High-Pressure Oxidation of Ruthenium as Probed by Surface-Enhanced Raman and X-Ray Photoelectron Spectroscopies

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Surface-enhanced Raman spectroscopy (SERS) combined with X-ray photoelectron spectroscopy (XPS) has been utilized to study the oxidation of ruthenium at ambient pressure (1 atm) and elevated temperatures (25-300°C). The SERS probe provides in-situ vibrational information regarding surface oxide bonding. While the XPS probe necessarily involves ex-situ measurements (i.e., transfer to and from ultrahigh vacuum), it provides valuable complementary information on the metal and oxygen electronic states. Ruthenium surfaces were prepared by electrodepositing ultrathin films (about three monolayers) onto electrochemically roughened (i.e., SERSactive) gold substrates. Insight into the in-situ oxidation process was obtained by probing the changes of surface speciation by SERS upon heating Ru in flowing O₂. A pair of SERS bands at 470 and 670 cm⁻¹ appear in the spectrum acquired for a freshly electrodeposited film, which are assigned to different stretching modes of hydrated RuO₂ formed during sample transfer to the gas-phase reactor. However, a fully reduced Ru surface (i.e., devoid of oxide features) could be formed by adsorbing a protective CO adlayer in an electrochemical cell followed by heating to 200°C in vacuum so to thermally desorb the CO. While the initially oxidized (i.e., RuO₂) surface was stable to further oxidation upon heating in O2, adsorbed atomic oxygen was detected at 200°C from the appearance of a SERS band at 600 cm⁻¹ and a XPS O(1s) peak at 531.7 eV. In contrast, the higher oxides RuO₄ and possibly RuO₃ were produced only upon thermal oxidation of the fully reduced Ru surface. Evidence for RuO₃ formation includes the appearance of a 800 cm⁻¹ SERS band at 200°C which correlates with the advent of a Ru(3d_{5/2}) peak at 282.6 eV. The surface was further oxidized to RuO₄ at 250°C, as deduced from the formation of a 875 cm⁻¹ band and a Ru(3 $d_{5/2}$) peak at 283.3 eV. While RuO₃ and RuO₄ were exclusively formed at temperatures higher than 250°C, RuO₂ was produced upon cooling to room temperature, possibly via the decomposition of RuO₄. © 1997 Academic Press

INTRODUCTION

Ruthenium is an important catalyst in chemical industry, having applications in hydrogenolysis (1), hydrogenation of benzene (2), and Fischer–Tropsch synthesis (3). The

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low overpotential for the electrooxidative generation of O_2 and Cl_2 also makes ruthenium an important electrocatalyst. The activity and selectivity of ruthenium catalysts depend greatly on the oxidation state of the metal, different ruthenium oxides exhibiting distinct physical and catalytic properties (4). For example, Bond *et al.* reported the effect of oxidation followed by low-temperature reduction on a supported Ru catalyst, enhancing the turnover frequency of hydrogenolysis of ethane by a factor of 200 at $160^{\circ}C$ (1).

The interaction between ruthenium and oxygen has therefore been the subject of extensive investigation. Chemisorption of oxygen in ultrahigh vacuum (UHV) on ruthenium single crystal surfaces has been well documented (5–13). Thomas *et al.* observed atomic oxygen adsorbed on Ru(001) by using Electron Energy Loss Spectroscopy (EELS) (11). For low exposures, oxygen adsorbs dissociatively but incorporation into the bulk occurs to a limited extent. The other mainstream approach involves the utilization of surface-specific techniques to characterize different stoichiometric ruthenium oxides. For instance, Mar *et al.* studied the effect of various preparative routes to RuO₂ on the resulting Raman spectra (14).

Ruthenium, however, is not as noble as other platinumgroup transition metals. From a technological standpoint, the formation of RuO_4 , which is known to be a volatile oxide, is of primary concern as it is the origin of catalyst loss in oxidative reaction systems (15). Given that most of the fundamental studies have been limited to UHV conditions in which ruthenium does not oxidize extensively, it is important to extend such investigations closer to practical reaction conditions, such as continuous-flow gaseous environments at elevated temperatures (25–500°C) and pressures (1 atm).

Over the past decade, we have demonstrated that surface-enhanced Raman spectroscopy (SERS) can provide powerful information regarding adsorbate vibrations for metal-gas as well as electrochemical interfaces under technologically relevant conditions, especially at higher (ambient) gas pressures. Although SERS is traditionally considered applicable only to the coinage metal surfaces Cu, Ag, and Au, following earlier work for electrochemical surfaces by Leung and Weaver (16, 17), we have extended it to a number of catalytically important transition metals such as Pt, Pd, and Rh in the gas phase (18–26) by similarly electrodepositing them as thin films on roughened gold. The sensitivity of SERS to probe metal–oxygen vibrational modes, usually found in the low frequency region between 200 and 1000 cm⁻¹, also makes it a valuable technique for monitoring surface oxidation of transition metals (21, 27).

While SERS can yield insight into the nature of surface bonding, X-ray photoelectron spectroscopy (XPS) provides a valuable complementary technique for assigning oxidation states and stoichiometry of the oxides. There are a number of XPS studies of various distinct Ru oxides; the oxidation-state specificity of the emitted electron energies facilitates the assignment of the detected SERS bands (28– 34). In contrast to SERS, however, XPS necessitates the use of UHV conditions, so that examination of metal oxides formed in high-pressure gas environments requires the surface to be transferred into UHV prior to scrutiny by XPS.

