

Rh-Promoted Methanol Decomposition on Cerium Oxide Thin Films

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Methanol adsorption and reaction have been studied on Rh-deposited cerium oxide thin films under UHV conditions using temperature-programmed desorption and synchrotron soft X-ray photoelectron spectroscopy. The methanol behavior was examined as a function of the Ce oxidation state, methanol exposure, and Rh particle size and coverage. When Rh nanoparticles were deposited on the ceria films, methanol decomposed on Rh to CO and H below 200 K. H atoms recombined and desorbed between 200 and 300 K. CO evolved from Rh deposited on fully oxidized ceria between 400 and 500 K. However, on reduced ceria films, the CO on Rh further decomposed to atomic C. Methanol adsorbed on the ceria films deprotonated to form methoxy as the only intermediate on the surface. This methoxy decomposed and desorbed as CO and H₂ at higher temperatures regardless of the ceria oxidation state. Compared with the methanol reaction on Rh-free ceria thin films, formaldehyde formation from methoxy was completely suppressed after Rh deposition. Our results indicate that Rh can promote the decomposition of methoxy adsorbed on the ceria and that decomposition of methoxy intermediates occurred at the metal/oxide interfaces. On the other hand, the reduced ceria can promote total methanol decomposition on Rh.

1. Introduction

The metal/oxide interface is important in many areas of research, such as heterogeneous catalysis, chemical gas sensors, and electronic devices. Metal nanoparticles supported on oxide substrates have been extensively studied as model systems for understanding the surface chemistry of commercial heterogeneous catalysts. Not only do small metal particles provide a greater surface area and more active sites for reactions, but their reactivity can also differ greatly from that of the bulk metals due to their specific size and structure. This size/structure-dependent chemistry is attributed to the unique electronic properties of nanosized particles.^{1,2}

Although the morphology of the metal particles is of paramount importance in catalysis, the interactions between the metal particles and the oxide supports have also been shown to be crucial for controlling the reactivity of oxide-supported metal particles. This is because oxide supports can directly or indirectly participate in the reaction. For instance, there may be a spillover or spill-on effect occurring during a reaction. The active species formed on the metal particles can migrate to the oxide support and react to form products, or surface species can diffuse from the support onto the particles, which modifies the overall reaction. In some reactions, the particle/support interface provides the active site for the reaction. The reaction intermediates are bound to both the particles and the oxide support to react. There may also be electron transfer between the nanoparticles and the oxide support, which can significantly affect the electronic properties of the small particles, thus changing their chemical reactivity. Furthermore, encapsulation of the metal particles by the oxide support can also occur when metal is deposited on a reducible oxide.^{3–6}

It is important to gain a fundamental understanding of the reactivity of the oxide-supported metal particles, especially if

there are any changes due to an interaction between the metal particles and the support. Our group has been engaged in this area of research using ceria-supported Rh particles as model systems.^{7–12} We have found that when Rh is supported on ceria, reaction channels open up for adsorbed molecules that are not observed when they are adsorbed on either the metal or the oxide separately. These new channels can take several forms. First, molecules on the metal can react directly with the oxide to produce oxidized desorption products. For example, ethylene decomposes on Rh to hydrogen and C on Rh-loaded ceria thin films. The adsorbed C on the Rh reacts with the O in the ceria to produce CO.^{7,13} Second, molecules on the metal may not interact directly with the oxide but may undergo reactions that do not occur in the absence of the oxide. This is evident in the adsorption of CO on Rh supported on ceria.^{9–11} In the absence of the oxide, CO adsorbs nondissociatively on Rh. CO also adsorbs nondissociatively on the Rh nanoparticles deposited on fully oxidized ceria films. However, if the ceria is partially reduced, CO dissociates on the Rh particles, producing atomic C that can be observed by core-level photoemission. The mechanism for the promoted dissociation is unclear. Structural and electronic modifications have been proposed.¹¹ Alternatively, CO adsorbed on Rh at the Rh/CeO_x interface may react with O vacancies in reduced ceria, which promotes dissociation.¹¹

Conversely, Rh particles can affect the reactions that occur in molecules adsorbed on the ceria support. We have observed that Rh promotes the decomposition of OH, leading to the desorption of H₂ at lower temperatures on ceria.¹⁰

In the present paper, we report our recent findings of methanol adsorption on ceria-supported Rh. Methanol is one of the few molecules we have studied that will adsorb and react in a vacuum with both the fully oxidized and reduced ceria surfaces.¹⁴ CH₃OH dissociates to produce CH₃O and OH on the ceria. These surface species react to produce water at low temperatures and formaldehyde at elevated temperatures on fully oxidized ceria and CO, H₂, and formaldehyde on reduced ceria.

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However, after Rh deposition, the methoxy that adsorbed on the ceria always decomposes to CO and H₂ rather than CH₂O. The desorption temperatures and intensities of CO and H₂ are dependent on the reduction of the ceria films. The data suggest that the methoxy species on the ceria react at the Rh/ceria interface. Methanol adsorbed on Rh decomposes to CO and H₂ below 200 K. On fully oxidized ceria, CO desorbs molecularly from the Rh. However, reduced ceria films can promote further CO decomposition to atomic C, which was not observed for the methanol reaction on Rh single crystals.^{15–17} Methanol decomposition behavior is further discussed as a function of methanol exposure and Rh particle size and coverage in the present paper.

2. Experimental Section

The experiments were performed in two different UHV chambers. The temperature-programmed desorption (TPD) experiments were performed in a chamber at Oak Ridge National Laboratory (ORNL). The temperature was ramped at 3 K/s, and the sample was biased -70 V to prevent electrons generated by the mass spectrometer ionizer from stimulating reactions at the surface. The chamber was further equipped with a cylindrical mirror analyzer and a Mg anode X-ray source. Ce 3d XPS was used to determine the Ce oxidation state.^{14,18} Soft X-ray photoelectron spectroscopy (SXPS) was performed in a chamber at the National Synchrotron Light Source at Brookhaven National Laboratory. Experiments were conducted on beamline U12A. C 1s SXPS spectra were recorded using 410 eV excitation. The binding energies were referenced relative to the Ru(0001) Fermi edge. Other extrinsic factors that could influence peak position, such as charging or band bending, were checked by recording the Ce 4d spectrum.¹⁴

