This divergence increases further at 350 °C, above which the rates even for the lower CO pressures become immeasurably fast. For oxide removal below 300 °C, zero-order rate constants, k_0 , were also obtained from the linear (i.e., the longer-time) portions of the $I_{ox}-t$ data. Arrhenius plots extracted from these data reveal an activation energy of 11 ± 2 kcal mol⁻¹ with a preexponential factor of about 1000 s⁻¹.



Figure 8. Arrhenius plot of temperature-dependent rate constants, k_1 , for the initial removal of oxide upon sudden exposure to 760 (circles), 76 (squares), and 7.6 Torr (triangles) of CO, extracted from SERS data as in Figures 4 and 6. (See text for other details.)

has no observable effect on these zero-order kinetics. A number of experiments were also performed involving CO-induced reduction of oxides formed on the "thicker" Rh films described above. However, no appreciable differences between these kinetics and those for the thinner films could be discerned, in contrast to the behavior with H_2 (vide supra).

Given that these data provide detailed insight into the transient reactivity of surface oxide toward gaseous CO reactant, it is of interest to relate this information to both the temperaturedependent surface speciation and overall kinetics for the wellstudied catalytic oxidation of CO by O₂. Experiments were therefore performed to determine under which conditions oxide and/or adsorbed CO forms in the presence of flowing mixtures of CO and O₂. Rhodium surfaces were heated in a stepwise periodic fashion in various O₂:CO mixtures (19:1 to 1:10) at 1 atm with a flow rate of 200 cm³ min⁻¹, SER spectra being recorded at each temperature until a time-independent response was attained (requiring ca. 3 min). Figure 9 shows typical temperature-dependent SER spectra acquired upon heating a Rh surface in a 19:1 O₂:CO mixture. At 100 °C (bottom spectrum) the 460 cm⁻¹ ν_{Rh-CO} band is seen to be dominant, indicating the extensive presence of CO adsorbed on atop sites. A weak broad band is also discernible at 670 cm⁻¹, similar to the SERS feature observed previously during CO oxidation on Rh.^{6d} This band was assigned to a bending vibration of a surface carbonate species, based partly on the 20 cm⁻¹ frequency downshift observed upon ¹⁸O₂ isotopic substitution.^{6d} Evidence for a surface carbonate species has also been noted in a study of CO oxidation on Rh(111), from vibrational bands at 750, 900, and 1400 cm⁻¹ formed during reaction under net oxidizing conditions.^{7c} While the present Raman spectra remain largely unchanged up to 150 °C, further heating to 200 °C yields a diminution of the 460 cm⁻¹ band intensity (Figure 9). Furthermore, the concomitant onset of Rh surface oxidation is signaled by the growth of the broad overlapping $\nu_{\rm Rh-O}$ feature centered around 540 cm⁻¹, assigned as before to Rh₂O₃. The 460 cm⁻¹ band is removed completely by 350 °C, as expected from thermal CO desorption, although the 540 cm⁻¹ oxide feature remains. While the temperature at which the surface begins to oxidize under this reactant flow is essentially identical to the case of pure O_2 (vide supra), the *extent* of oxidation at a



Figure 9. Temperature-dependent SER spectra obtained during exposure of rhodium to 200 cm³ min⁻¹ of a 19:1 O₂/CO mixture at 1 atm. The spectral acquisition time was 20 s. (See text for other details.)

given temperature is apparently less, as gleaned from the typically lower ν_{Rh-O} band intensities seen here in the presence of CO.

Furthermore, decreasing the O₂/CO ratio to 10:1 and below yielded temperature-dependent SER spectra that are essentially *identical* with those seen in the presence of pure CO. Thus, the 530 and 670 cm⁻¹ bands are now absent, the spectra exhibiting only the familiar ν_{Rh-CO} and ν_{C-O} vibrations at 470 and 2030 cm⁻¹, respectively. These bands are removed within the temperature range 250–350 °C, as observed with O₂-free gaseous CO. Interestingly, then, the temperature-dependent formation of oxide during the ambient-pressure catalytic oxidation of CO on Rh requires a large O₂ excess and is very sensitive to the O₂/CO pressure ratio. Adsorbed CO, on the other hand, is formed extensively even in the presence of a large (20-fold) oxygen excess, at least at temperatures below where thermal desorption proceeds.