Our group previously utilized combined SERS and XPS measurements to investigate the ambient-pressure thermal oxidation of rhodium (21). Comparative inspection of the temperature-dependent SERS and corresponding XPS spectra demonstrated the ability of this approach to identify specific oxides formed beyond initial oxygen chemisorption, especially Rh_2O_3 . Such tactics should be even more valuable for examining the thermal oxidation of ruthenium, owing to the anticipated existence of a wider variety of ruthenium oxides. We report herein such a study of thermal oxidation of ruthenium by means of SERS combined with XPS. Of central interest is to identify various ruthenium oxides formed as a function of the elevated reaction temperature under technologically relevant conditions, i.e. 1 atm of oxygen.

EXPERIMENTAL

The preparation of SERS-active thin film samples followed a procedure used previously (17-19) involving electrodeposition of ruthenium on roughened gold. Gold discs of diameter 6 mm were cut from 0.1-mm-thick gold foil (Johnson Matthey) and polished using alumina powder. They were then put into an electrode holder that exposed 10 mm² of the surface in 0.1 *M* KCl solution, followed by oxidation-reduction cycles to produce a SERS-active gold surface by following essentially the procedure described in Ref. (35). Ruthenium thin films were deposited from a 5×10^{-4} MRuCl₃ solution in 0.1 MHClO₄ at -0.1 V versus saturated calomel electrode (SCE), the cathodic charge being monitored so as to obtain the desired film thickness, usually about 3 monolayers. The surface was then transferred to an ambient-pressure gas reactor (ca 1 atm), mounting on a sample holder which is capable of raising the surface temperature up to 600°C by resistive heating. Laser excitation at 647.1 nm was provided by a Kr⁺ laser (Spectra Physics). The scattered light was collected by a three-stage spectrometer (Triplemate) equipped with a charge-coupled device (CCD) detector. The frequencies of the Raman scattered light were calibrated by a neon light emitting diode.

The XPS experiments were performed on similar Ru thin films. The sample (10 mm \times 10 mm) was mounted on a molybdenum holder. The XPS instrument was a Perkin-Elmer PHI 5300 connected to a PHI 04-800 high-pressure catalytic reactor, capable of heating the sample up to 600°C at 1 atm. After the surface oxidation was performed under the desired conditions, the sample was cooled down to 25°C and then transferred to the UHV main chamber at 10^{-9} Torr for spectral acquisition. Spectra were collected using a magnesium X-ray source operated at 15 kV and 300 W, an analyzer pass energy of 8.95 eV and with a channel-plate detector. The spectrometer was calibrated from the known binding energy of the Au $(4f_{7/2})$ level, 84.0 eV. The XPS spectra were computer fitted in order to determine the chemical states of specific species present on the samples. Curve-fitting was carried out using a nonlinear least squares fitting program with a Gaussian/Lorentzian sum function, with the spin-orbit splitting of the Ru (3d) doublet constrained to be 4.2 eV. The Ru XPS spectra were further fitted with exponential tails to account for the peak asymmetry arising from core-hole coupling (36).

RESULTS

Raman Spectroscopy

Freshly deposited ruthenium films examined by SERS in the gas-phase reactor under vacuum conditions (10^{-6} Torr) exhibited vibrational peaks at ca 470 and 670 cm⁻¹, suggesting the presence of surface impurities or an oxide film formed during the transfer from the electrochemical cell to the reactor (*vide infra*). Consequently, we attempted to engender surface reduction by heating in H₂. Figure 1A shows typical temperature-dependent SER spectra of a freshly electrodeposited Ru sample heated in a continuous flow of H_2 at 100 cm³ min⁻¹. (Note that the spectra shown in Fig. 1A and subsequently are displayed in an upwardstacked sequence.) No change was detected upon dosing H₂ at ca 25° C, the SERS bands at 470 and 670 cm⁻¹ remaining (bottom spectrum). The surface temperature was increased progressively up to 150°C, holding at each temperature for 3 min before the spectra was acquired. By 100°C, a SERS band at 600 cm^{-1} appeared, whereas the 470 and 670 cm^{-1} bands were still present as shoulders, resulting in a broad and convolved peak. No significant change was detected at 150°C and further temperature increases were avoided as some attenuation in SERS activity was experienced when heating in H₂ at higher temperatures. Subsequent cooling to room temperature left the 600 cm^{-1} band as the major residual feature.



FIG. 1. (A) Temperature-dependent SER spectra for a Ru film in 100 cm³ min⁻¹ H₂ at 1 atm. The film was prepared by electrodeposition on roughened gold (Method I). (B) Subsequent temperature-dependent SER spectra obtained in flowing O_2 (100 cm³ min⁻¹) at 1 atm.

The ruthenium was then reoxidized in flowing O_2 at 100 cm³ min⁻¹; Fig. 1B shows typical spectra as a function of temperature. No observable change to the 600 cm⁻¹ band was discerned at 25°C. After the sample was oxidized at 250°C, followed by cooling to room temperature, however, several SERS peaks were detected at 470, 600, 670, and 800 cm⁻¹ (Fig. 1B, top spectrum). This reappearance of the 470 and 670 cm⁻¹ peaks suggests they originate from an oxide, since they are thermally removed in the presence of H₂ but can be regenerated by heating in O₂.