Highly ordered CeO₂(111) films were grown in situ on Ru(0001) as has been described previously.^{14,19} Briefly, CeO₂(111) was produced by depositing Ce metal in an O₂ ambient of 2×10^{-7} Torr while the Ru was at 700 K. The Ce flux was monitored by a mass spectrometer during deposition to ensure reproducible results. After deposition the sample was annealed at 1000 K for 1 min. A sharp hexagonal LEED pattern of the film was always obtained after the film growth. The ceria films were estimated to be ca. 5 nm thick on the basis of the attenuation of the Ru AES or Ru 3d XPS intensities. In general, the films used in the SXPS experiments may have been slightly thicker than those used in the TPD experiments. Reduced cerium oxide films (CeO_x, $1.5 < x < 2$) were produced by growing a film at a lower oxygen pressure or by exposing a CeO₂(111) film to methanol as described previously.¹⁴

Rh was deposited from a resistively heated evaporative source while the sample was maintained at 300 K and then annealed to 800 K. The home-built Rh evaporator consisted of ca. 2 cm of 0.25 mm diameter Rh wound around a 0.25 mm diameter W wire. The Rh flux was monitored by a mass spectrometer during deposition, and the flux was calibrated by evaporating Rh onto clean Ru(0001) and recording the Rh and Ru AES intensities (ORNL) or the Rh 3d intensity (NSLS) as a function of the Rh exposure. Rh on Ru has been shown to grow in a layer-by-layer manner.¹³ The data indicated very distinct inflection points in plots of the AES or XPS intensities vs Rh exposure (not shown). These inflection points correspond to the completion of a Rh monolayer on the Ru(0001) surface. For a 10 min deposition, the Rh coverage is estimated to be 8 ± 1 nm⁻². (Note that 8 nm⁻² = 0.5 monolayer (ML) relative to Rh(111) and 1.0 ML relative to CeO₂(111).) A 10 min deposition of Rh was used in this study unless otherwise mentioned. The surface

area of the Rh after the deposition was measured from CO adsorption experiments. The surface was exposed to a saturation dose of CO at 200 K, and TPD was performed to determine the amount of CO adsorbed. CO does not adsorb significantly on ceria.²⁰ The Rh surface area can be determined from the amount of CO detected from TPD data and comparing it to the CO desorption intensity from the clean Ru(0001) substrate.

CH₃OH (Alfa Aesar, 99.9%) was purified through many freeze–pump–thaw cycles. Its purity was checked by a mass spectrometer. There were no impurities found in methanol except a trace amount of water at very high exposures. Methanol exposure was carried out through a laser-drilled aperture connected to a long tube, which has an inner diameter of 1 cm and can be positioned at the crystal face. The exposure was controlled by the pressure in the ballast behind the aperture as well as the exposure duration. A 200 s methanol dose was used for all the studies unless otherwise mentioned to ensure a saturation coverage on the surface. The exposure was estimated to be equivalent to ca. 20 L. All exposures were conducted while the sample was at 100 K.

3. Results

3.1. Methanol Decomposition on Ceria Thin Films. To better understand methanol decomposition on the Rh-deposited ceria films, methanol decomposition was first carried out on bare ceria thin films. The results are briefly summarized here since detailed results have been presented elsewhere.¹⁴ Our data indicate that methanol reaction on ceria thin films depends on the ceria oxidation state. On the fully oxidized ceria surface (CeO₂), only water, methanol, and formaldehyde were produced after methanol adsorption at 100 K. H₂, water, CO, formaldehyde, and methanol were monitored at masses 2, 18, 28, 29, and 31, respectively, as shown in Figure 1a. Besides formaldehyde, mass 29 also has a contribution from the cracking of methanol. The mass 29 signal below 300 K is primarily associated with methanol. However, mass 29 at 570 K is primarily due to the formation of formaldehyde. Water evolved from the surface with a peak at 200 K. The physisorbed methanol multilayer desorbed around 140 K, and chemisorbed, recombinative methanol also evolved from the surface at 200 K. A small amount of methanol was also produced at 570 K. No other products such as H₂ or CO were detected from the fully oxidized ceria. However, H₂ and CO were the major products from methanol reaction on reduced ceria (CeO_{1.8}) as shown in Figure 1b. Both species desorbed from the surface around 650 K. The desorption temperature varied slightly due to the degree of reduction of the ceria films. The low-temperature side of the H₂ peak contains H₂ formation due to H recombination from the surface hydroxyls produced from methanol decomposition.¹⁴ Some water was still produced on the reduced ceria film. However, with increasing ceria film reduction, the water yield decreased and H₂ production increased correspondingly. CH₂O and CH₃OH that formed at elevated temperatures desorbed at a slightly lower temperature than CO/H₂.

C 1s SXPS spectra were collected to monitor surface species after methanol adsorption at 100 K as well as after heating of the surface to different higher temperatures. Shown in Figure 2a is the C 1s region recorded as a function of the annealing temperature. On the fully oxidized film, a spectrum centered at 287.2 eV was observed after heating to 200 K to desorb methanol multilayers. Further heating the surface to 500 K only caused a decrease in the peak intensity, but did not change the peak position, which indicates that only one species was present

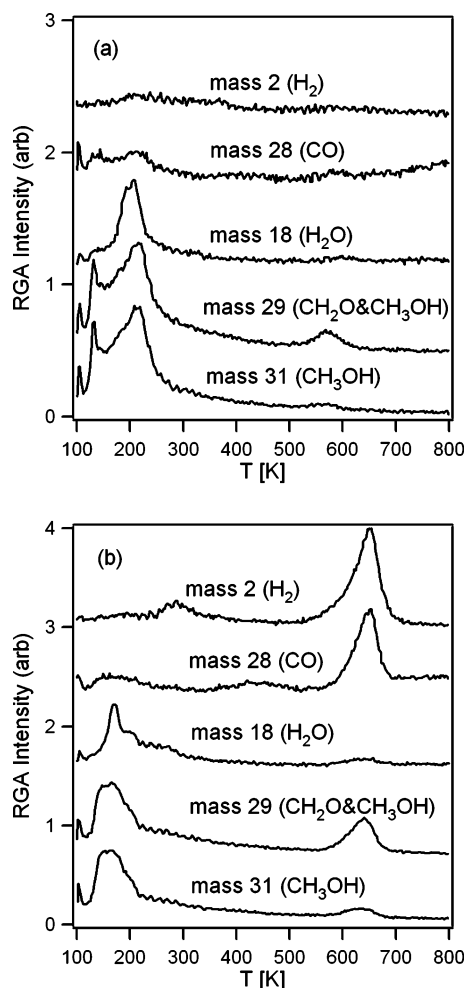


Figure 1. Temperature-programmed desorption data for a saturation dose of methanol at 100 K and heated with a linear ramp of 3 K/s on (a) a fully oxidized $\text{CeO}_2(111)$ surface and (b) a reduced $\text{CeO}_{1.8}(111)$ surface.