The steady-state rates of CO₂ formation for a number of reactant ratios were also obtained via mass spectrometric monitoring of the gas-phase flow composition, in order to compare the kinetics for the overall catalytic rates with those for the transient CO oxidation by oxide as considered above. The procedure utilized was identical to that outlined for the temperature-dependent SERS experiments described above. The steady-state CO oxidation rates were extracted from the MS data in the conventional form of "turnover frequencies" (molecules site⁻¹ s⁻¹), deduced by assuming a surface reaction site density of 2 \times 10¹⁵ sites cm⁻². The steady-state CO₂ production rates deduced on this basis, for example, at 250 and 300 °C for a 9:1 O2:CO reactant ratio at 1 atm are 140 \pm 50 and 270 \pm 50 molecules site⁻¹ s⁻¹, respectively. The CO oxidation kinetics are similar to those observed previously in this laboratory on polycrystalline Rh as well as being in approximate accordance with reports for single-crystal surfaces.⁷ A direct comparison of the CO₂ formation rates with the rate constants for transient oxide removal presented above can be made with a knowledge of the oxide surface concentration, Γ_{ox} , involved in the latter measurements. Assuming that $\Gamma_{ox}\approx 2$ \times 10¹⁵ atoms cm⁻², i.e., equal to the number of surface sites,

yields values of the CO₂ production rates (molecules site⁻¹ s⁻¹) from transient CO reduction of the surface oxide that are numerically equal to the k_1 (s⁻¹) values in Figure 8. For initial oxide reduction at 300 °C at the same CO partial pressure (76 Torr) as above, $k_1 \approx 0.3$ s⁻¹, corresponding on this basis to a transient CO₂ production rate of 0.3 molecules site⁻¹ s⁻¹. We therefore deduce that the steady-state catalytic production rate of CO₂, at least for the above conditions, is very much (10³fold) higher than for transient oxide removal.

Discussion

A notable feature of the present results is the dramatic differences in the transient kinetics of oxide removal by gaseous H_2 and CO. In addition to the much more rapid oxide reduction rates induced by H_2 , the markedly dissimilar oxide coverage—time functionalities signal that distinctly different mechanisms govern these processes. In interpreting the results, it is appropriate to first compare them with the (albeit sparse) literature information on these important processes.

Surface Rh₂O₃ reduction by 1 Torr of CO at 145 °C has been investigated using imaging atom probe mass spectrometry.^{12c} An initial first-order rate constant of 0.1 s^{-1} was extracted by measuring the amount of oxygen on the surface at different points during the reaction. This value is similar to that observed here at 150 °C with 7.6 and 76 Torr of CO (Figure 8). Several kinetic and UHV-based temperature-programmed desorption (TPD) investigations have examined removal of adsorbed atomic oxygen by H or CO.9,10,21,22 The rate constants for reaction of adsorbed oxygen with hydrogen tend to be at least 100-fold higher than those with CO at a given temperature. This is in harmony with the $10-10^2$ -fold larger rates measured here for H₂-induced oxide removal in the "postinduction" time regime, as compared to those found for initial reduction with CO under similar conditions. It is nonetheless important to recall the distinction between adsorbed oxygen atoms and a surface oxide. The latter, but not the former, entails disruption of the metal substrate atoms to form a distinct "surface phase" where the oxygen atoms are located at least partly within the metal lattice, so that oxide reduction requires displacement from this film.

The most striking characteristic of oxide removal by hydrogen, yet not with CO, is the induction period observed prior to the rapid decay in oxide coverage (cf. Figure 2). This behavior, along with the marked effects of pressure and temperature, can most readily be rationalized in terms of a "nucleation/growth" type of reaction mechanism. Taking into account the findings from numerous UHV-based investigations involving surface reactions between oxygen and hydrogen on Rh, a plausible mechanistic sequence for the oxide removal is

$$O^{2-} \leftrightarrow O_{(ads)}$$
 (1)

$$H_{2(g)} + 2S \leftrightarrow 2H_{(ads)}$$
(2)

$$H_{(ads)} + O_{(ads)} \Longrightarrow OH_{(ads)} + S$$
(3)

$$OH_{(ads)} + H_{(ads)} \Longrightarrow H_2O_{(g)} + 2S$$
(4)

or
$$2OH_{(ads)} \rightarrow H_2O_{(g)} + O_{(ads)} + S$$
 (5)

where S denotes a free site and O^{2-} represents the lattice oxide. Step 5 is included because it has been shown under UHV conditions to be important when the coverage of adsorbed oxygen is high,²¹ as is probably the case here.