Table 1 summarizes some literature vibrational spectroscopic data for several ruthenium oxides, including the well-known RuO_2 and RuO_4 species. The 470/670 cm⁻¹ pair observed here have comparable frequencies to the characteristic normal Raman bands of RuO_2 , located at 515 and 626 cm⁻¹ (14, 37). However, firmer assignment of these and other bands requires parallel interpretation of SERS and XPS results and will be addressed below in the Discussion.

Since H_2 pretreatment of the freshly electrodeposited sample leaves a residual species with a SERS band at 600 cm⁻¹ (Fig. 1A), an electrochemical reduction step was utilized as an alternative means to obtain an oxide-free Ru surface. A pretreatment procedure achieving this objective involves applying a reducing potential, -0.3 V versus SCE, to the freshly deposited Ru sample after transfer to 0.1 *M* HClO₄. The electrode was then sparged with CO so to modify the surface, thereby protecting the sample from atmospheric contamination during final transfer to the gas-phase reactor. (Electrochemically reduced surfaces transferred through air without CO modification still exhibited partial oxidation as seen from the reappearance of the 470/670 cm⁻¹ bands.) We will refer to this latter pretreatment procedure as "Method II," with the tactic described above involving simple transfer of a freshly deposited Ru film being dubbed "Method I."

The effect of this Method II pretreatment on the SER spectra, as well as the subsequent gas-phase oxidation, is shown in Fig. 2. After the sample had been transferred

TABLE 1

Published Vibrational Modes of Various Ru Oxides, Oxyanions, and Adsorbed Oxygen on Ru

Species	ν (Ru-O) stretching modes (cm ⁻¹)	Reference	Technique	
Adsorbed	600	а	SERS	
atomic oxygen	585	10	EELS	
	575-595	5	EELS	
	520-600	11	EELS	
RuO ₂	470/670	а	SERS	
	510/630	а	SERS	
	515/626	14	Raman	
	528/646	37	Raman	
RuO ₃	800	а	SERS	
RuO_4^{2-}	808	45	Raman	
RuO ₄	875	а	SERS	
	878	44	Raman	
	881	45	Raman	

^a Data from this work for comparison.





FIG. 2. Temperature-dependent SER spectra for thermal oxidation of a metallic Ru surface. The initial oxide-free surface was prepared by electrochemical reduction and protected by CO adsorption during the transfer to the reactor (Method II): (a) CO-covered Ru surface; (b) reduced Ru surface at 25° C after CO was desorbed by heating to 200° C in vacuum; (c–e) spectra obtained in O₂ after ramping temperature to values indicated; (f) after cooling to 25° C.

to the reactor, two vibrational modes were observed at 500 and 550 cm^{-1} (spectrum a), diagnostic of the ruthenium-carbon stretching modes v(Ru-CO) of adsorbed CO (17). The sample was then heated to 200°C in a vacuum (10^{-6} Torr) to remove the CO; the resulting spectrum exhibits no discernable features in the 300- 900 cm^{-1} region (spectrum b), indicative of the desired formation of an oxide-free Ru surface. To initiate oxidation, the surface temperature was raised incrementally in flowing O_2 at 100 cm³ min⁻¹. At 200°C, three bands are evident, centered at 510 and 630 cm^{-1} with a more intense feature at 800 cm^{-1} (spectrum c). A new feature emerged at 875 cm⁻¹ when the temperature was further increased to 250°C (spectrum d). By 300°C, there was an intensity increase of the 875 cm⁻¹ peak relative to the 800 cm⁻¹ band (spectrum e). To facilitate comparison between corresponding XPS and SERS experiments. the SERS sample was subsequently cooled down to 25°C, mimicking the data acquisition procedure required for the ex-situ XPS measurements outlined below. Interestingly, along with the remnants of both the 875 and 800 cm^{-1} peaks, the resulting SER spectrum shows not only the reappearance, but also an intensification, of the characteristic RuO₂ bands at 510 and 630 cm^{-1} (spectrum f). Significantly, the results of this experiment (Fig. 2) are dissimilar to that involving H₂ pretreatment (Fig. 1B) in that in the former case two behaviorally distinct features were detected at 875 and 800 cm⁻¹ but the 600 cm⁻¹ band was absent. As seen in Table 1, the 875 cm⁻¹ band has a similar frequency to the normal Raman band of RuO₄. However, the identification of the 800 cm⁻¹ peak is not straightforward (see below).

Given these rich SER spectral changes induced by thermal oxidation of the initially reduced ruthenium surface prepared by Method II (Fig. 2), experiments were also performed by similarly heating the initially partially oxidized (i.e., Method I) Ru surface in oxygen, prepared as for Fig. 1A. A typical temperature-dependent set of SER spectra obtained in this fashion is shown in Fig. 3. The spectrum was unaffected by dosing O_2 at room temperature, but the 600 cm^{-1} band is seen when the temperature was higher than 200°C, remarkably similar to when the same surface was heated in H₂ (Fig. 1A). Furthermore, the features at 875 and 800 cm⁻¹ were not seen, contrasting the behavior for oxidation of the initially reduced surface (Fig. 2). Prompted by the broadness and asymmetry of the resulting band, the spectrum that was acquired after subsequent cooling to 25°C was deconvolved (Fig. 3, top spectrum). It is evident that both the features originally present, at 470 and 670 cm^{-1} , also provide contributions to the final spectrum.