on the surface. At 600 K, there were no C-containing species remaining on the surface. The surface species at 287.2 eV is assigned to methoxy, which is consistent with the O 1s SXPS and C k-edge NEXAFS data.¹⁴ The C 1s SXPS results also agree well with studies from methoxy adsorption on other oxide surfaces such as TiO_2 ²¹ and MgO .²²

Methoxy was also determined to be the only reaction intermediate on the reduced ceria surface ($\text{CeO}_{1.8}$). As shown in Figure 2b, a C peak at 287.3 eV was evident after methanol adsorption at 100 K followed by heating of the surface to 200 K, which is consistent with methoxy adsorption on the oxidized ceria surface. After heating to 300 K, the peak shifted to 287.9 eV. There was little change in the spectra collected between 300 and 500 K. However, the C peak shifted back to the lower binding energy after heating to 600 K. By 700 K, all C desorbed from the surface. Despite the shift in the SXPS spectra, the O 1s spectra and NEXAFS data confirmed that methoxy was the sole intermediate present on the surface.¹⁴ It was speculated that the slight shift in the C 1s peak position may have been due to the differences in methoxy adsorption sites on the surface.¹⁴

3.2. Methanol Decomposition on Rh Deposited on a Fully Oxidized Ceria Thin Film. Rh (10 min deposition, $8 \pm 1 \text{ nm}^{-2}$) was deposited on a fully oxidized ceria film. The Rh surface area was ca. 3.3 nm^{-2} , indicating a Rh dispersion of 40–50%. The Rh surface area was determined by integrating the TPD intensity from a saturation coverage of CO and comparing it to

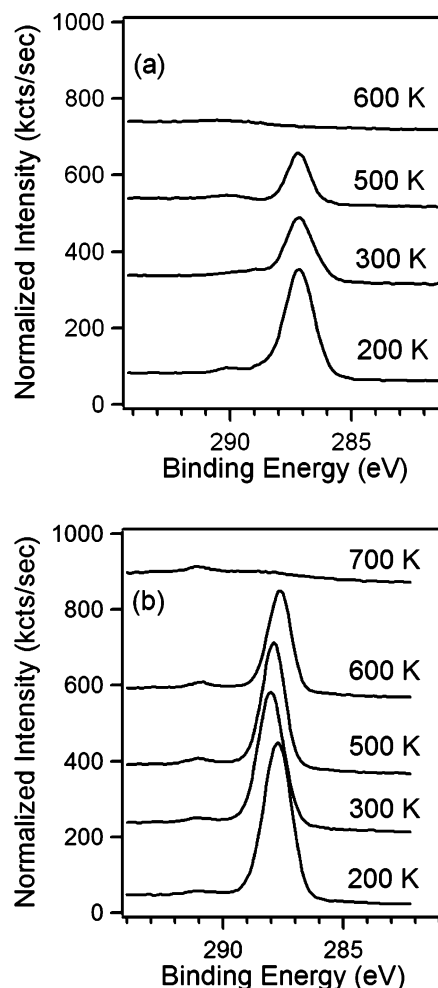


Figure 2. C 1s soft X-ray photoelectron spectra from a saturation dose of CH_3OH at 100 K on (a) a fully oxidized $\text{CeO}_2(111)$ surface and (b) a reduced $\text{CeO}_{1.8}(111)$ surface and annealed as indicated.

the TPD intensity from CO on the $\text{Ru}(0001)$ substrate as discussed previously.⁷

Following methanol adsorption at 100 K, CO and H_2 were observed as major reaction products as shown in the TPD spectra (Figure 3a). Masses 2, 18, 28, 30, and 31 were monitored for H_2 , H_2O , CO, CH_2O , and CH_3OH , respectively. No other products were detected during the reaction. Broad desorption features of H_2 between 200 and 300 K as well as CO between 400 and 500 K were observed, which resemble those from methanol decomposition on Rh single crystals.^{15,17} The integrated CO and H_2 intensities indicate that the amount of methanol that decomposed to CO and H_2 on the Rh particles was 1.6 nm^{-2} or 0.5 ML relative to the Rh surface area. This is larger than anticipated since only 0.2 ML of methanol decomposes to CO on either $\text{Rh}(111)$ ¹⁵ or $\text{Rh}(100)$.¹⁷

The sharp CO and H_2 peaks coincident at 540 K were new features considering that no CO or H_2 was formed at this temperature either from a fully oxidized ceria film or from Rh single crystals. We propose that this occurs from methoxy decomposition at the Rh/ceria interface as discussed in detail below. Furthermore, CH_2O , the major product from the reaction of methanol on the oxidized ceria film, was completely suppressed on the Rh-deposited surface. Water was still a major product evolving from the surface in a broad feature with a peak at 190 K. At this methanol exposure, a multilayer was formed that desorbed from the surface at about 135 K. By 240 K, all chemisorbed methanol desorbed.

