Methanol Oxidation on Palladium Compared to Rhodium at Ambient Pressures as Probed by Surface-Enhanced Raman and Mass Spectroscopies

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The influences of surface speciation upon the catalytic oxidation kinetics of methanol on palladium under ambient-pressure flowreactor conditions was examined by surface-enhanced Raman spectroscopy (SERS) combined with mass spectrometry (MS) and compared with corresponding data on rhodium. The former technique provides uniquely sensitive surface vibrational information under real-time (\approx 1 s) in situ conditions, by utilizing ultrathin catalyst films electrodeposited onto an inert SERS-active gold substrate. These transition-metal surfaces exhibit sufficiently robust SERS activity to enable temperature-dependent spectral measurements over the range 25-500°C. Parallel kinetic measurements undertaken with MS show the occurrence of methanol decomposition (to CO and H₂) in the absence of O₂ on both Pd and Rh. While the presence of a molar deficiency of O₂ yields methanol oxidation (to form CO₂ and H₂) in addition to methanol decomposition on Rh, only the latter occurred (at slower rates than Rh) on Pd. These dissimilar reaction selectivities are consistent with the absence of surface vibrational features on the latter surface and the observed presence of adsorbed CO on the former. The behavior can be rationalized by the paucity of adsorbed atomic oxygen, O_(ad), on Pd compared with Rh arising from the greater ability of the latter to dissociatively chemisorb O₂. Both catalysts induced exhaustive methanol oxidation (yielding CO₂ and H₂O) in a heavily O₂-rich reactant mixture, although Pd again yielded less facile reaction kinetics. In addition, a significant catalyst deactivation occurred upon heating Pd in this reactant mixture, which was entirely absent on Rh. The corresponding temperature-dependent SER spectra indicate the formation of palladium oxide (PdO) by 350°C, which was retained entirely upon subsequent cooling. While an oxide (Rh₂O₃) was also seen by SERS to form on Rh by 350°C under these conditions, this species was removed upon subsequent cooling. Transient SERS measurements following sudden exposure of such oxidized surfaces to a methanol gas stream revealed that PdO was entirely unreactive toward methanol even at 350°C, while, in contrast, Rh₂O₃ was removed entirely within ca. 5 s. This remarkable difference in oxide reactivity, which accounts for the Pd catalyst deactivation, was deduced to be due primarily to the inability of methanol to yield a suitable adsorbed "oxygen scavenger" by dissociative chemisorption on Pd. The possible involvement of a methoxy intermediate in the reaction on Pd under O_2 -rich conditions, as suggested by the SERS data, is also discussed. $$\odot$$ 1998 Academic Press

INTRODUCTION

The catalytic oxidation of methanol on noble transition metals has drawn considerable attention, due partly to environmental concerns regarding control of volatile organic compound formation from industrial processes as well as automobile emissions standards. Fundamentally, it serves as a relatively simple model catalytic system, involving issues such as how different bond cleavage routes (C–O or O–H) may determine product selectivity. An understanding of the oxidation pathways on different metals can also provide mechanistic insight into the reverse reaction (i.e., CH₃OH synthesis on supported noble metal catalysts from CO/CO₂ with H₂) as well as other catalytic oxidation processes.

Two metals which have received interest with regard to catalytic methanol oxidation are palladium and rhodium. The decomposition of methanol on Pd (1-12) and Rh (13-15) single crystals in ultrahigh vacuum (UHV) at low temperatures has been studied extensively, to gain fundamental insight into the initial steps of the reaction. It is generally accepted that methanol decomposes readily at room temperature via the formation of a methoxy intermediate (metal-OCH₃) to form adsorbed CO and H. In particular, experiments involving the predosage of O₂ prior to CH₃OH exposure (attempting to mimic practical reaction conditions) are common and have revealed that on most transition metals the extent of methanol adsorption as well as surface methoxy stability are increased on both Pd (16-18) and Rh (19, 20). Considering the large differences between UHV experiments and those more relevant to technological catalysis, it is important to garner mechanistic and surface chemical information under higher-pressure conditions. However, there have been relatively few studies of catalytic methanol dissociation and oxidation on Pd

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(21–24) and Rh (24–26), particularly with regard to *in situ* monitoring of adsorbed species (23). The highest reactant partial pressures that have been examined during kinetic investigations are \approx 0.1–1 Torr and reveal that CO₂ and H₂O are the major products (21–26) during reaction of mixtures containing a molar excess of oxygen. In contrast, exhaustive methanol oxidation can be hampered in excess methanol gas (26). It is consequently of substantial interest to account for these and other kinetic observations in terms of the surface speciation and reactivity under reaction conditions.

With its superior surface sensitivity, especially at high (ambient or beyond) gas pressures, surface-enhanced Raman spectroscopy (SERS) can offer a unique view of the surface species present under such technologically relevant conditions. In earlier studies from our laboratory, we have demonstrated that the SERS effect can be extended to adsorbates on transition metals, including Pd (27) and Rh (28), by electrodepositing them as thin films on roughened gold substrates. Such surfaces were subsequently shown to exhibit stable as well as intense SERS activity also in the gas phase, even at elevated temperatures (29-40). As a result, the wide vibrational frequency range afforded by SERS may be exploited to yield information regarding gassurface interactions for reactive systems at high pressures that are not easily accessible with more conventional methods. By correlating the presence and reactivity (or otherwise) of surface species with gas-phase reaction products as monitored by mass spectrometric (MS) analysis, information can be obtained regarding the possible role of the adsorbed molecules in the reaction pathway (24, 37, 38, 40). The advent of charge-coupled device (CCD) technology along with the intrinsically intense SERS signals also allows the acquisition of spectral sequences on a rapid (≈ 1 s) time scale, thereby enabling us to probe the temporal evolution of surface species by transiently perturbing the system parameters (e.g., temperature, reactant ratio) in a gas-flow reactor arrangement and monitoring the real-time spectroscopic response.