Besides studies aimed at the gas-solid interface, as already noted SERS is also invaluable (and indeed better known) for scrutinizing adsorption at metal-solution interfaces (16, 17, 27). Consequently, related aqueous electrochemical SERS experiments were performed to discern any similarities, or differences, between the oxidation of ruthenium in these two environments. The SERS-active Ru



FIG. 3. Temperature-dependent SER spectra for thermal oxidation of hydrated RuO₂ (prepared by Method I) by exposing to 100 cm³ min⁻¹ O_2 at 1 atm.



FIG. 4. Electrochemical SER spectra obtained for a Ru film in 0.1 M HClO₄ as a function of applied potential (vs SCE). The surface was initially reduced at -0.3 V (bottom spectrum) prior to raising the potential to where O₂ evolution occurs (+1.16 V), and subsequently reduced again at -0.3 V.

film was prepared as described above, the surface then being transferred rapidly to a SERS cell with aqueous 0.1 M HClO₄ as supporting electrolyte. Figure 4 shows selected SER spectra for the ensuing electrooxidation of ruthenium as a function of electrode potential (vs SCE) which was altered in a stepwise fashion. The 470 and 670 cm^{-1} bands, initially present at the open circuit potential, were found to be entirely removed when a reducing potential at -0.3 V was applied, yielding a spectrally featureless surface (bottom spectrum). Upon increasing the potential to +0.6 V, the simultaneous reappearance of the 470 and 670 $\rm cm^{-1}$ bands indicates that they are arising from electrooxidation (by water) of the Ru surface. Given that oxidation of an originally reduced Ru surface in dry O₂ requires elevated temperatures (Fig. 2), this finding in Fig. 4 suggests that the initial room-temperature oxidation observed following transfer through (wet) air (Fig. 1A, bottom spectrum) also involves an electrochemical mechanism, perhaps involving a water film on the surface. An additional SERS band at 580 cm^{-1} emerged at +1.16 V (Fig. 4) corresponding to the point where O₂ evolution reaction occurs on the Ru electrode in acidic medium (38). The surface was subsequently reduced by decreasing the potential. At +0.8 V, a 800 cm⁻¹ feature was detected. In addition, the 470 and 670 $\rm cm^{-1}$ bands reappeared at +0.6 V, and they vanished when the potential was lowered to -0.3 V (Fig. 4), indicating that the electrochemical oxidation/reduction processes are chemically reversible.

Photoelectron Spectroscopy

The XPS experiments were performed primarily on ruthenium thin films deposited on smooth gold foils. Roughened gold substrates, as in the SERS experiments, were also used but the results showed no significant differences from those with smooth surfaces. The sample could be transferred without exposure to air between a UHV chamber for spectral acquisition and a high-pressure (1 atm) reactor, where temperature-dependent surface oxidation was undertaken in a similar fashion to the SERS experiments. XPS peaks arising from Ru(3d) and O(1s)photoelectrons were examined, as they are the most intense of the ruthenium and oxygen signals in the photoemission spectrum. Unfortunately, there is an overlap between the $Ru(3d_{3/2})$ and the C(1s) peak at ca 284.5 eV, the latter being due to surface carbonaceous contamination. In view of this, all samples were initially heated in flowing O₂ at 400°C for 30 min to remove the carbonaceous species, followed by reduction in H₂ at 300°C to obtain a metallic Ru surface. Consequently, then, this surface can be compared most directly with that prepared by means of Method II above.

The XPS analysis of different Ru oxides has been well documented, and Table 2 summarizes selected published results from other studies. Figure 5 shows typical curve-fitted Ru(3*d*) doublet and O(1*s*) singlet XPS spectra obtained from a temperature-dependent oxidation experiment performed on an initially metallic ruthenium surface in 1 atm of O₂. After the gas-phase oxidation/reduction pretreatment, the Ru(3*d*_{5/2}) peak was located at 280.3 eV (Fig. 5a); this value is comparable to the binding energy of a metallic ruthenium surface (32–34). Corresponding O(1*s*) signals were found at 532.5 and 534.0 eV, possibly arising from surface impurities (*vide infra*).

As shown in Fig. 5, a noticeable attenuation of the $Ru(3d_{5/2})$ peak at 280.3 eV was observed upon oxidation at 200°C, along with the emergence of another two peaks at 281.0 and 282.6 eV. The corresponding O(1s) XPS spectrum consists of a major new peak at 531.7 eV and another at 530.0 eV. The latter is characteristic of lattice oxide (31, 33) and the coincidence with the binding energy upshift of the Ru(3d) peak suggests surface oxidation. Upon further increasing the oxidation temperature to 250°C, an additional $Ru(3d_{5/2})$ peak was found at 283.3 eV but the 281.0 eV component remains dominant. The extent of surface oxidation was greater, as indicated by the increase of the intensity of the oxidic O(1s) peak at 530.0 eV. The surface was completely oxidized upon subsequently raising the temperature to 300°C as implied from the disappearance of the Ru metal peak at 280.3 eV. The relative intensity of the 283.3 eV to the 282.6 eV peak also increased. Similarly to the SERS data, XPS band assignments will be addressed further in the Discussion section below.