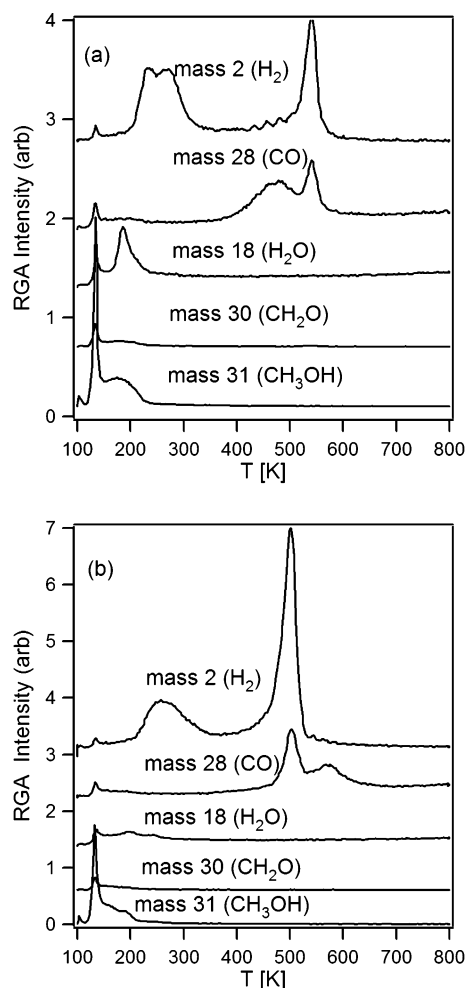


Figure 3. Temperature-programmed desorption data for a saturation dose of methanol at 100 K and heated with a linear ramp of 3 K/s on Rh deposited on (a) a fully oxidized $\text{CeO}_2(111)$ surface and (b) a reduced $\text{CeO}_{1.8}(111)$ surface.

C 1s SXPS spectra are shown in Figure 4a collected after methanol was dosed at 100 K followed by heating of the surface to successive temperatures between 200 and 600 K. At 200 K, a broad spectrum was observed, which can be fit with a main peak at 287.2 eV and a shoulder peak at 286.2 eV. As mentioned previously, the peak at 287.2 eV is due to the adsorption of a methoxy species on the ceria surface. The new shoulder peak at 286.2 eV is attributed to molecular CO adsorbed on the Rh particles according to our previous CO adsorption studies on ceria-supported Rh particles.^{10,11} The appearance of this shoulder peak indicates that methanol adsorbed on Rh decomposed to molecular CO and H below 200 K. Both methoxy and CO were present on the surface up to 400 K. Heating to 500 K removed all CO from the Rh surface and left only methoxy on the ceria. By 600 K, all C desorbed from the surface. These results confirm that the CO and H_2 desorption at 540 K in Figure 3a came from methoxy adsorbed on the ceria.

3.3. Methanol Decomposition on Rh Deposited on a Reduced Ceria Thin Film. The same amount of Rh was deposited on a reduced ceria surface ($\text{CeO}_{1.8}$). On the basis of CO titration, the Rh surface area was ca. 4.1 nm^{-2} . It is not clear whether the increased surface area is due to greater Rh dispersion or irreproducibility in the Rh doser. Following methanol adsorption (Figure 3b), broad H_2 desorption from the Rh particles between 200 and 300 K was still observed. The H_2 desorption intensity is similar to what was observed on Rh/

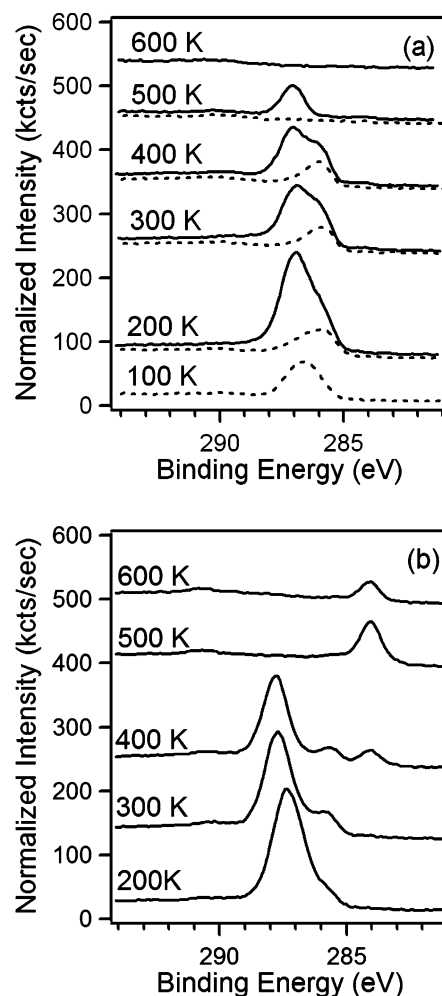


Figure 4. C 1s soft X-ray photoelectron spectra collected from CH_3OH decomposition on Rh deposited on (a) a fully oxidized $\text{CeO}_2(111)$ surface after a saturation dose of CH_3OH (solid lines) and a subsaturation dose (dashed lines) at 100 K and (b) a reduced $\text{CeO}_{1.8}(111)$ surface after a saturation dose of CH_3OH at 100 K followed by heating to various temperatures as indicated.

CeO_2 (Figure 3a). However, the broad CO desorption feature between 400 and 500 K observed from decomposition of methanol on Rh deposited on the oxidized ceria was absent. Instead, a new CO peak was detected at 570 K, which was formed by the recombination of atomic C on Rh and O from the ceria surface as suggested by SXPS data shown later. The sharp coincident CO and H_2 peaks at 500 K resemble the peaks at 540 K from the Rh-deposited oxidized ceria except that they are shifted 40 K lower. They are also shifted significantly lower compared to the CO and H_2 peaks at 650 K from the reduced ceria surface without Rh (Figure 1b). Besides CO and H_2 , a small fraction of water was also detected. Similar to the methanol reaction on the oxidized ceria surface with Rh, formaldehyde production was not observed after Rh deposition on the reduced ceria surface.

The C 1s SXPS data (Figure 4b) clearly show three C species present on the surface. The spectrum at 200 K contains a main feature at 287.2 eV and a shoulder peak at 286.1 eV. As discussed previously, they are assigned to methoxy on ceria and CO adsorbed on the Rh particles, respectively. Upon heating of the surface to 300 K, the CO peak increased its intensity and the methoxy peak shifted its position to a higher binding energy of 287.9 eV. This shift in the methoxy binding energy was observed during methanol decomposition on the reduced