We have recently reported a SERS study of methanol oxidation on Rh (39). In addition to detecting Rh_2O_3 formation *in situ* under reaction conditions, it was shown that this species was highly reactive toward gas-phase methanol. The role of the oxide along with other adsorbates detected by SERS during this reaction has also been investigated further in a detailed SERS study combined with reaction kinetics obtained by MS (40). Herein is presented a combined SERS–MS examination of methanol oxidation on Pd in comparison with corresponding findings on Rh, with emphasis placed on the effects of surface oxygen and lattice oxide on reaction rates and selectivity. The findings demonstrate how the less facile oxidation kinetics on Pd compared with Rh, along with different reaction selectivities, can be understood on the basis of a relatively nonreactive oxide on the former surface as well as a weaker ability of Pd to dissociatively chemisorb the methanol as well as oxygen reactants.

EXPERIMENTAL

The procedure for preparing SERS-active samples has been detailed previously and involves electrodeposition of Pd and Rh ultrathin films (about three to five monolayers) on electrochemically roughened gold substrates (27, 28). Gold disks (10 mm in diameter) were cut from 0.1-mmthick gold foil (Johnson Matthey) and polished with alumina powder. They were subsequently placed into an electrode holder that exposed 10 mm² of surface in 0.1 M KCl solution, followed by oxidation-reduction cycles to produce a SERS-active gold substrate (41). Palladium films were deposited from a 0.05 M PdCl₂ solution in 0.1 M HClO₄ at +0.1 V vs saturated calomel electrode (SCE). Similarly, Rh films were deposited from a 0.05 M RhCl₃ solution in 0.1 M HClO₄ at +0.1 V vs SCE. The desired film thickness was controlled by monitoring the cathodic charge during deposition.

The high-pressure reactor is a six-way cross equipped with a turbomolecular pump (Balzers TPH 060) yielding a base pressure of 10^{-6} Torr. The pressure over the entire range is measured using a combination of Pirani and cold-cathode gauges (Balzers PKR 250), controlled by a Balzers TPG 252 pressure controller. Inside the sample holder, a solid piece of stainless steel is surrounded by a coil of thin nichrome wire to provide resistive heating. Through the center of this heater is a K-type thermocouple which is in intimate contact with the sample and leads to a programmable temperature controller (Omega CN2041). Reactants were delivered through a manifold which allows mixing of up to four gases. Methanol vapor in argon carrier gas was generated by sparging Ar through liquid methanol. (This procedure yielded a maximum methanol partial pressure in the gas stream of ca. 110 Torr.) The reactants utilized were 99.9% pure MeOH (Fisher) and gases of ultrahigh purity grade (Airco). Methanol oxidation experiments were performed at ambient pressure (1 atm) and elevated temperatures (25-500°C). Two reaction mixtures with different O₂/CH₃OH ratios were utilized (one with large O₂ excess and the other being marginally richer in CH₃OH).

Laser excitation at 647.1 nm for SERS was provided by a Kr⁺ laser (Spectra Physics). The scattered light was collected by a three-stage spectrometer (Triplemate) equipped with a CCD detector (Photometrics). The Raman frequencies were calibrated by lines from a neon light-emitting diode.

Corresponding mass spectrometric experiments were performed separately in a small (ca. 4 cm^3) stainless-steel reactor which could be pumped down to 10^{-6} Torr. A bundle of gold wire (99.998% pure, Johnson Matthey) was used

as the substrate rather than the gold foil used in SERS experiments, in order to produce a larger surface area (about 7 cm²), to facilitate the kinetic measurements. [Although we have previously undertaken MS analysis simultaneously with SERS (e.g., Ref. 37), the parallel MS experiments were employed instead here to optimize the sensitivity of the kinetic measurements.] The Pd and Rh thin films on this gold substrate were prepared exactly as for the SERS experiments (*vide supra*). The gas-phase composition during the reaction was measured by leaking the gas outlet into a quadrupole mass spectrometer (Lybold Inficon IPC-50).

RESULTS AND DISCUSSION

Since results for methanol oxidation on Rh will be available elsewhere (40), we only summarize the most important findings for this catalyst as they compare with those for Pd. Both SERS and MS results obtained from corresponding experiments on Pd and Rh surfaces are presented together to facilitate such comparisons. Pure methanol decomposition will be discussed first, followed by methanol oxidation using two reactant mixtures, one deficient in O_2 and the other in excess O2. Steady-state MS and SERS results are presented as a function of surface temperature and will be interpreted in concert to link observed reaction rates measured by the former technique with the presence of adsorbates sensed by the latter. Finally we describe transient SERS experiments performed on a seconds time scale to determine the reactivity of the Pd and Rh oxides formed during the reaction toward pure gas-phase methanol, to gain further insight regarding their probable kinetic role toward methanol oxidation.