Additional XPS experiments (results not shown) were also performed to correlate the SERS and XPS results in

TABLE 2

Approach	Ru surface oxidation			Stoichiometrically known Ru oxides		This work
Reference Reference	(34)	(7)	(40)	(32)	(28)	
energy (eV) Ru(3 $d_{1/2}$)	$Au(4t_{7/2}) = 84.0$	$\operatorname{Ru}(3d_{5/2}) = 279.96$	$Au(4f_{7/2}) = 84.0$	$Au(4t_{7/2}) = 84.0$	$\operatorname{Au}(4t_{7/2}) = 84.0$	$Au(4t_{7/2}) = 84.0$
$Ru RuO_2 RuO_3 RuO_4$	280.2 281.9	279.96 280.7 281.7 282.6	280.0 280.7 282.4	280.0 280.7 282.5 283.3	279.91 280.68 282.38	280.3 281.0 282.6 283.3
O(1 <i>s</i>) Adsorbed atomic oxygen Lattice oxygen	531.0 529.4	529.9 528.9	529.2	531.5 529.4		531.7 530.0
Remarks	High-pressure oxidation of ruthenium powder.	NO2 was used to obtain high atomic oxygen coverage.	Electrooxidation Ru and RuO ₂ surfaces.	Characterization of pure stoichiometric RuO4 and RuO2.	Characterization of various supported Ru catalysts.	High-pressure oxidation of Ru thin film in flowing O ₂ .

Literature XPS Binding Energies (eV) of Various RuO_x Species

order to aid identification of the 600 cm⁻¹ SERS band found upon heating initially oxidized Ru surfaces (cf. Fig. 1A). Analogously to the SERS experiment shown in Fig. 3, an electrodeposited Ru sample (prepared by Method I) was exposed to O₂ at 250°C without the aforementioned thermal oxidation/reduction pretreatment. The resulting XPS O(1s) spectrum shows no difference to the one as shown in Fig. 5c, which has the major 531.7 eV peak and a shoulder at 530.0 eV, but the presence of the carbon peak makes the $Ru(3d_{5/2})$ signal difficult to interpret.

DISCUSSION

The data presented in this study demonstrates the inherent complexity of the surface oxidation. The assignments of various SERS and XPS peaks, deduced to arise from RuO₂, RuO₃, RuO₄, and an adsorbed oxygen species, will be discussed separately. Furthermore, several issues concerning the oxidation process itself will be addressed. These include: (1) In the presence of O_2 , what is the origin of the behavioral difference between heating an initially partly oxidized and a reduced Ru surface? (2) What is the role of adsorbed oxygen in the selective formation of various Ru oxides? (3) What is the thermal stability of the higher valent oxides?

RuO₂

Ruthenium dioxide (RuO₂) has a rutile structure and it is also the most thermally stable species among the family of Ru oxides (4, 15). Being a conductive oxide, it is infrared inactive, but normal Raman spectra yield Eg and A1g modes at 528 and 644 cm⁻¹, respectively (14, 37). Consequently,

as already mentioned the two similar SERS bands at 510 and 630 cm^{-1} detected upon oxidizing a reduced (Method II) Ru surface to 200°C (Fig. 2c) are attributed to RuO₂. This assignment is strongly supported by the corresponding XPS data (Fig. 5b) in that the upshift of the major $Ru(3d_{5/2})$ peak from the metallic value at 280.3 to 281.0 eV at 200°C in oxygen is consistent with the formation of RuO_2 , as seen by comparison with literature XPS data for bulk-phase RuO₂ (Table 2).

It is known that RuO₂ behaves as a hygroscopic oxide (4). Therefore, the 470 and 670 cm^{-1} SERS bands formed by Ru electrooxidation at +0.6 V are suggested to arise from hydrated RuO₂. Despite the lack of any vibrational spectroscopic data for direct comparison, there are ultraviolet photoelectron spectroscopy (UPS) (39) and XPS (40) studies of the same system which support the formation of hydrated RuO₂ under similar electrochemical conditions.

Recall that apparently similar 470 and 670 cm⁻¹ bands were also detected upon thermal reoxidation of a partially reduced Ru surface by H_2 (Fig. 1B). Although it appears less likely that hydrated oxide would form at the metal-gas interface than in an aqueous electrochemical environment, the presence of water may be accounted for by the reaction between H₂ and the lattice oxygen during the reduction of the oxide. At first glance, one is also tempted to ascribe the O(1s) peak observed at 532.5 eV (with a shoulder at 534.0 eV) following H₂ reduction but prior to thermal oxidation to water or possibly OH species in view of the high binding energies. However, water should desorb well below room temperature on ruthenium in UHV, eliminating this possibility. While the assignment is certainly unclear, we note that a O(1s) band at a similarly high binding energy,

O(1s)

Ru(3d)



FIG. 5. Ru(3*d*) and O(1*s*) XPS spectra obtained upon progressive thermal oxidation of a reduced Ru thin film deposited on a smooth gold substrate. The deposited film in (a) was pretreated by oxidation in O_2 at 400°C to remove surface carbon followed by reduction in H_2 at 300°C. Spectra shown (b-d) obtained following oxidation in 100 cm³ min⁻¹ O_2 at 1 atm at temperatures indicated and transferral to UHV in each case. The uppermost trace in each spectrum represents overlapping of the data and the best-fit curve. Exponential tail functions are shown as an example in Fig. 5a, accounting for the asymmetry of the Ru(3*d*) peaks due to corehole coupling (see text), but they are not shown in Figs. 5(b-d) for the sake of clarity.