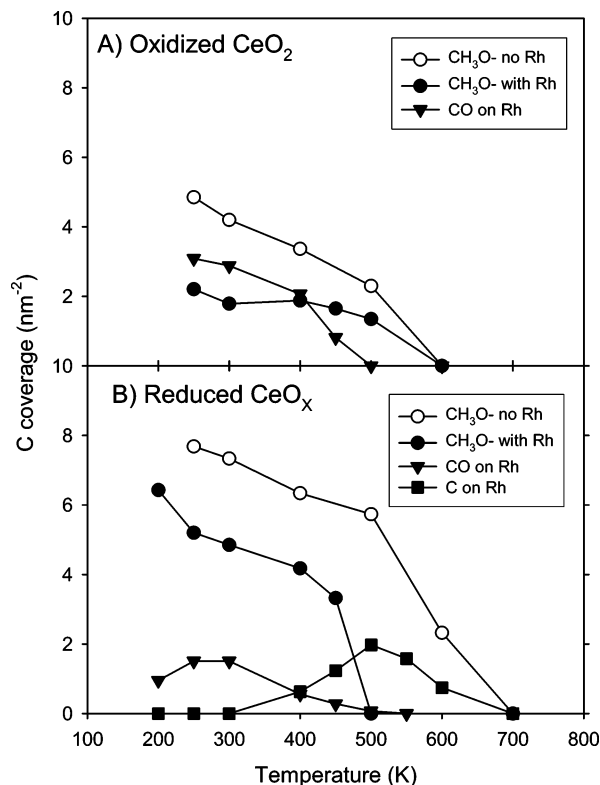


Figure 5. Surface densities of various C-containing species derived from the C 1s spectra: (A) on a fully oxidized CeO_2 surface, (B) on a reduced CeO_x surface. The open circles indicate the methoxy coverage in the absence of Rh, while the filled symbols are from a Rh-covered surface.

ceria surface without Rh (Figure 2b). After heating to 400 K, a new C peak appeared at 284.2 eV and the intensity of the CO peak decreased. This new peak was assigned to atomic C on Rh formed from CO decomposition.^{10,11} This atomic C was not observed on methanol decomposition on pure Rh surfaces^{15,17} or Rh particles supported on the oxidized ceria. By 500 K, the atomic C was the sole species left on the surface. All of the methoxy desorbed from ceria by 500 K. The atomic C was removed from the Rh by 700 K.

A quantitative comparison of the concentrations of the various surface species is shown in Figure 5. The components in the C 1s spectra were fit using the program FitXPS. The coverage was calibrated using the SXPS intensities from CH_3SH on Ru-(0001) and CeO_x as discussed previously.¹⁴ The methoxy coverages on Rh-free oxidized and reduced ceria surfaces are shown by the open circles in parts A and B, respectively, of Figure 5. The key feature from this quantitative analysis is that the methoxy species have a density equivalent to ca. 50% of the O anion density on the oxidized surface and 100% of the O anion/vacancy sites on the reduced surface. When Rh is present, the amount of methoxy decreases as Rh covers some of the available absorption sites on the ceria. Consistent with the TPD data, the coverage of CO on Rh is greater than would have been anticipated on the basis of the decomposition of methanol on Rh(111)¹⁵ or Rh(100).¹⁷ All of the CO adsorbed on the Rh at 300 K converted to atomic C at 500 K.

3.4. Methanol Coverage Dependence. Methanol decomposition was carried out on Rh particles supported on a mostly oxidized ceria surface ($\text{CeO}_{1.95}$) as a function of the methanol exposure. H_2 and CO TPD spectra for four methanol doses were collected and are compared in Figure 6. Methanol desorption (not shown) was not detected until a 100 s exposure with multilayer methanol appearing after a 200 s exposure. For a

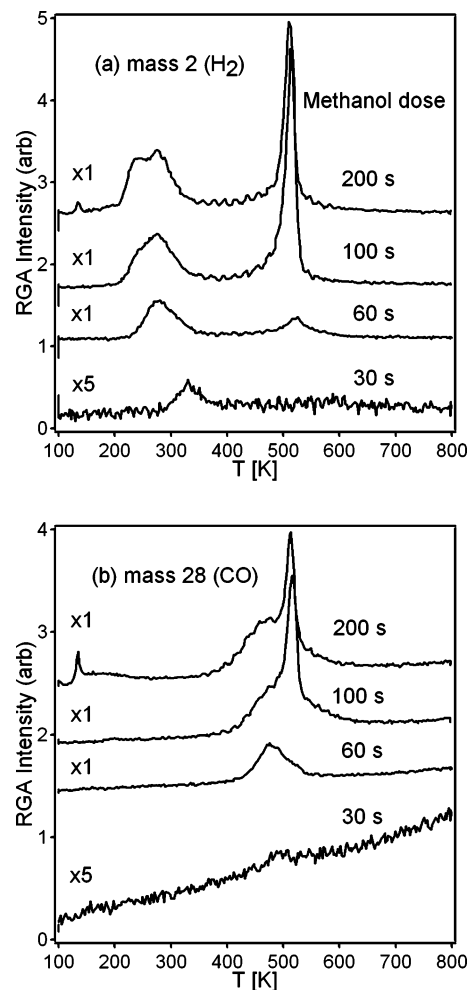


Figure 6. Temperature-programmed desorption spectra for (a) H_2 and (b) CO from Rh on an oxidized ceria surface ($\text{CeO}_{1.95}$) after various methanol exposures as indicated at 100 K.

very low dose of methanol (30 s), only a trace amount of CO and H_2 was produced in temperature ranges consistent with methanol decomposition on Rh. For a 60 s methanol dose a H_2 peak appeared at 520 K and a CO shoulder emerged at a similar temperature. These were likely due to methoxy decomposition at the Rh/ceria interface. However, the majority of adsorbed methanol decomposed on the Rh particles to produce CO at 476 K and H_2 at 278 K. More methanol decomposition occurred on Rh following a 100 s exposure, but there was a significant increase in methanol decomposition at the Rh/ceria interface that produced sharp, intense CO and H_2 peaks at about 512 K. For a 200 s methanol dose, methanol reactions both on Rh and at the Rh/ceria interface were saturated.