Freshly deposited samples used in both SERS and MS experiments were first pretreated by heating in H_2 at 150°C for 5 min to remove traces of adsorbed chloride from the deposition solution and obtain a reduced Pd or Rh surface. This procedure produced a featureless SERS background in the 200–1000 cm⁻¹ region while leaving some weak SERS bands between 1300 and 1600 cm⁻¹ due to residual carbonaceous contamination. Complete removal of these bands requires thermal oxidation and subsequent reduction at high temperatures, which typically results in severe loss of SERS activity. Therefore, this latter pretreatment step was not used here.

Methanol Decomposition

It is desirable to examine initially the interaction of both Pd and Rh with oxygen-free methanol gas in order to reveal how this molecule decomposes in the absence of the oxidant. After samples (either Pd or Rh) were subjected to the H₂ pretreatment, the reactor was evacuated and subsequently flushed with Ar. Samples were then heated in a methanol-saturated Ar stream (15% CH₃OH/85% Ar by volume) at 100 cm³ min⁻¹ and 1 atm, during which the gas-

phase composition was monitored by MS. The experimental protocol involved a series of ca. 50°C temperature ramps (starting from 25 up to 500°C), holding at each temperature until the MS signals reached a constant level. These MS experiments revealed that methanol decomposes to yield exclusively CO and H₂ on both Pd and Rh (40), with the onset of detectable product formation at 350 and 250°C, respectively. After excursions to 500°C, the temperature was decreased incrementally to detect any thermally induced deactivation of the catalyst. (The total time consumed for the increasing and decreasing temperature segments was about 40 min in both cases.) The CO production rates on Rh were drastically decreased (to ca. 10%) from the corresponding values measured during the initial upward temperature ramp, probably due to the progressive deposition of carbon on the surface at higher temperatures (vide infra). The methanol decomposition rates on Pd were decreased to about 25% of the values measured with increasing temperature during the subsequent cooling segment.

Corresponding SERS experiments involved essentially the same protocol as that utilized for the MS measurements. The surface temperature was increased in a stepwise fashion, with SER spectra acquired using an integration time of 20 s after a time-independent spectral response was achieved (requiring ca. 2-3 min). Identical heating procedures were utilized in all experiments described below unless otherwise noted. No spectral featuress below ca. 1000 cm⁻¹ were evident upon methanol dosing at 25°C on both Pd and Rh, suggesting the absence of adsorbed species (at least at moderate to high coverages) under these reaction conditions. (On both Pd and Rh, however, broad SERS bands around 1350 and 1580 cm⁻¹ developed under these conditions, indicative of surface carbon formation.) Furthermore, no additional SERS bands were observed on either surface even upon increasing the temperature into the range where gaseous CO production could be detected (350-500°C for Pd and 250-500°C for Rh).

Methanol Oxidation: O2-Deficient Case

We next examine the occurrence of nonoxidative methanol decomposition and oxidation by O_2 in the presence of a molar excess of methanol. Figure 1A displays an Arrhenius plot extracted from steady-state MS results obtained for a Pd surface exposed to 100 cm³ min⁻¹ of a methanol-rich mixture (13.5% CH₃OH/76.5% Ar/10% O₂ by volume) at 1 atm. The only products detected by MS under these conditions were CO and H₂, with the onset of detectable reaction occurring at 250°C. A constant activation energy of 7 (±1) kcal mol⁻¹ was obtained from 300 to 500°C. In contrast to the O₂-free case, *essentially identical* T-dependent kinetics were observed during the upward and subsequent downward temperature segments; i.e., no significant hysteresis was observed. The rates of CO formation



FIG. 1. (A) Arrhenius plot extracted from MS measurements of temperature-dependent CO production rates from a flowing mixture $(100 \text{ cm}^3 \text{ min}^{-1})$ of 13.5% CH₃OH/10% O₂/76.5% Ar at 1 atm on Pd. (B) As for A, but for CO and CO₂ production rates during exposure of Rh to a 250 cm³ min⁻¹ reactant flow.

are converted to turnover numbers (molecules site⁻¹ s⁻¹) in Fig. 1A by assuming a surface site density of 1.8×10^{15} sites cm⁻².

Similarly, Fig. 1B displays MS results obtained for exposing Rh to the same excess methanol mixture as described above, but at a faster reactant flow rate, 250 cm³ min⁻¹. While gaseous CO and H₂ were detected on Rh beginning at ca. 250°C, in contrast to the Pd case, CO₂ production along with H₂ (but not H₂O) was also observed by 200°C. At a given temperature, the rates of CO formation on Rh are about two to three times faster than the same reaction on Pd. Similarly to Pd, these kinetics displayed essentially no T-dependent hysteresis. The activation energy for CO₂ formation on Rh is 12 (±1) kcal mol⁻¹ from 200 to 350°C, above which the reaction rates level off (Fig. 1B). However, the CO formation rates increase continuously throughout the entire temperature range (250–500°C), although exhibiting a lower activation energy of 8 (±1) kcal mol⁻¹.