533.5 eV, was also observed in our earlier SERS/XPS study of rhodium oxidation following heating in UHV (21). This was tentatively attributed to "subsurface oxygen" or possibly SiO₂ formed from Si impurities in the metal.

Adsorbed Oxygen

The 600 cm^{-1} Raman band detected when a Method I Ru film was exposed to either reducing (Fig. 1A) or ox-

idizing condition (Fig. 3) is assigned to adsorbed oxygen. The frequency of this vibrational mode is in agreement with an EELS feature reported by Thomas et al. (11) when O_2 was adsorbed dissociatively on Ru(001). This band was assigned to the metal-oxygen stretch of adsorbed atomic oxygen and found to be coverage-dependent, varying from 520 cm⁻¹ at low coverage to 600 cm⁻¹ at saturation. A similar 600 cm⁻¹ SERS band emerging at elevated temperatures (Fig. 3) can be interpreted as arising from dissociative adsorption of oxygen on the oxide surface. The thermal stability of this surface oxygen is in harmony with the UHV studies in that it is not desorbed in the latter environment until ca 750° C (6, 8). Although the present 600 cm⁻¹ band refers to an at least partly oxidized surface, rather than a clean metal surfaces as studied in Refs. (6) and (8), our assignment is strengthened by noting that this band also appears on partially reduced Ru (Fig. 1A). The appearance of a similar 600 cm⁻¹ band at the onset of reduction of hydrated RuO₂ in H₂ at 100°C (Fig. 1A) suggests that this adsorbed oxygen may be involved in the reaction as an intermediate.

Again, this tentative assignment is made firmer by comparison with the XPS data. The XPS results also show there exists a corresponding major O(1s) peak component at 531.7 eV besides the one associated with lattice oxygen at 530.0 eV. This relatively high O(1s) binding energy, indicating it originates from a less electron-rich oxygen, which has been previously assigned to chemisorbed atomic oxygen (32, 34). We therefore assign both the 531.7 eV O(1s)XPS peak and the 600 cm⁻¹ SERS band to adsorbed atomic oxygen, given that they were both detected upon heating RuO₂ in O₂.

An additional feature is also noticed in the higher-binding energy side of the O(1s) peak of the oxidized surface (Figs. 5b-d). Its identity is not as clear. One possibility ascribes it to remnant of the adsorbed species which was evident prior to thermal oxidation (Fig. 5a). The other possibility is that it may arise from core-hole coupling which would yield an asymmetrical broadening of the XPS peak towards higher binding energy, yielding so-called "shakeup" peaks (41-43). This effect has been shown previously in numerous spectra of adsorbate atoms on metal surfaces (41). However, it is known that the stronger the adsorbatesubstrate interaction, the less marked this effect will be (41, 42). Considering the high thermal stability of the 530.0 and 531.7 eV peaks (Fig. 5d), they should be associated with strongly bonded species. Moreover, a previous study by Fuggle et al. has addressed the appearance of shake-up lines in the XPS spectra for oxygen adsorption on Ru(001) (43). A similar asymmetric broadening is evident in the higher binding-energy side of the O(1s) peak, as well as a satellite peak at ca 10 eV higher energy. The former was assigned to another adsorbed species (43). On this basis, then, we are inclined to similarly attribute the high-energy asymmetry in our O(1s) peak to the presence of another adsorbed state.

RuO_4

Ruthenium tetraoxide (RuO₄) has been used as an oxidizing agent in organic chemistry (44). It is also identified as the major corrosion product involved in oxygen evolution on ruthenium electrodes (38, 45). Several infrared (IR) (46) and Raman (47, 48) spectra of RuO₄ have been reported, with the latter showing a symmetric stretching mode at 880 cm⁻¹. As already mentioned, this finding therefore suggests an assignment of the SERS band observed here at 875 cm^{-1} to RuO₄. This band is only discernable upon oxidation of a reduced Ru surface (prepared by Method II) at temperatures higher than 250°C (Fig. 2). Again, this assertion is strengthened by inspecting the corresponding XPS $\operatorname{Ru}(3d_{5/2})$ spectra (Fig. 5c), in which the additional 283.3 eV peak emerging at 250° C is also characteristic of RuO₄ (32). When the surface temperature was further in to 300°C, both the SERS and XPS results show an increased production of RuO₄. Once RuO₄ was formed, it is stable at temperatures as high as 300°C, as well as upon subsequent cooling to room temperature.

As far as the formation of RuO_4 as a corrosion product is concerned, the 875 cm⁻¹ band was not detected at the potential of O₂ evolution (+1.16 V vs SCE) in the electrochemical SERS experiment (Fig. 4). This observation apparently contradicts a recent *in-situ* IR spectroscopic study (38) of the same system in which an IR band at 920 cm⁻¹, assigned to RuO₄, was observed under similar conditions. We tentatively account for this discrepancy by suggesting that the infrared band observed in Ref. (32) arises from a solution species; note that SERS is an intrinsically surface-specific technique. The additional appearance of the 580 cm⁻¹ peak at +1.16 V is indicative of gold oxidation (27), thereby providing evidence for Ru film dissolution so to reveal the underlying gold substrate.