Prior to introduction of hydrogen, the surface is essentially completely oxidized to form Rh₂O₃ (vide supra) as well as being saturated with atomic oxygen on available metallic sites.^{13b} Under these conditions step 1 can be thought of as being essentially in equilibrium. This situation results in a very low probability for dissociative adsorption of H₂, given that two adjacent metal sites are required for step 2. However, the atomic hydrogen that is eventually formed will readily react with nearby adsorbed atomic oxygen to form water, which is then desorbed.^{10,21} The increasing number of free metal sites formed by this process should trigger more extensive hydrogen adsorption, leading to a rapidly accelerated depletion of surface oxygen. The marked temperature dependence of the induction time (Figure 2) supports the notion that reactions along the lines of steps 3-5 are occurring during this initial period. Oxide removal will be initiated on this basis when the adsorbed atomic oxygen concentration decreases to a level that causes step 1 to be driven irreversibly, thereby decomposing the oxide lattice. Thereafter, reactions 3-5 most likely proceed at the boundaries of oxide/oxygen island structures, as has been proposed by several investigators.^{14a,b,10a,20,21} Perhaps the most direct evidence supporting such a mechanism is found in recent photoemission electron microscopic measurements, which show that surface oxygen removal by hydrogen during the $H_2 + O_2$ reaction on Rh(110) at ca. 10⁻⁵ Torr proceeds via moving reaction "fronts".23 Most importantly, however, such a mechanistic sequence can account for the striking "autocatalytic" nature of the observed oxide-reduction kinetics.

As noted above, hydrogen reduction of the "thicker" oxide film features longer induction periods as well as slower ensuing oxide-removal kinetics. This may be rationalized by the notion that thicker films are likely to be more contiguous. Framed in the context of the "nucleation/growth" mechanism proposed above, such oxide films would have fewer surface metal sites available initially for dissociative H₂ adsorption, resulting in longer induction times, as are observed. A possibly analogous effect was found by Vis et al.,14b who showed using temperatureprogrammed reaction that large (>60 Å) oxidized Rh particles were more resistant to reduction by H₂ than are smaller supported crystallites. Indeed, reactions between adsorbed atomic oxygen and hydrogen also exhibit a significant surfacestructure dependence. For instance, an activation energy of 5.3 kcal mol⁻¹ was found for rate constants obtained on Rh(111),^{10c} whereas a somewhat higher (7.4 kcal mol⁻¹) value was extracted from kinetic data on the (110) face.^{10b}

Given that the oxide removal kinetics are essentially identical when employing 1% or 0.1% H_2 mixtures, it is interesting as well as surprising that the rates are accelerated so dramatically toward higher reductant pressures (i.e., ≥76 Torr). One explanation is that a new, more facile, pathway for oxide removal is afforded by the increased H₂ partial pressure. For instance, the concentration of a surface intermediate (e.g., OH) might be increased, thereby allowing a reaction step such as (5) to become preferred. A more novel, although speculative, possibility is the involvement of "subsurface" as well as adsorbed atomic hydrogen in the reaction pathway. Such a species, entailing diffusion of hydrogen atoms into the metal lattice, has been invoked in a number of surface science studies on several transition metals,²⁴ including rhodium.^{24d} The formation of subsurface hydrogen, H_{sub}, will be more likely at large H₂ exposures or higher gas pressures and at surfaces containing numerous steps, kinks, etc., as should abound on the polycrystalline films examined here. Once formed, H_{sub} may react with the oxygen within the lattice, thereby circumventing

the need for step 1 to occur prior to the formation of OH species. Especially given that step 1 may well be at least partly rate limiting under some conditions (vide infra), the occurrence of such a pathway may account for the notably accelerated oxide reduction rates at higher H₂ pressures. The formation of H_{sub} may also contribute to, or even be responsible for, the "nucleation/growth" oxide-removal kinetics seen at lower H₂ pressures and possibly also observed kinetic sensitivity to the Rh film "thickness". Thus, the "nucleation centers" might conceivably be defects, etc., in the oxide film where hydrogen atoms can more readily enter the surface lattice. Reaction between H_{sub} and O²⁻ can then be envisaged to "spread out" from such centers, undermining the surface lattice structure and thereby facilitating further oxide reduction.