Corresponding SERS experiments during reaction of this methanol-rich mixture on both metals were also performed. As for the oxygen-free case, no spectral features were detected on Pd between 25 and 500°C. However, markedly different results were obtained for a Rh surface, in that two SERS bands at 465 and ca. 2000 cm⁻¹ were observed even upon dosing the methanol-rich mixture at 25°C. These features are assigned to the ν_{Rh-CO} and ν_{C-O} stretching vibrations, respectively, of atop (i.e., terminal) adsorbed CO (40). Both bands remained until 350°C and disappeared at higher temperatures (results not shown; see Ref. 40). This

observation of adsorbed CO contrasts the SERS findings for pure methanol exposure on Rh, in which no adsorbates were detected, and indicates that additional surface chemistry occurs as a result of the presence of oxygen. Significantly, neither the Pd nor the Rh surfaces displayed SERS bands at 1300–1600 cm⁻¹ in the presence of oxygen, indicating the lack of surface carbon formation under these conditions.

Summarizing the influence of O_2 on the kinetic data noted above, the major effect in the case of Pd is that the temperature required for (nonoxidative) methanol decomposition to CO is lowered by about 100°C in the presence of 10% O₂ (Fig. 1A), with the T-induced hysteresis being removed. However, on Rh the presence of O₂ also results in CO₂ formation (Fig. 1B), although it has little influence on the temperature at which gaseous CO was first detected (ca. 250°C). Insight into such effects of O₂ on the methanol decomposition kinetics on these metals can be obtained by comparing the results with previous studies involving methanol exposure on clean and O-covered surfaces in UHV. It has been shown that predosed oxygen assists methanol decomposition on both Pd (16-18) and Rh (19, 20) for two reasons. First, oxygen provides an additional methanol decomposition pathway involving the abstraction of the methanolic hydroxyl hydrogen by coadsorbed atomic oxygen, O(ad), to form surface hydroxyl and methoxy (16-20):

$$CH_3OH_{(ad)} + O_{(ad)} \Rightarrow CH_3O_{(ad)} + OH_{(ad)}.$$
 [1]

Second, the thermal stability of methoxy is increased by the presence of neighboring oxygen atoms [16–20].

This promotion effect of O_(ad) on methanol decomposition can partly explain the observed differences between Pd and Rh regarding selectivity and surface speciation under reaction conditions. One can account for both the CO₂ formation (Fig. 1B) and the presence of adsorbed CO observed on Rh, but not on Pd, in terms of the higher affinity of the former surface for oxygen. A previous study of dioxygen dissociation trends on noble transition metals by means of temperature-programmed desorption (TPD) has shown that oxygen adsorbs more extensively on Rh than Pd (42). Furthermore, atomic oxygen formed in such a fashion exhibits a higher thermal stability on Rh. Consequently, then, the appearance of CO-related SERS features on Rh upon methanol-rich mixture dosage at room temperature (vide *supra*) may well arise from the oxygen-induced methanol decomposition pathway [1]. The smaller affinity of Pd for O_2 should yield much lower $O_{(ad)}$ coverages and therefore can readily explain the lack of formation of adsorbed CO on Pd as a result of limited methanol decomposition. Further supporting this notion, a given rate of gaseous CO formation from methanol decomposition requires a roughly 50°C higher temperature on Pd than on Rh (Figs. 1A and 1B).

Such higher $O_{(ad)}$ coverages on Rh can also account for the formation of CO_2 (Fig. 1B) in the presence of O_2 via oxidation of adsorbed CO. Along the same lines, the presence of only a very low $O_{(ad)}$ coverage on Pd can account for the exclusive formation of gaseous CO (Fig. 1A). The presence of 10% O_2 , however, lowers the apparent activation energy for CO formation on Pd from roughly 14 (±3) kcal mol⁻¹ during the upward temperature segment (from 350 to 450°C) for pure methanol decomposition, down to 7 (±1) kcal mol⁻¹. At least the observed ca. 100°C diminution in temperature required for the detectable onset of gaseous CO formation on Pd when O_2 was present could therefore also be due to the influence of the O-assisted decomposition [1].

Methanol Oxidation: O2-Rich Case

Figure 2A displays the Arrhenius plot extracted from steady-state MS results obtained while heating a Pd surface in a 100 $\text{cm}^3 \text{min}^{-1}$ flow of a reaction mixture containing a large excess of O2 (3% CH3OH/80% O2/17% Ar by volume). Essentially an exhaustive oxidation of methanol was achieved so that CO₂ and H₂O were the exclusive products, with first detectable reaction occurring at 250°C (Fig. 2A, open circles). This observation contrasts the kinetic results obtained for the excess methanol case (Fig. 1A), in which CO and H₂ were the only products. Furthermore, the apparent activation energy of the reaction is 5 (± 1) kcal mol⁻¹ between 250 and 400°C during the upward temperature sequence (open circles, Fig. 2A), lower than that for CO formation in the excess methanol mixture. Interestingly, when the surface temperature of Pd was lowered incrementally from 500°C the reaction rates (filled circles) exhibited some hysteresis with respect to the preceding increasing

В А 300°C 500°C 400°C 200°C 500°C 400°C 300°C **Turnover Number (Molecules site⁻¹ s⁻¹)** 100 Turnover Number (molecules site⁻¹ s⁻¹) CO, Formation CO₂ Formation ф 10 φ φ 10 φ 1.2 1.9 2 1.3 1.4 1.5 1.6 1.7 1.8 1.8 1.2 1.4 1.6 2 2.2 1000/T (1/K) 1000/T (1/K)

FIG. 2. (A) Arrhenius plot extracted from MS measurements of CO_2 production rates from a flowing mixture (100 cm³ min⁻¹) of 13.5% CH₃OH/10% O₂/76.5% Ar at 1 atm on Pd. Open and filled symbols refer to rate measurements obtained during stepwise heating and subsequent cooling segments, respectively (See text for details). (B) As for A, but for Rh exposed to 250 cm³ min⁻¹ of reactants. (Note that the rates during subsequent cooling on Rh were the same as those during the heating segment.)

temperature segment (open circles). As already noted, this was not observed in the excess methanol case (Fig. 1A).