C 1s SXPS spectra were recorded after a lower dose of methanol (ca. 40% of the methanol exposure used in section 3.2) at 100 K and after heating to elevated temperatures on Rh deposited on a fully oxidized ceria film. The resulting C 1s spectra are indicated by the dashed lines in Figure 4a. A broad C spectrum was observed at 286.7 eV after methanol adsorption at 100 K. The binding energy of this peak lies between those associated with methoxy on ceria and CO on Rh and is tentatively assigned to methoxy on Rh. Heating the surface to 200 K caused the spectrum to shift to a lower binding energy, with a main peak at 286.0 eV and a shoulder at 286.7 eV. As discussed above, the peak at 286.0 eV is due to CO adsorption on Rh. The intensity loss of the peak at 286.7 eV is primarily the result of methoxy decomposition on the Rh. Further heating

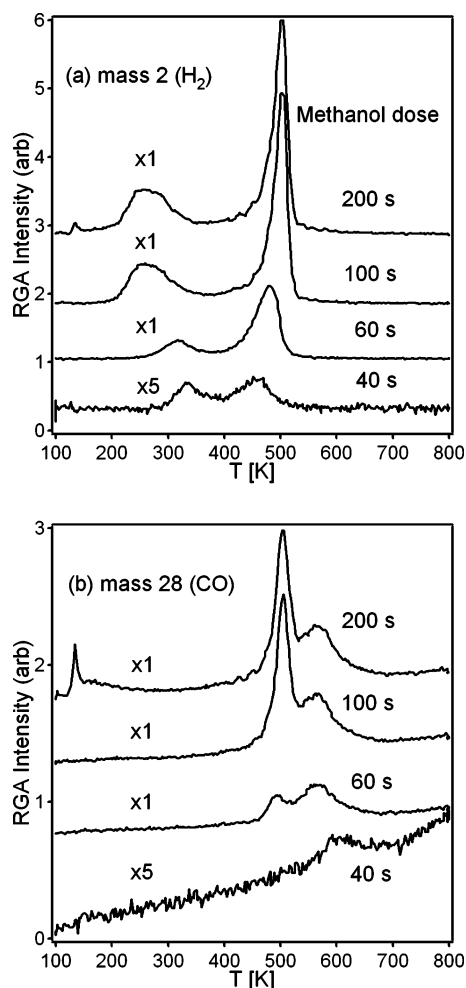


Figure 7. Temperature-programmed desorption spectra for (a) H_2 and (b) CO from Rh on a reduced ceria surface ($\text{CeO}_{1.75}$) after various methanol exposures as indicated at 100 K.

of the surface to 300 K removed all the methoxy at 286.7 eV and left only the CO peak at 286.0 eV. This peak remains unchanged until the CO desorbs between 400 and 500 K.

TPD experiments were also performed on Rh particles supported on a reduced ceria surface ($\text{CeO}_{1.75}$) as a function of the methanol exposure. The resulting H_2 and CO TPD spectra are compared in Figure 7. For the lowest methanol dose (40 s), only hydrogen and CO desorption were observed. Hydrogen evolved from the surface with two peaks, 330 and 457 K, while CO desorbed via a single peak at 592 K. The absence of CO desorption between 400 and 500 K indicates that this low dose of methanol experienced a total decomposition to atomic H and C on Rh particles. Hydrogen atoms recombined and evolved from Rh at 330 K. Atomic carbon and oxygen reacted to give CO at 592 K. As for the hydrogen peak at 457 K, it may be due to the hydrogen evolving from the ceria surface. Hydroxyls formed from water or methanol dissociation on reduced ceria without Rh produce H_2 between 500 and 700 K.^{10,14} However, the presence of Rh on the surface can facilitate H_2 desorption at a lower temperature.¹⁰ Methanol may dissociate on the ceria to produce hydroxyls on the ceria with the methoxy migrating onto the Rh. Alternatively, the methanol may decompose on the Rh with the H migrating onto the ceria. It has been shown in the literature that H can migrate to the ceria surface from the Rh particles.²³ An additional CO desorption peak was detected after a 60 s methanol dose. The H_2 peak at 320 K and the CO peak at 565 K were due to methanol decomposition on Rh

particles. The H_2 peak at 480 K and the CO peak at 493 K resulted from methoxy decomposition at the Rh/ceria interface and hydroxyl decomposition on the ceria. The reactivity of a 100 s methanol dose on the reduced ceria was quite similar to that of the 200 s dose previously described (Figure 3b). For the 100 s dose, monolayer methanol desorption was observed, but multilayers were not formed.

3.5. Rh Particle Size and Coverage Dependence. Methanol decomposition was also investigated as a function of the Rh morphology (structure and size) and coverage on ceria since previous studies indicate that the chemical reactivity of metal particles deposited on oxide surfaces can be dependent on the particle morphology.^{1,2,24–26} Although the growth of Rh on ceria is unknown, we have attempted to change the Rh particle size by varying the postannealing temperatures. Two sizes of Rh particles were prepared on a reduced ceria surface ($\text{CeO}_{1.75}$) by depositing Rh for 20 min at 300 K and then first heating the surface to 800 K and then 1000 K. Titration of the Rh surface area by adsorption and TPD of CO indicated that after annealing to 1000 K the Rh surface area was only half of that after annealing to 800 K. It has previously been shown that the Rh Auger and XPS intensities and CO desorption intensity decrease after annealing of the Rh nanoparticles to elevated temperatures.¹¹ These observations indicate that the Rh particles are growing three-dimensionally and that the Rh surface area is decreasing upon annealing.

The surface was exposed to methanol at 100 K after each annealing step. TPD spectra of H_2 and CO from methanol decomposition on both surfaces are compared in Figure 8. The integrated peak areas suggest that both surfaces produced the same amount of CO and H_2 in total. However, it is clear that the CO and H_2 production around 500 K, which results from methoxy decomposition on ceria at the Rh/ceria interface, increases after heating of the surface to 1000 K. Conversely, H_2 at 250 K and the CO shoulder peak at 560 K from methanol decomposition on Rh decrease upon heating to 1000 K. These results are consistent with a decrease in the Rh surface area and an increase in the exposed ceria surface area after annealing at 1000 K.

We also investigated methanol behavior as a function of the Rh coverage on a reduced ceria surface ($\text{CeO}_{1.75}$). Three Rh coverages were used by varying the deposition time at 300 K (5, 10, and 20 min). All surfaces were annealed to 800 K after Rh deposition. CO and H_2 TPD spectra (data not shown) collected following methanol adsorption on these three ceria-supported Rh surfaces show that CO at 560 K and H_2 between 200 and 300 K from Rh increase upon the increase of Rh loading on the surface. However, the CO and H_2 production at 500 K from the decomposition of methoxy on ceria at the Rh/ceria interface decreased. C 1s SXPS spectra show similar results (data not shown). Specifically, the only change as a result of increased Rh coverage is an increase in the CO or C on Rh and a decrease in the methoxy on ceria.

