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# NOTE

# Raman Spectral Evidence of Reactive Oxide Formation during Methanol Oxidation on Polycrystalline Rhodium at High Gas Pressures

The interaction of methanol with transition-metal surfaces has been a subject of much interest over the past decade. This has in part stemmed from the desire to investigate the fundamental aspects of $CH_3OH$ production from syngas (i.e., $CO + H_2$), in addition to its proposed use in fuel cells and as an alternative automobile fuel. Furthermore, the inherent chemical richness present in such a simple molecule makes it a prime candidate for fundamental studies of adsorption, dissociation, and reaction.

One of the transition metal catalysts which has exhibited promise for methanol oxidation is rhodium. Several studies have examined adsorption of methanol on clean (1–5) and oxygen-covered (2, 5) Rh single crystal surfaces. They show that $CH_3OH$ dissociation proceeds through a stable methoxy ($-OCH_3$) intermediate to form adsorbed carbon monoxide at low (<250 K) temperatures, as evidenced by electron energy loss spectroscopic measurements (1, 2). Furthermore, the low desorption temperatures of methanol (≈200 K) and methoxy (≈250 K) as measured by TPD suggest that the coverages of these species at higher temperatures during the methanol oxidation reaction will be small. However, there are no studies in which surface species on Rh have been monitored spectroscopically *in situ* during reaction of oxygen with elevated partial pressures of methanol. The highest pressure (≈0.1–1 Torr) investigations available have examined the kinetics of both methanol dissociation (6, 7) and oxidation (7, 8) over polycrystalline (6, 7) and supported Rh catalysts (7, 8).

In this communication we present an *in situ* surface-enhanced Raman spectroscopic (SERS) investigation of the adsorbed species present on a polycrystalline Rh surface during methanol oxidation at high reactant partial pressures. We have shown previously that SERS is a valuable tool for investigating heterogeneous catalytic reactions at high gas pressures and elevated temperatures (9–18). The ability to detect low-frequency (<800 $cm^{-1}$) surface-adsorbate vibrations and the inherent temporal resolution of the technique provide here new information regarding the presence of adsorbed species, particularly lattice oxide, during methanol oxidation. Intriguingly, the oxide exhibits *high* reactivity toward methanol and probably plays a significant role in the reaction mechanism.

Catalysts were prepared by electrochemically depositing 4–5 monolayers of Rh on a SERS-active Au foil (99.95% Pure, Johnson Matthey), as described previously (9–18). The reactor and Raman spectroscopic equipment utilized for the *in situ* SERS measurements have also been detailed previously (14–18). Methanol was introduced into the reactor by bubbling Ar through the liquid phase, which resulted in equilibrium saturation of the flowing room-temperature gas. Various reactant ratios were achieved by subsequently mixing the resulting stream with oxygen and/or argon. The reactants utilized in this study were 99.9% pure MeOH (Fisher) and gases of ultra-high-purity grade (Airco).

The electrochemically deposited Rh thin films were pretreated by heating to 150°C in 100 $cm^3\ min^{-1}$ of $H_2$ for about 5–10 min. This procedure resulted in a clean SERS background in the 200–1000 $cm^{-1}$ range, but retained weak features in the 1300–1600 $cm^{-1}$ region due to surface carbonaceous residues. Complete removal of these bands required prior high-temperature oxidation, which typically resulted in severe disruption of the film and substantial loss of SERS activity following reduction with $H_2$; this was therefore not used as part of the pretreatment procedure.

While several reaction conditions were examined in order to determine which surface species are present, only the case of excess oxygen at 1 atm total pressure is considered here. Figure 1 shows typical SER spectra for a reduced Rh surface heated in a mixture of 80% $O_2$/17% Ar/3% $CH_3OH$ at 1 atm total pressure. The sample was held at each temperature until the spectra became time independent (ca. 2–3 min), at which point a SER spectrum was recorded using a 20-s acquisition time. The spectrum obtained at 100°C (bottom) reveals a weak band at 250 $cm^{-1}$, along with a very broad sloping baseline. Upon heating the surface there was essentially no change in the spectra until 250°C, where the baseline diminished and the 250 $cm^{-1}$ band intensity increased. This feature is assigned to a species formed from methanol dissociation. The assignment is based in part on the observed absence of frequency downshifts upon isotopically substituting the gas mixture with $^{18}O_2$, $CH_3OD$, or $CD_3OD$. The 250 $cm^{-1}$ peak intensity increased slightly upon heating to 350°C and was attenuated at higher temperatures. Additionally, surface oxidation