Shown in Fig. 2B is the Arrhenius plot extracted from corresponding steady-state MS results obtained while heating Rh in the excess O_2 mixture. Again, a large (250 cm³ min⁻¹) flow rate was used. As on Pd, an exclusive production of CO_2 and H_2O was observed, yielding an apparent activation energy of 7.5 (±1) kcal mol⁻¹. These kinetics on Rh therefore show a different product selectivity and a lower activation energy in comparison with reaction in the excess methanol mixture (Fig. 1B).

However, there are several significant differences evident between the kinetics of methanol oxidation on Pd and Rh in the excess oxygen mixture. First, the latter surface is more catalytically active than the former, exhibiting a two- to three-fold higher reaction rates at a given temperature. Perhaps more intriguing, however, is the hysteresis observed in the temperature-dependent CO_2 formation kinetics on Pd (Fig. 2A), the effect *not* being observed for the corresponding measurements on Rh (Fig. 2B). This thermally induced catalyst deactivation on Pd suggests an alteration of the surface state and will be discussed in light of the corresponding SERS results (*vide infra*).

It is of interest to consider likely reasons for the substantially different product selectivities on both Pd and Rh observed in changing from an O_2 -deficient to an O_2 -rich reactant mixture. The observed gaseous reaction products indicate the occurrence of the following three overall reactions:

$$CH_3OH_{(g)} \Rightarrow CO_{(g)} + 2 H_{2(g)}$$
 [2]

$$CH_3OH_{(g)} + 1/2 O_{2(g)} \Rightarrow CO_{2(g)} + 2 H_{2(g)}$$
 [3]

$$CH_3OH_{(g)} + 3/2 O_{2(g)} \Rightarrow CO_{2(g)} + 2 H_2O_{(g)}.$$
 [4]

Thus, while exhaustive methanol oxidation [4] is observed under excess oxygen conditions on both metals, only the partial oxidation process [3] along with some nonoxidative methanol decomposition [2] are observed in a molar excess of methanol on Rh and only the nonoxidative reaction [2] for the latter condition on Pd. As already noted, the ability of Rh to catalyze reaction [3] under the latter condition is probably due to the higher O₂ affinity of this metal. Changing from excess methanol to a very low CH₃OH/O₂ molar ratio also lowers the apparent activation energy from 12 to 7.5 kcal mol⁻¹ for CO₂ production on Rh, suggesting a mechanistic change. Although switching from the higher to low CH₃OH/O₂ molar ratio also decreases the activation energy on Pd, from 7 to 5 kcal mol^{-1} , the reaction also changes from exclusive CO/H₂ to CO₂/H₂O formation under these conditions.

At least the results on Rh may be rationalized by considering the above interpretation regarding the possible effects that $O_{(ad)}$ exerts on the surface processes governing methanol oxidation. Exposing either metal to an 80% O_2 mixture presumably yields relatively high O_(ad) coverages, causing the O-assisted methanol decomposition pathway [1] to become dominant. Since such a step would likely be more energetically favorable than the "unassisted" fragmentation route, this notion can explain the lower activation energies observed for CO₂ production under excess oxygen conditions (40). Furthermore, this interpretation is supported by the exclusive detection of gaseous H₂O product, rather than H_2 , along with CO_2 (i.e., exhaustive oxidation) under excess O2 conditions. The formation of water during the reaction probably arises by combining adsorbed H and OH, the latter being produced in O-assisted methoxy formation. Indeed, high selectivities toward H₂O versus H₂ production have been observed in UHV studies of methanol dissociation on oxygen predosed Rh(111) surfaces (19, 20).

In the wake of the information regarding kinetics and product selectivity obtained from the above MS experiments, corresponding SER spectra were collected with an eye toward correlation of the observed gas-phase product formation with surface speciation. Figure 3A shows typical temperature-dependent SER spectra obtained for a Pd film exposed to the excess O_2 reaction mixture, again obtained using a similar protocol to that used with the corresponding MS measurements. A band at 255 cm⁻¹ was detected upon dosing of reactants at 25°C (bottom spectrum), the intensity of which begins to attenuate by 200°C, being removed completely at higher temperatures. While no spectral features were observed between 250 and 300°C, raising the temperature further yields the appearance of a pair of SERS bands at 500 and 700 cm⁻¹. These features were stable at



FIG. 3. (A) Temperature-dependent SER spectra obtained during exposure of Pd to 100 cm³ min⁻¹ flow of 13.5% CH₃OH/10% O₂/76.5% Ar at 1 atm. The spectral acquisition time was 20 s. (B) As for A, but for Rh with 250 cm³ min⁻¹ reactant flow.

temperatures as high as 500° C and remained upon cooling to 25° C (Fig. 3A, top spectrum). Similar bands have been observed previously with SERS during thermal oxidation of Pd with pure O₂ (37) and are assigned to palladium oxide (PdO) based partly on similarities with the normal Raman spectra of the bulk material (43, 44).