We now turn to a consideration of the oxide reduction pathways with CO. One striking difference in the reduction kinetics with CO compared with H2 is the complete absence of a discernible induction period with the former reductant. Unlike hydrogen, the adsorption of atop CO should require only one free metal site. As a result, this reductant would be expected to rapidly access the available surface sites and react with nearby oxygen to form CO₂. Indeed, both Figures 3 and 6 show that adsorbed CO is spectroscopically detectable within the first spectral acquisition period (0.5 s), indicating facile adsorption under the conditions employed here. The ability of CO to initiate the reaction promptly upon introduction to the surface is also clear from the kinetic data. However, it should be noted that no significant CO-induced reaction occurs on the time scales commensurate with the induction periods observed with H₂ reductant (Figure 2), when the comparisons are made at the same temperature and reductant pressure. Consequently, then, the observed lack of an "induction period" for CO-induced oxide reduction does not reflect a greater intrinsic ability of CO to initiate the reaction.

The second major difference between the kinetic profiles for oxide removal by CO as compared to H₂ can be characterized in general by the apparent "autoinhibition" appearance of the former $I_{ox}-t$ curves (e.g., Figure 7) at lower temperatures (\leq 300 °C), this curvilinear response contrasting the "autocatalytic" form of the latter data (Figure 2). The rapid buildup of substantial CO coverages appears to play a major role in inducing the curvilinear shape of the oxide coverage-time profiles (Figure 7). Figure 10 shows the relative coverages of CO and oxide (filled and open symbols, respectively), extracted from the point at which the oxide removal kinetics switch from an initial rapid decay to the much more sluggish zero-order character (cf. Figure 7) plotted versus temperature, for reduction with 760 and 76 Torr of CO (circles and squares, respectively). The onset of zero-order removal kinetics is seen to occur uniformly at a CO coverage (θ_{co}) of about 0.8, regardless of the pressure or temperature employed. (Note that this relative coverage is obtained by normalizing the ν_{Rh-CO} band intensity to the final asymptotic value achieved during a given experiment.) The initial introduction of CO onto the surface is likely to yield rapid reduction of nearby adsorbed oxygen, triggering net removal of oxide from the metal lattice via step 1. Along with such reactive adsorption, a fraction of the newly adsorbed CO will remain unreacted and thereby rapidly build up to high coverages, as indicated by the vibrational data. Such dense, possibly even close-packed, CO domains will cover an increasing fraction of the surface, effectively limiting the locations where oxide removal via reaction with adsorbed CO can proceed to island edges or other unoccupied sites in the CO adlayer. The reaction rate is therefore depressed by an overabundance



Figure 10. Relative intensities of ν_{Rh-O} oxide (open symbols) and ν_{Rh-CO} adsorbed CO (filled symbols) bands for oxide and adsorbed CO, respectively, during transient oxide removal by CO at 760 (circles) and 76 Torr (squares) at the point where initial rapid oxide decay kinetics transforms to slower zero-order decay (see text).

of the adsorbed reductant, limiting severely as well as buffering the availability of surface sites where the escaping oxide can react (as adsorbed oxygen) with a juxtaposed CO molecule. Such a "site-limited" mechanism can readily account for the observed zero-order dependence in oxide, the kinetics being determined primarily by the CO adlayer morphology.

Further inspection of Figure 10 shows that the relative oxide coverage at which this "adsorbed CO-inhibited" pathway emerges is significantly higher as the CO pressure is increased from 76 to 760 Torr (open squares and circles, respectively). This effect is consistent with the above mechanism in that the higher CO pressure yields a markedly more rapid initial θ_{co} increase. Given that the initial rate of oxide removal is only slightly enhanced under these conditions (Figure 8), a greater fraction of the oxide will become "trapped" by the enveloping CO adlayer and will therefore be obliged to be reduced (more sluggishly) within this adsorbate matrix.