RuO3

The existence of RuO₃ has been the subject of controversy in many XPS studies (29–32). To our best knowledge, there has not been any reported characterization of RuO₃ as a discrete stoichiometric oxide. As shown in Fig. 5b, the Ru($3d_{5/2}$) peak has a dominant component at 281.0 eV as well as a minor one at 282.6 eV. While the assignment of the former peak to RuO₂ is well-accepted, that of the latter is not as clearcut. The higher binding-energy component at 282.6 eV has been previously proposed as arising from RuO₃ (29, 30, 32), which is believed to be present on RuO₂ bulk-phase sample as a surface defect.

This interpretation, however, has been challenged by Cox *et al.* who suggest an alternative hypothesis involving core–hole coupling (31). Specifically, these authors claim that both XPS spectral components are due to RuO₂, with

the lower binding-energy peak at 281.0 eV corresponding to RuO_2 screened by metallic conduction electrons. This asymmetric appearance of the XPS spectra is also consistent with core-hole coupling which requires the atom to have unfilled states above the Fermi level (49). As shown in Fig. 5a, the Ru metallic peak was curve-fitted, including an exponential tail function to account for the asymmetry.

Core-hole coupling is most commonly observed on *d*-metals, the spectra of most oxide surfaces being symmetric. However, since RuO_2 is a metallic oxide that therefore also has a partially filled conduction band (4), corehole coupling may also occur on this surface. Nonetheless, the *increased* intensity of the $\text{Ru}(3d_{5/2})$ peak shoulder at 282–283 eV upon oxidation (Figs. 5b–d) suggests that the 282.6 eV feature in the deconvoluted spectra emerging by 200°C signals the formation of another species, which has a higher Ru valency than that of RuO_2 . Therefore, the curve-fitting procedure of the Ru(3d) peak of the oxidized sample includes an exponential tail as well as allowing for contributions from other chemical components.

Additional insight into this issue in the present case, however, can be gleaned by examining the corresponding SERS data. Significantly, these results favor the former interpretation, suggesting the presence of RuO₃ as well as RuO₂. Thus upon inspecting the SER spectrum at 200° C (Fig. 2c), a SERS band was detected at 800 cm^{-1} besides the RuO₂ bands at 510 and 630 $\rm cm^{-1}$. Comparing the corresponding SERS (Fig. 2c) and XPS (Fig. 5b) results at 200°C correlates the characteristic RuO_2 peaks at 510/630 cm⁻¹ and 281.0 eV, respectively, so that it is likely that the remaining peaks at 800 cm^{-1} and 282.6 eV both arise from another species. While the 800 cm^{-1} band is not present in the vibrational spectra of RuO_2 and RuO_4 , it has a frequency slightly lower than that of RuO_4 (875 cm⁻¹), suggesting the presence of intermediate Ru oxidation state, such as in RuO₃. Indeed, the frequency of the symmetric stretches of several Ru tetraoxy compounds has been shown to follow the sequence: RuO₄ $(880 \text{ cm}^{-1}) > \text{RuO}_4^ (825 \text{ cm}^{-1}) > \text{RuO}_4^{2-}$ (810 cm^{-1}) (48).

An apparently similar 800 cm⁻¹ band was also detected in the electrochemical SERS experiment (Fig. 4) which we tentatively assign to RuO_4^{2-} , a well-known Ru(VI) oxy anion (38, 48). In this regard, the formation of RuO_4^{2-} at +0.8 V may occur via reduction of the RuO_4 produced in the oxygen evolution reaction (at +1.16 V). Interestingly, an analogous consecutive formation of different Ru oxycompounds is found by thermal means in the gas-phase system in that RuO_4 (875 cm⁻¹) was only detected upon further raising the temperature after forming the 800 cm⁻¹ band species (Fig. 3). This leads to the suggestion that the latter acts as a precursor to the formation of RuO_4 . However, while it is less likely that a charged species like RuO_4^{2-} will be present at the metal–gas interface, the similarity of the 800 cm⁻¹ band frequency to that of RuO_4^{2-} suggests, instead, that the two species share the same oxidation state. Based on this line of reasoning, therefore, we tentatively assign the 800 cm^{-1} feature to RuO_3 .

Behavioral Differences between Initially Reduced and Partly Oxidized Ru Surfaces toward Thermal Oxidation

Comparison of the SERS findings which involve thermal oxidation of a reduced Ru and a RuO₂ oxide surface display remarkable differences in the ensuing surface composition. While the initially RuO₂ surface (prepared by Method I) yielded primarily surface oxygen (600 cm^{-1}) upon oxidation (Fig. 3), metallic Ru (formed by Method II) is vulnerable toward oxidizing to the higher valent oxides RuO₃ or RuO₄ (Fig. 2). This behavioral difference is consistent with the notion that RuO₂ acts as a protective layer against further oxidation (50). Considering that the formation of either RuO₃ or RuO₄ involves the incorporation of oxygen into the metal via place exchange, it would appear that oxygen can penetrate more easily into a Ru metal than a RuO₂ surface.