Typical temperature-dependent SER spectra obtained during similar exposure of the Rh surface to the excess O₂ mixture are displayed in Fig. 3B. Dosage of the reaction mixture at 25°C resulted in a weak SERS band at 250 cm^{-1} . There was essentially no change upon heating until 250°C, whereupon the intensity of this band increased up to 350°C before decreasing somewhat at higher temperatures (Fig. 3B). The thermal stability of the species responsible for this 250 cm^{-1} feature on Rh is therefore much higher than the adsorbate yielding the otherwise similar 255 cm⁻¹ band on Pd. Furthermore, the advent of the 510 and 560 cm⁻¹ bands on Rh at temperatures higher than 350°C (Fig. 3B) is indicative of the formation of another species. This pair of SERS features are assigned to v_{Rh-O} stretches of Rh₂O₃, based on both a previous combined SERS and X-ray photoelectron spectroscopy (XPS) study of Rh surface oxidation (33) and the normal Raman spectra of bulk rhodium oxide (33, 43). In the contrast to PdO, however, both Rh₂O₃ SERS features disappeared when the sample was cooled to room temperature (Fig. 3B, top spectrum).

The above SERS results obtained during reaction in the O₂-rich mixture on Pd and Rh therefore again show some notable similarities and differences. No SERS bands associated with adsorbed CO were detected on either metal under these conditions. While ca. 250 cm⁻¹ SERS bands were evident on both metals upon reactant dosing at 25°C, these features exhibit a marked difference in thermal stability. (The assignments of the band on Pd, along with its possible role in the methanol oxidation reaction, will be discussed below.) Another common feature of the results for Pd and Rh is the emergence of oxide-related SERS bands at temperatures higher than 350°C. These appear to be the first in situ observations of oxide formation on such metals during methanol oxidation. Interestingly, however, the temperature at which both metals begin to oxidize under O₂-rich reaction conditions (ca. 350°C) is 150 to 200°C higher than those observed during thermal oxidation of these surfaces by pure O_2 (33, 37). A plausible explanation is that, rather than being incorporated into the metal lattices, surface oxygen preferentially reacts with CH₃OH and its dissociation products. Significantly, the observed exclusive formation of CO₂ and H₂O, i.e., reaction [4] at these temperatures (Figs. 2A and 2B), lends support to this supposition.

Interestingly, the *complete retention* of PdO upon cooling in the presence of the O_2 -rich reactant mixture, versus the *removal* of Rh_2O_3 upon cooling, can account for the temperature-dependent kinetic hysteresis observed on Pd and its absence on Rh (Figs. 2A and 2B). Thus the lower

 CO_2 production rates on the former surface during the downward-temperature portion (Fig. 2A, filled circles) are likely due to blocking of metal surface sites by PdO. In contrast, the disappearance of the Rh oxide hands upon cooling (Fig. 3B, top spectrum) indicates reactive removal at lower temperatures by methanol, resulting in regeneration of the metallic sites for the reaction to proceed. Indeed, as we have recently shown (39, 40), the Rh₂O₃ formed in the O₂-rich mixture is extremely reactive with pure gas-phase methanol; discussion of this issue is the topic of the next section.

Transient SERS Experiments

Prompted by the desire to elucidate whether the oxide formed at higher temperatures is involved directly in the methanol oxidation catalysis, the transient reduction kinetics of Rh₂O₃ and PdO by pure methanol were investigated by means of SERS. The experimental procedure has been described in detail elsewhere (39, 40) and exploits the sub second time resolution afforded by SERS. [While the SER spectra cannot be used as a reliable monitor of oxide coverage, this is likely to be high, at least circa one monolayer, partly on the basis of XPS measurements for Rh₂O₃ (33).] Oxide surfaces were initially formed by heating in the O₂rich reaction mixture at 500°C. The flow was then switched to pure Ar at this temperature, so to displace the gas mixture from the reactor. The surface was then cooled to the desired temperature, and the gas flow suddenly switched to a methanol-containing Ar stream (39, 40). Figures 4A and 4B show ensuing time-dependent SER spectra acquired following exposure of PdO and Rh₂O₃, respectively, to $1200 \text{ cm}^3 \text{ min}^{-1}$ of 15% methanol in Ar at 350°C.

Intriguingly, the Pd oxide is *entirely nonreactive* with methanol even at 350° C as evidenced by the lack of any change in the intensity of the oxide bands even over a ca. 10 min time scale (Fig. 4A). In striking contrast, Rh₂O₃ shows *very high reactivity* toward gas-phase methanol, being removed entirely within 5 s following the onset of methanol exposure under the same conditions (Fig. 4B). This rapid reduction of rhodium oxide by methanol has been attributed to the efficient removal of adsorbed oxygen by methanol fragments, such as adsorbed CO, thereby driving the conversion

$$O^{2-} \Rightarrow O_{(ad)}$$
 [5]

irreversibly toward the right (40). (The lattice oxide is denoted by O^{2-} in reaction [5].) Two distinct kinetic regimes were identified by examining the Rh_2O_3 removal kinetics as a function of methanol partial pressure as well as temperature (40). At higher methanol pressures and/or lower temperatures, reaction [5] appeared to be rate determining, yielding an apparent activation energy of 12 (±2) kcal mol⁻¹