It remains to consider the first-order oxide removal kinetics at temperatures (\geq 300 °C) where the buildup of adsorbed CO is either absent or insufficient to substantially autoinhibit the process. Interestingly, the thermal desorption of CO coincides with the marked divergence of the rate constants for initial oxide removal seen for different reductant pressures under these conditions (Figure 8). This marked upward curvature in the Arrhenius plots suggests that an inherently more facile reaction pathway becomes available at higher temperatures, especially for the highest CO pressure. The reasons for this behavior, however, are unclear. One possible explanation is that a CO pressure-sensitive surface restructuring may be occurring which increases the reactivity of the lattice oxide. While this notion is speculative, even Pt(111) as well as (110) has recently been observed to undergo surface restructuring in ambient CO pressures at elevated temperatures.^{2a}

As already mentioned, it is of substantial interest to relate the present observations regarding surface oxide reactivity to CO oxidation by O_2 , particularly since this process is of archetypical importance in heterogeneous catalysis. Surface oxide formation is believed to poison catalytic CO oxidation on Rh at elevated temperatures when O_2 is in stoichiometric excess.²⁵ As Figure 9 shows, surface rhodium oxide forms at around 200 °C during CO oxidation even in a large (ca 20fold) excess of O_2 . The present finding falls within the range of reactant pressures reported to be required for oxide formation.^{7,25} The present observed effectiveness of pure CO for oxide reduction (cf. Figures 4, 5, and 7) might appear at first sight to be at odds with such findings. However, O_2 supplies a copious amount of atomic oxygen to the surface under reaction conditions, pushing the equilibrium of reaction 1 toward the left. Thus, the oxide is "pinned" under such circumstances by the presence of large quantities of adsorbed oxygen.

Also of significance is the substantial presence of adsorbed CO at lower temperatures even with such O₂-rich mixtures (Figure 9). The additional presence of carbonate under these conditions, as implied from the weak 670 cm^{-1} band, is in harmony with suggestions from kinetic data that this adsorbate is involved centrally in the CO oxidation pathway on oxiderich rhodium, even that the observed overall reaction involves rate-limiting carbonate decomposition.7d (However, unambiguous evidence that this species, rather than reaction between coadsorbed oxygen and CO to form CO2 directly, provides the kinetic bottleneck is apparently lacking.) While the smaller extent of surface oxidation seen in comparison with CO-free O₂ suggests that the presence of the CO adlayer impairs oxide formation, another factor limiting this process may well be the reverse reaction, i.e., oxide reduction by CO. Given that extensive CO adsorption is seen here to strongly inhibit oxide reduction (vide supra), the observed occurrence of surface oxidation under these reaction conditions is probably due as much to CO-induced retardation of the forward direction of step 1. The above observation that the steady-state catalytic CO_2 formation rates are markedly (103-fold) faster than for COinduced oxide removal eliminates the oxide, perhaps not surprisingly, from contention as a bona fide reaction intermediate. However, this situation does not alter the likelihood that the kinetics of CO-induced oxide removal play a major role in determining the conditions for which oxide is present under catalytic reaction conditions.

Finally, it is instructive to compare the present rates of rhodium oxide reduction by H₂ and CO with those from our recent kinetic study using methanol,^{5c} in order to ascertain which chemisorbed alcohol fragment may be responsible for oxide removal in the latter process. Overall, the temperaturedependent rates of rhodium oxide removal by methanol are comparable to the initial reduction rates observed here with CO at similar gas pressures. An interesting difference, however, is that the methanol-induced oxide removal exhibits first-order decay kinetics even down to low oxide coverages.^{5c} Also, while adsorbed CO is seen to form on Rh under steady-state catalytic conditions using methanol-rich CH₃OH/O₂ mixtures, this species is not detected spectroscopically during transient oxide reduction in pure methanol. Consequently, while these findings suggest that adsorbed CO may well be the "active reductant" in the methanol reaction, it is not formed in sufficient quantity to autoinhibit the process, as is the case with gaseous CO.

From the observed kinetic behavior, we proposed that the rate-determining step for oxide removal at high methanol pressures and/or lower temperatures was the irreversible release of oxygen from the surface lattice (step 1), the chemisorbed methanol fragment(s) acting as an "adsorbed oxygen scavenger" and hence quenching the reverse process.^{5c} The observed similarity in the initial oxide reduction rates with CO and methanol lends some support to this notion. Furthermore, given that methanol dissociative chemisorption should yield adsorbed H as well as CO, the strikingly more facile oxide reduction kinetics observed here with H₂ strongly suggest that the former

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fragment does *not* act as the predominant reductant for methanol-induced oxide removal. Most likely, this inability of adsorbed H to react with oxide stems from a severe competition for surface sites with other chemisorbed methanol fragments. Nevertheless, the observation that pure H₂ provides a much more potent scavenger for surface rhodium oxide than *either* CO or methanol supports the hypothesis that hydrogen can induce a reduction pathway that circumvents the need for the oxygen to be displaced from the metal lattice prior to reaction.