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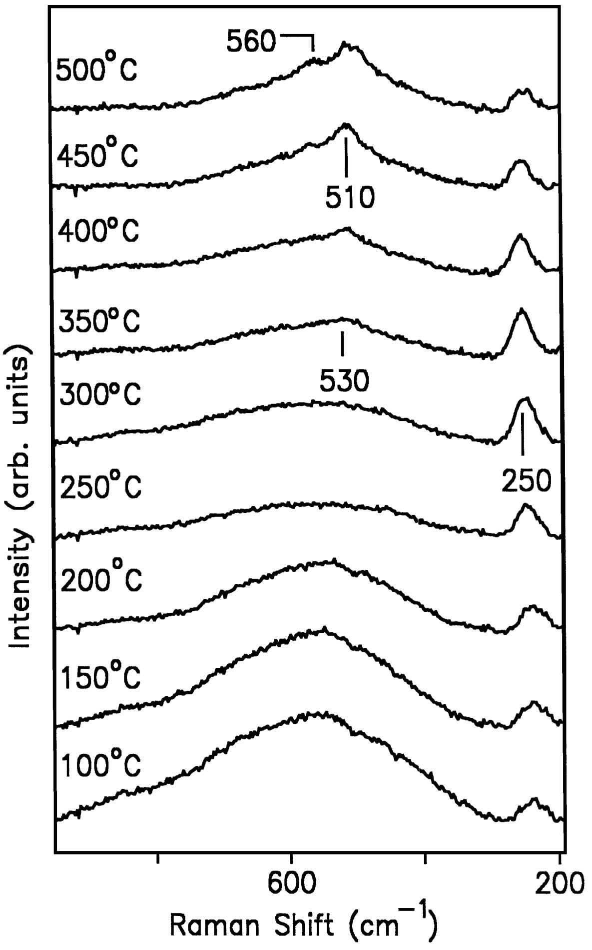

**FIG. 1.** Temperature-dependent SER spectra obtained during exposure of Rh to 100 cm$^3$ min$^{-1}$ of 80% $O_2$/17% Ar/3% $CH_3OH$ at 1 atm total pressure. The spectral acquisition time was 20 s.

commenced by 350°C, as evidenced by the appearance of a broad ca. 530 cm$^{-1}$ feature. A clearcut identification that the species responsible for this band is formed from $O_2$ was made from observations of the expected ca. 20 cm$^{-1}$ downshift upon substitution with $^{18}O_2$. An earlier detailed study utilizing X-ray photoelectron spectroscopy as well as SERS identified the oxide formed by $O_2$ exposure as $Rh_2O_3$ (13). Although methanol apparently plays no role in the formation of the oxide feature in Fig. 1, similar experiments performed in its absence (as in Ref. (13)) show stronger ca. 530 cm$^{-1}$ SERS bands over the 200–350°C temperature range, indicating some oxide–methanol reaction. Upon further heating this broad ca. 530 cm$^{-1}$ feature became better defined, revealing a sharp band at 510 cm$^{-1}$ along with a shoulder at 560 cm$^{-1}$ by 500°C. To our knowledge this is the first *in situ* observation of surface oxide formation during methanol oxidation on Rh.

Given the interesting reactive removal of oxide by methanol implied above, a number of experiments were performed that involved monitoring the transient removal of oxide by real-time SERS following the stepwise addition of methanol gas at various temperatures. The following protocol was employed. After heating a Rh surface in 80% $O_2$/17% Ar/3% $CH_3OH$ at 1 atm total pressure to 500°C, the reactor was flushed with pure Ar and the sample cooled to the desired reaction temperature. As the temperatures investigated are significantly lower than those reported for thermal desorption of oxygen from Rh (19–21), this procedure resulted in a surface covered by $Rh_2O_3$. Samples were subsequently exposed to pure methanol by switching the pure Ar gas flow to 1200 cm$^3$ min$^{-1}$ of 15% $CH_3OH$ in Ar. Typical time-resolved SER spectra obtained at 350°C following such a gas-flow switch are shown in Fig. 2. A spectral acquisition time of about 0.5 s was utilized in order to monitor the process with sufficient temporal resolution. At $t = 0$ s