FIG. 4. (A) Time-dependent SER spectra of an oxide-covered Pd surface at 350°C following introduction of 1 atm 15% CH₃OH/85% Ar at 100 cm³ min⁻¹. The oxides were initially formed in an O₂-rich reaction mixture and then flushed with Ar before suddenly introducing the CH₃OH/Ar stream (at time *t*=0). The spectral acquisition time was 10 s. (B) Similarly to A, but for an oxide-covered Rh surface at 350°C following sudden introduction of 1 atm 15% CH₃OH/85% Ar at 1200 cm³ min⁻¹. The spectral acquisition time was 0.5 s.

and a preexponential factor of 3.5×10^4 s⁻¹. However, at lower methanol pressures (ca. 10 Torr and below) and/or higher temperatures, the reaction rate became almost T independent, attributed tentatively to a rate-determining step involving adsorptive formation of the methanol fragment or reaction with adsorbed oxygen (40).

The nonreactivity of PdO toward methanol observed here is remarkable since this species should be less stable than Rh_2O_3 in terms of "dissociation pressures" [the O_2 partial pressure in equilibrium with a dissociating bulk-phase metal oxide at a given temperature (45, 46)]. This unexpected stability of the palladium oxide may be due to the fact that it is a thin film (about three to five monolayers). Indeed, oxides grown on such films have been reported to be more thermally stable than their bulk-phase analogues (47, 48). A recent SERS study of Ru oxidation also revealed a marked difference in stability between thin-film and bulkphase RuO_4 (49).

An alternative explanation for the nonreactivity of PdO toward methanol is that the surface concentration of the "adsorbed oxygen scavenger" species [i.e., methanol fragment(s)] is very low on Pd, as a result of the relative impotence of this surface toward dissociative chemisorption of methanol, perhaps together with lower coverages of adsorbed oxygen itself (*vide supra*). These circumstances would clearly yield very slow rates for reaction [2]. Significantly, evidence strongly favoring the dominant importance of the former factor was obtained from transient SERS ex-

periments that showed that PdO is *rapidly removed* (within ca. 10 s) even at 250° C by dosing either with 1 atm of CO or H₂. [In the former case, removal of the characteristic PdO SERS features is accompanied by the appearance of a band at around 650 cm⁻¹, tentatively attributed to adsorbed carbonate (cf. Ref. 38).] The Rh₂O₃ film was also found to be reactive toward both CO and H₂ under these conditions (50).

Given that Rh_2O_3 is found to be efficiently removed by methanol, the question remains whether Rh_2O_3 participates importantly in the methanol oxidation reaction. This issue has been investigated in detail elsewhere (40) by utilizing a kinetic analysis to model the Rh_2O_3 removal by methanol. It was found that the removal rates were about two orders of magnitude lower than the rates of methanol oxidation, suggesting that Rh_2O_3 is *not* a major reaction intermediate, even though its reactive nature prevents the oxide from acting as a surface "poison" in the manner of PdO.

Spectroscopic Evidence for Adsorbed Methanol Fragments

While the assignments of the SERS bands detected at higher temperatures to oxides are straightforward, discerning the identity of the apparently reactive species responsible for the 255 cm⁻¹ SERS feature on Pd constitutes a significant challenge. The band was removed by 250°C (Fig. 3A), with the corresponding MS data revealing first detectable CO_2 production at the same temperature (Fig. 2A). These results therefore suggest that the species responsible for the 255 cm⁻¹ feature may be an active surface intermediate in methanol oxidation. One possibility is that it arises from the ν_{Pd-O} stretch of adsorbed atomic oxygen from dissociative adsorption of O₂. However, we observed the absence of a discernable frequency downshift upon ¹⁸O₂ isotopic substitution, eliminating this possibility. Molecularly adsorbed methanol also seems an unlikely candidate due to its extremely low thermal stability; it has been found to desorb in UHV by 150 K (11).

Surface methoxy (Pd-OCH₃) is another possible candidate. This speculation is partly based on its comparable frequency to the values obtained from EELS studies (1, 3, 8). These UHV investigations find, however, that methoxy is not stable on Pd at temperatures above 25°C, decomposing to adsorbed CO and H. Nevertheless, the fact that no SERS feature associated with adsorbed CO [which has a characteristic ν_{Pd-CO} band at 360 cm⁻¹ (37)] was observed at 25°C, coupled with the lack of detectable CO or CO₂ formation at this temperature, suggests that the 255 $\rm cm^{-1}$ band may be an adsorbate with a molecular structure between CH₃OH and CO. Adsorbed methoxy therefore appears to be a prime candidate; possible alternative adsorbates such as Pd-CH₂O and Pd-CHO appear to be less stable (6). It is interesting to note that Pd is incapable of dissociating methanol to form CO in aqueous electrochemical environments (51), contrasting the extensive dissociation observed on Rh electrodes (52, 53).