4. Discussion

Methanol decomposition on ceria-supported Rh particles exhibits reaction channels that do not occur on either pure ceria thin films or Rh single crystals. The reaction products, desorption temperatures, and surface species observed for methanol adsorbed on these various surfaces are summarized in Table 1. On pure ceria, CH_3OH dissociates to produce CH_3O and OH on both oxidized and reduced surfaces by 200 K.¹⁴ The OH species produce water at low temperatures on fully oxidized ceria. Water formation decreases and H_2 production increases

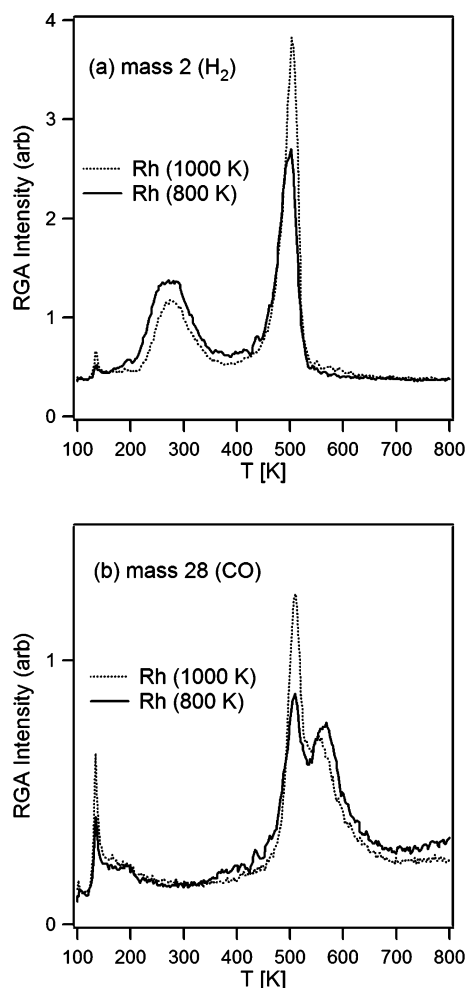


Figure 8. Temperature-programmed desorption spectra for (a) H_2 and (b) CO collected after a saturation dose of methanol on Rh on a reduced ceria surface ($\text{CeO}_{1.75}$) as a function of the annealing temperature before methanol adsorption.

TABLE 1: Summary of Methanol Reaction and Intermediates on CeO_x , Rh Single Crystals, and Rh/ CeO_x

surface	adsorbate detected	reaction product	desorption temp (K)	from Rh, CeO_x , or Rh/ CeO_x
CeO_2	methoxy	$\text{H}_2\text{CO}/\text{CH}_3\text{OH}$	570	CeO_2
		H_2O	200	
CeO_x	methoxy	H_2/CO	650	CeO_x
		H_2O	200	
		$\text{H}_2\text{CO}/\text{CH}_3\text{OH}$	635	
$\text{Rh}(111)^{15}$	methoxy, CO	H_2/CO	320/495	Rh
$\text{Rh}(100)^{17}$	methoxy, CO	H_2/CO	326/521	Rh
Rh/CeO_2	CO/Rh	H_2	200–300	Rh
		CO	400–500	
	methoxy/ CeO_2	H_2/CO	540	Rh/ CeO_2
		H_2O	190	CeO_2
Rh/CeO_x	CO/Rh, C/Rh	H_2	200–300	Rh
		CO	570	
	methoxy/ CeO_x	H_2/CO	500	Rh/ CeO_x
		H_2O	190	CeO_x

from the surface hydroxyls with the degree of the ceria film reduction. The CH_3O reacts with oxidized ceria to produce formaldehyde at elevated temperatures. Although on a reduced ceria surface formaldehyde is also produced, methoxy primarily decomposes to CO and H_2 .

The first step in methanol decomposition on $\text{Rh}(111)$ is also the formation of methoxy species on the surface as determined by TPD and HREELS.^{15,16} Upon heating to 210 K, the methoxy decomposes to CO and H . TPD data show CO and H_2 as the

sole reaction products. CO does not desorb upon formation; instead it desorbs at 495 K. H_2 desorbs at 320 K, which is limited by the kinetics of H atom recombination.¹⁵

Compared with these reaction pathways on ceria thin films and $\text{Rh}(111)$, new behavior was observed during methanol decomposition on Rh deposited on ceria. On one hand, the presence of Rh changes methanol decomposition on ceria itself. The formation of formaldehyde from methoxy was completely suppressed on both oxidized and reduced surfaces, and methoxy species on ceria decomposed to CO and H_2 regardless of the degree of ceria reduction. Furthermore, the CO/H_2 desorption temperature was much lower than the CH_2O , CO , or H_2 desorption temperature observed on bare $\text{CeO}_x(111)$. Our data suggest that methoxy adsorbed on ceria decomposed at the Rh/ceria interface. We did not observe two decomposition channels in which some of the methoxy decomposed at lower temperatures to CO and H_2 while the remainder of the methoxy was unaffected by Rh and formed CH_2O at higher temperatures. The total decomposition of methoxy on the ceria at the lower temperature also did not depend on the amount of Rh or the Rh particle morphology. This suggests that the methoxy on the ceria diffuses to the available Rh and reacts. Since methanol adsorbed on Rh decomposes to CO and H , it is perhaps not surprising that methoxy at the Rh/ceria interface decomposes to CO and H_2 . On the other hand, the ceria substrate also affects the methanol decomposition on Rh. When Rh is deposited on reduced ceria, the ceria support promotes total methanol decomposition on Rh to atomic C , O , and H . This was not observed during methanol decomposition on $\text{Rh}(111)$.^{15,16}

Superficially, when Rh is deposited on the fully oxidized ceria, the ceria support does not seem to alter the methanol reaction on the Rh particles. Methanol decomposition on those supported Rh particles is similar to that on Rh single-crystal metal surfaces.^{15–17} Our data show that CO and H_2 are the sole reaction products from methanol decomposition on the Rh particles supported on the fully oxidized ceria. The decomposition of methanol to CO and H on Rh occurred around 200 K since our TPD and XPS data show onset of H_2 desorption and the formation of CO at this temperature, respectively. The $\text{C } 1s$ SXPS experiments at lower methanol exposure (Figure 4a, dashed line) indicate that decomposition to CO is not complete at 100 K but is largely complete by 200 K. CO desorption occurred in a temperature range similar to that in which CO desorbs from $\text{Rh}(111)$.