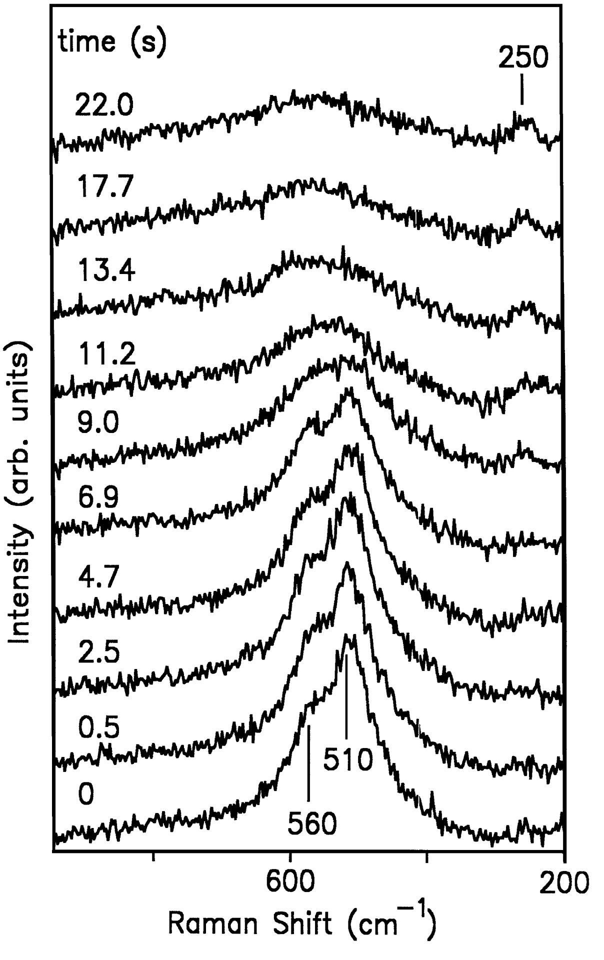

**FIG. 2.** Temporal SER spectra of an oxide-covered surface following gas-phase switch from 1200 cm$^3$ min$^{-1}$ pure Ar to 1200 cm$^3$ min$^{-1}$ 15% $CH_3OH$ in Ar. The surface was previously heated in the fashion described for Fig. 1 to 500°C and the reactor flushed out with argon and cooled to the temperature of interest before methanol addition. The spectral acquisition time was 0.5 s.

(bottom spectrum), the presence of surface oxide is clearly evidenced by the pair of features at 510 and 560 $cm^{-1}$. However, these bands began to decrease by around 5 s and were finally removed by ca. 20 s. The temporal response of this species to stepwise changes in gas composition is the fastest that we have observed with SERS to this date.

Identical experiments performed at other temperatures (not shown) revealed a strongly temperature-dependent behavior, thus encouraging a kinetic analysis of the oxide removal. In order to estimate the temporal changes in oxide coverage for a given experiment, the intensity of oxide features at various times was normalized to the initial value. Thus the overall intensity of the 510 and 560 $cm^{-1}$ oxide features in each spectrum of Fig. 2 was divided by their value at $t = 0$ s. The validity of this approach rests on the assumption that the SERS band intensities vary roughly linearly with surface concentration, a situation which has been verified for several other simple metal–adsorbate vibrations (22). Figure 3 shows the time-dependent changes in the relative oxide coverage during the above-mentioned transient experiments performed at 250, 300, and 350°C. The results for each temperature represent an average of data obtained over several experiments.

For all three temperatures there is a short induction period followed by a near-exponential decay in the oxide coverage. The time required for the reactor $CH_3OH$ partial pressure to increase (ca. 25 s to reach 50% of the final concentration) most likely causes the observed delay. To determine if the oxide is playing a catalytic role during methanol oxidation, the kinetics of the removal process were analyzed. By estimating the absolute coverage of oxide, a turnover frequency of around 0.1 is obtained for removal at 250°C. This is considerably lower (ca. 2 orders of magnitude) than the turnover frequencies for $CO_2$ formation under the conditions utilized in Fig. 1, obtained from mass spectrometer data.

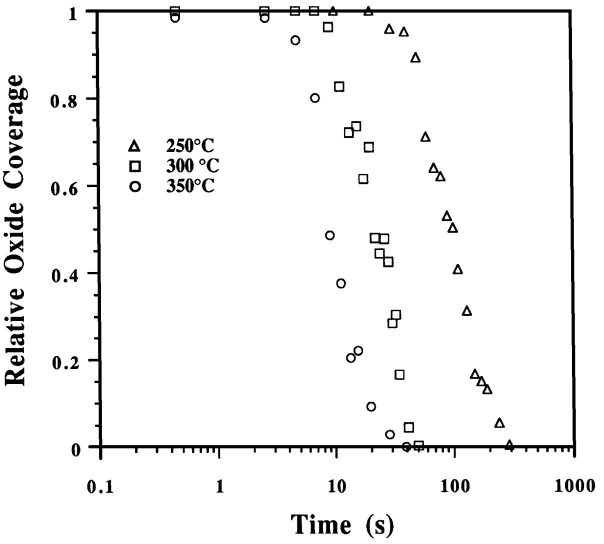

**FIG. 3.** Semi-log plot of the coverage of $Rh_2O_3$ (left axis) as a function of time at 250 (triangles), 300 (squares), and 350°C (circles) following the initiation of methanol gas flow. Coverages, as deduced from SERS intensities (see text), are normalized to the maximum (i.e., initial) values. Data employed are as shown in Fig. 2.

In conclusion, the presence of surface oxide was detected for the first time on polycrystalline Rh during the high-pressure oxidation of methanol. Moreover, the oxide ($Rh_2O_3$) is highly reactive toward methanol and may play an important role in the oxidation mechanism. In a future publication we shall extend the work reported here by presenting complementary real-time SERS and mass spectral results obtained under several reaction conditions. In this fashion we will attempt to link the behavior of adsorbates (particularly oxygen and carbon monoxide) to the observed reaction rates and selectivity.

## ACKNOWLEDGMENT

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