Indeed, the detection of surface methoxy on Pd even at room temperature and above is not unprecedented. Christmann *et al.* (9) have reported the existence of a thermally stable methoxy on Pd(110) upon CH₃OH exposure, which only decomposes to CO at 250°C under UHV conditions. Moreover, a recent study using static secondary ion mass spectrometry (SIMS) noted the presence of surface methoxy upon methanol dosage on Pd(111) even at 25°C (10), thereby exhibiting a greater thermal stability than that reported previously (1-4). It was found that maintaining a significant surface concentration of methoxy requires a continuous gas-phase methanol supply, the species being removed when the dosing was terminated (10). This observation partly supports the assignment of the 255 cm⁻¹ band to methoxy, since the present study involves a continuous gas-flow environment that is very different than that utilized for UHV investigations, which typically involve only a finite initial dosing of reactants. However, the present 255 cm⁻¹ band on Pd remained upon switching the gas flow from O₂-rich methanol to pure argon at 25°C. This feature was subsequently removed only upon heating to ca. 200°C in Ar, i.e., at a similar temperature to its disappearance in the O_2 -rich methanol mixture (Fig. 3A).

This discrepancy regarding the stability of the methoxy in UHV and in the present high-pressure gas environment may be accounted for in terms of site availability. Any adsorbed methoxy (Pd–OCH₃, bonded through O) must find an empty adjacent site in order to further dissociate and form adsorbed CO (Pd–CO, bonded through C) (6). This may explain why CO is readily observed upon methanol decomposition in UHV, where the adsorbates are presumably surrounded by numerous free adjacent sites. On the other hand, the probable higher coverages obtained under our high-pressure conditions most likely hinder such a surface reaction, resulting in a paucity of adsorbed CO (and hence the lack of detectable CO₂ production on Pd) at temperatures below 250°C.

This hypothesis is also supported by the findings of Rebholz and co-workers (5, 10, 17), who reported that the surface methoxy coverage on Pd(111) is directly proportional to the methanol partial pressure. This implies that the present high-pressure reaction conditions should result in high coverages of this species. This is especially plausible given that the presence of excess oxygen facilitates the formation and aids the stability of methoxy (*vide supra*) (17). Second, an induction period for methoxy dissociation was found, revealed by a ca. 200-s delay in the formation of adsorbed CO upon methanol exposure (10). Given that methanol decomposes initially on the clean surface to form CO, it was suggested that the latter species inhibits further decomposition (probably due to the aforementioned lack of adjacent sites) (10). As a consequence, methoxy should build up to a detectable concentration in the presence of coadsorbates, as may well be encountered with our ambient-pressure reaction conditions.

The observation of an apparently similar SERS band, centered at 250 cm⁻¹, on Rh (Fig. 3B) should also be noted in this context. However, the high thermal stability of the species responsible for this feature, as seen by its survival even up to 500° C (Fig. 3B) argues strongly against attributing it to methoxy. While the assignment of the 250 cm⁻¹ band on Rh is uncertain (40), its markedly narrower bandwidth than the 255 cm⁻¹ feature on Pd also suggests that these two vibrational modes arise from different methanol fragments.

CONCLUDING REMARKS

The present results demonstrate how the availability of *in situ* surface vibrational information as furnished by SERS, along with parallel information on the temperaturedependent kinetics, can provide novel insight into the surface chemical factors responsible for the differences in catalytic activity and selectivity toward methanol oxidation observed on Pd versus Rh. A critical virtue of the SERS technique in this context is the ability to extract rapid (≈ 1 s) sequences of surface vibrational spectra even under technologically relevant catalytic conditions. Specifically, the chief deductions are as follows.

(a) The lack of methanol oxidation, in addition to decomposition (CO/H₂ formation), on Pd for the methanolrich reaction mixture is consistent with the apparent paucity of adsorbed methanol fragments as gleaned from the absence of detectable vibrational bands. In contrast, the facile production of CO₂ and H₂, as well as CO/H₂ formation, on Rh is consistent with the presence of adsorbed CO as observed by SERS under these conditions.

(b) In the oxygen-rich reactant mixture, the hysteresis in the temperature-dependent kinetics of CO_2 and H_2O formation observed on Pd, but not on Rh, can be accounted for by the nonreactive nature of the oxide seen by SERS to be formed on the former surface, versus the reactive properties of the corresponding oxide produced on the latter.

(c) The ability of SERS to extract real-time kinetic information for adsorbates, even on a ca. ≈ 1 s time scale, following a sudden introduction of the methanol reductant, enables the remarkable stability of surface PdO, as contrasted by the facile reactivity of Rh_2O_3 , to clearly be delineated.

(d) The differences in catalytic activity and selectivity between Pd and Rh and on a given metal between the excess methanol and O_2 -rich reactant mixtures, along with corresponding dissimilarities in surface speciation as gleaned from SERS, can be rationalized in terms of the differing ability of these catalysts to dissociatively chemisorb oxygen. (e) The possible involvement of a methoxy (or related) intermediate in the reaction mechanism on Pd, as gleaned tentatively from the appearance of a 255 cm⁻¹ surface-adsorbate vibration, is scrutinized. Likely reasons are considered for the greater thermal stability of such species observed in the present ambient-pressure reaction environment compared with the UHV conditions examined previously.

Overall, then, the combined application of SERS and MS in this manner appears to be a potent as well as novel approach enabling the elucidation of long-sought-after relationships between catalyst performance and surface chemistry under technological relevant (i.e., high-pressure gas flow) reaction conditions. Further applications along these lines to other industrially as well as fundamentally significant heterogeneous catalytic processes are under way in our laboratory.

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