Further, comparing the results from oxidation of reduced Ru (Fig. 2) and a sample previously covered with adsorbed oxygen (Fig. 1B), it is found that RuO_4 was formed in the former experiment while in the latter one the highest oxide detected was RuO_3 . Along with the observation, noted above, that a RuO_2 surface was covered with adsorbed oxygen upon oxidation but without formation of higher oxides, these experiments suggest that surface oxygen may act as a barrier against further diffusion. This deduction is related to the claim (8, 9) that dosed oxygen is trapped in the subsurface region without further oxidation on Ru(001) in UHV.

Thermal Stability of RuO₃ and RuO₄

As seen by inspecting Fig. 2, the exclusive presence of RuO_3 and RuO_4 at temperatures above 250°C is interesting as well as informative. This is surprising in that bulk-phase RuO_4 sublimes at 40°C (4). The thermal stability of the surface oxide was therefore investigated further by prolonged heating at 300°C. No significant attenuation of either the 800 cm⁻¹ and 875 cm⁻¹ bands was detected. Indeed, a recent study reports that desorption of gas-phase RuO_3 into UHV did not occur until above 500°C after forming a high coverage of atomic oxygen on Ru(001) (8).

While the complementary SERS and XPS spectra appears to be in harmony in terms of surface speciation, there is a significant apparent difference in the distribution of different Ru oxides as probed by the two techniques. As seen in Fig. 5c, the Ru($3d_{5/2}$) XPS spectra has a dominant 281.0 eV component at 250°C, suggesting that the surface is composed primarily of RuO₂. However, the corresponding SERS data show only weak 510 and 630 cm⁻¹ bands arising from RuO₂ (Fig. 2d). This discrepancy may arise from the fact that the XPS and SERS data were actually collected at different surface temperatures. It is important to realize

that while SERS is an *in-situ* technique; this is not the case for XPS analysis where spectra were acquired *at room temperature* after transfer from the high-pressure reactor cell. On the other hand, however, inspecting the SER spectrum in which a Ru metallic sample had been cooled down to room temperature after oxidation at 300°C (Fig. 2f), shows the presence of three distinct oxides, including RuO₂, RuO₃, and RuO₄, thereby agreeing nicely with the corresponding XPS spectra (Fig. 5d).

As shown from our *in-situ* SERS results, the higher-valent oxides RuO_3 and RuO_4 were selectively formed at temperatures above 200°C. As far as the formation mechanism of RuO_2 is concerned, the decomposition of RuO_4 upon cooling is a likely candidate (32). This explains why the 281.0 eV $\text{Ru}(3d_{5/2})$ peak attributed to RuO_2 tends to be the dominant component in such XPS studies, even following vigorous thermal oxidation. The thermal oxidation of the ruthenium surface in 1 atm of oxygen can therefore be summarized by the following reactions:

Oxidation

$$Ru_{(s)} + O_{2(g)} \Rightarrow RuO_{2(s)} + RuO_{3(s)} \quad (200^{\circ}C) \quad [1]$$

$$RuO_{3(s)} + O_{2(g)} \Rightarrow RuO_{4(s)} \qquad (250-300^{\circ}C) \quad [2]$$

Decomposition

$$RuO_{4(s)} \Rightarrow RuO_{2(s)}$$
 (25°C) [3]

CONCLUDING REMARKS

We have investigated the high-pressure oxidation of Ru by using combined SERS and XPS. While the *in-situ* capability of SERS yields real-time information regarding the change of surface speciation as a function of surface temperature, supporting evidence such as oxidation states of various Ru oxides is available from XPS analysis. The major conclusions are as follows.

(1) RuO₂, RuO₄, and possibly RuO₃ were detected upon thermal oxidation (25–300°C) of an initially reduced Ru surface in 1 atm of O₂. The SERS results show that RuO₃ and RuO₄ were exclusively formed at temperatures above 250°C, with RuO₄ decomposing upon cooling to form RuO₂. The latter gives rise to a XPS Ru(3 $d_{5/2}$) peak at 281.0 eV and a pair of bands at 510 and 630 cm⁻¹ in the SER spectrum.

(2) In contrast to a Ru metallic surface, no significant formation of RuO₃ and RuO₄ occurred upon thermal oxidation of a RuO₂ surface, suggesting that the latter oxide acts as a protective layer against further oxidation. Instead, both the SERS and XPS experiments suggest the formation of adsorbed oxygen on the RuO₂ surface at 200°C, as diagnosed by a 600 cm⁻¹ vibrational feature and a O(1*s*) peak at 531.7 eV, respectively.

(3) For the first time we have shown that RuO_3 and RuO_4 may be responsible for the high-binding-energy components of the $\text{Ru}(3d_{5/2})$ peak of an oxidized Ru surface, based on comparisons with the complementary SERS data. The $\text{Ru}(3d_{5/2})$ peak at 282.6 eV detected at 200°C correlates with a SERS band at 800 cm⁻¹; both are tentatively assigned to RuO₃. The surface was further oxidized to RuO₄ at 250°C, as deduced from the appearance of an 875 cm⁻¹ SERS bands and a corresponding 283.3 eV Ru($3d_{5/2}$) peak.

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