Concluding Remarks

The foregoing is believed to provide concrete evidence supporting our contention that the present SERS approach can yield detailed kinetic as well as surface speciation information for interfacial chemical processes for systems and experimental conditions (elevated temperatures, ambient gas pressures, etc.) that encompass those of direct relevance to "real-world" heterogeneous catalysis. Admittedly, quantitative kinetic analyses are hampered by incompletely known relationships between surface morphology, adsorbate coverage, etc., and the Raman signal intensities. The present film-deposition strategy may also turn out to be applicable only to polycrystalline metal or related interfaces, although encompassing numerous systems of catalytic interest. However, the excellent temporal resolution and surface sensitivity afforded by SERS, together with the intrinsic benefits of Raman spectroscopy in accessing vibrational modes spanning wide frequency ranges, conspire to grace the technique with unusual attributes for exploring mechanistic catalytic chemistry. Perhaps most importantly, when utilized in flow-reactor systems as employed here, the strategy provides a versatile in situ means of exploring the catalytic role of surface species in *both* transient and steady-state circumstances. This flexibility enables direct links to be forged between the kinetics of individual interfacial processes and the overall catalytic rates and mechanisms. Such a combination of temporal versatility and interfacial chemical specificity even in high-pressure gas or liquid systems is a unique hallmark of this approach. Thus, insight has been gained in the present study regarding the kinetics of oxide reduction by CO and H₂ (and previously methanol).^{5c} Such information gains more broad-based importance, for example, when considered in light of commonly proposed mechanisms for oxidation catalysis. The present findings suggest in this regard that the notion of lattice oxygen (i.e., oxide) participating directly in catalytic oxidation reactions, often known as the Mars-Van Klevan mechanism,²⁶ may be flawed, at least for rhodium.

Another factor contributing to our enthusiasm for the technique as an increasingly powerful tool for in situ surface chemical characterization in heterogeneous catalysis is the enhanced sensitivity of Raman spectroscopy in general, due especially to recent improvements in spectrometer and detector technology. It is therefore now feasible not only to exploit Raman spectroscopy for interfacial characterization even in the absence (or greatly diminished presence) of the SERS effect but also to explore a widening range of interesting interfacial materials by engendering *some* surface Raman enhancement by film deposition or other tactics. Especially when combined with other means of scrutinizing surface chemical speciation and kinetics applicable to technologically relevant interfaces, we believe that such novel SERS approaches stand poised to make substantial contributions to our broad-based understanding of heterogeneous catalysis in both high-pressure gaseous and liquid-phase environments.

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(18) A series of oxide reduction experiments were also performed utilizing CO of (ostensibly) similar purity which had been stored in a steel cylinder. It is well-known that such gas if not purified further can contain iron carbonyls, which may deposit on metal surfaces at elevated temperatures. Indeed, Rh surfaces heated in such CO in both the presence and absence of oxygen were observed to darken above 300 °C. Parallel XPS and SIMS surface analysis revealed that large amounts of iron, carbon, and oxygen were present. Oxide reduction experiments with this "contaminated" CO were therefore carried out only between 150 and 300 °C. While the initial oxide removal kinetics were found to be very similar under these conditions to those evaluated using Fe-free CO, the surface oxide was only incompletely reduced using impure CO. In addition to formation of adsorbed CO (460 cm^{-1}), a strong band at 670 cm⁻¹ was seen to grow in, especially at higher temperatures.

(19) In the rhodium surface oxidation experiments reported in ref 13b, the 290 cm⁻¹ band was often found to be of comparable intensity to the main 530 cm⁻¹ oxide feature. The former is apparently more resistant to CO-induced removal. This finding, together with the observed instability (or even nonappearance) of the 290 cm⁻¹ feature during rapid heating, suggested that the band is due to a distinct species, possibly chemisorbed or subsurface oxygen.^{13b} The involvement of oxygen in the 290 cm⁻¹ band was confirmed by an observed 15 cm⁻¹ downshift when formed with ¹⁸O₂ rather than ¹⁶O₂.^{6d} However, more recent experiments undertaken using a cleaner gas-handling/pumping system, including the present study, find that the 290 cm⁻¹ feature tends to be weak or even absent. It is therefore unclear at present whether this 290 cm⁻¹ band observed upon exposure of Rh films to O₂ is due to a species formed upon Rh oxidation as opposed to an adventitious (albeit O-containing) impurity.

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