Subtle differences compared to methanol adsorption and decomposition on Rh single crystals are evident, however. Compared with H_2 desorption from $\text{Rh}(111)$ or $\text{Rh}(100)$, H_2 desorbed at a lower temperature from ceria-supported Rh particles. A similar behavior was also observed during H_2 desorption from Rh or Pd particles supported on ceria.^{13,27} H_2 evolved from both the ceria-supported Rh particles¹³ and Pd particles²⁷ between 200 and 300 K rather than at 320 K from $\text{Rh}(111)$. This may be due to an intrinsic interaction between H and the nanosized Rh or Pd particles or an interaction between the ceria support and the metal particles. In addition, more methanol reacted and decomposed on the nanoparticles compared to the single crystals as indicated by the amount of CO formed on and desorbed from the Rh. On the Rh single crystals a significant amount of chemisorbed methanol desorbed from the Rh at low temperature. Apparently more of the adsorbed methanol decomposes to CO and H_2 on the Rh nanoparticles.

The reduced ceria support can promote total methanol decomposition on Rh. CO and H were initially formed on Rh upon methanol adsorption at 100 K followed by heating to 200

K. However, the CO dissociated to atomic C upon further heating. The degree of CO dissociation is greatly dependent upon the degree of reduction of the ceria support. The more the ceria is reduced, the greater the tendency toward CO decomposition on the supported Rh (data not shown). The promotion of molecular dissociation by Rh on reduced ceria was also observed for CO¹¹ and NO²⁸ on ceria-supported Rh particles. SXPS and TPD of CO adsorption on ceria-supported Rh have shown that CO adsorbs molecularly on Rh supported on a fully oxidized ceria substrate. However, nearly total decomposition can occur if the ceria substrate is highly reduced.¹¹ NO dissociation on Rh is also sensitive to the oxidation state of the ceria.^{12,28} NO partially decomposes on Rh deposited on the fully oxidized ceria in a manner similar to that of its decomposition on single-crystal Rh surfaces. However, Rh deposited on reduced ceria is more active for NO dissociation to N and O. The explanation for why reduced ceria promotes the decomposition of CO and NO is not clear. The behavior is most directly correlated with the degree of reduction of the Ce and is not closely correlated with the Rh coverage or morphology.^{11,28} The current results from methanol are consistent with these previous observations but do not contribute to an understanding of the mechanism involved.

The presence of Rh on the surface dramatically modifies the methanol behavior on ceria. Methoxy on ceria decomposed to CO and H₂ rather than formaldehyde on both oxidized and reduced ceria surfaces. We suggest this is due to the reaction occurring at the Rh/ceria interface, where Rh can facilitate more complete methoxy decomposition to CO and H₂. Our SXPS data show that methanol adsorbed on ceria formed methoxy species by 200 K. Upon heating to elevated temperatures (500–600 K), methoxy species disappeared from ceria and simultaneously CO and H₂ were produced in a single reaction channel as shown by our SXPS and TPD data, respectively. Since all the methoxy decomposed through this channel, the chemisorbed species must rapidly diffuse from isolated areas of the oxide to the interface to react. The methoxy species react at the Rh/ceria interface to form CO and H₂ before they can react on the bare ceria surface to form formaldehyde or CO and H₂. The rate of the reaction is most likely controlled by the energy barrier for the methoxy decomposition at the interface since all CO and H₂ were produced with a single peak. If the diffusion of methoxy was the controlling step for the decomposition, multiple temperatures for CO and H₂ desorption would be expected as methoxy adsorbed at the interface would react first followed by methoxy that diffused to the Rh at higher temperatures. Furthermore, the decrease in the desorption temperature of CO/H₂ with the increase of ceria film reduction is probably due to the lower energy barrier for methoxy decomposition at the Rh/reduced ceria surface. This is consistent with our former studies that show that Rh on reduced ceria is more reactive compared with Rh on oxidized ceria.^{11,28} The data also suggest that methoxy reacted at the Rh/ceria interface and not on top of the Rh particles. Methoxy reacted to form CO and H₂ at 500 K on reduced ceria even though the Rh particles were still covered with atomic C and CO (Figures 3b and 4b).

The observation that methanol adsorbed and decomposed only on the Rh particles and not on ceria at low methanol exposures (Figures 4a, 6, and 7) can be explained by a capture zone effect which has been observed in other reactions on oxide-supported metal particles.^{29,30} The capture zone effect describes the migration of reactants to the metal particles after they initially adsorb on the oxide support in a weakly chemisorbed or physisorbed molecular state. Each metal particle on the support

defines its own capture or collection zone, where adsorbates can reach the particles and adsorb or react. Methanol molecules can directly adsorb on Rh particles during methanol introduction at 100 K. However, methanol molecules that initially impinge on ceria can diffuse on the surface due to a weak interaction with the oxide and are collected by the Rh particles. C 1s SXPS spectra recorded after a lower dose of methanol (Figure 4a) show no evidence of the presence of methoxy on ceria. A species attributed to methoxy on Rh was observed upon adsorption at 100 K. This species fully decomposed to CO on Rh, which was the sole species observed between 300 and 500 K on the surface. TPD experiments at lower methanol exposures (Figures 6 and 7) similarly show the absence of desorption features related to methoxy adsorbed on ceria.

The decrease in CO and H₂ production on Rh particles annealed to 1000 K compared to Rh annealed to 800 K can be explained by the Rh surface area. CO adsorption experiments show that the Rh surface area after annealing to 1000 K is only half of that from Rh annealed to 800 K. It is known that annealing oxide-supported metal particles results in three-dimensional growth and thus less surface area for the particles is exposed for the reaction. As the Rh surface area decreases, there is more ceria surface area exposed. Therefore, more methoxy can be formed on the ceria which then reacts at the Rh interface, resulting in increased CO/H₂ formation at 500 K from the surface annealed to 1000 K. The increased CO and H₂ formation from methanol reaction on Rh with the increase of Rh coverage can also be explained by the increase in Rh surface area since the CO and H₂ yields correlate well with the Rh surface areas. With the increase of Rh coverage, the measured Rh surface area increases and the yields of CO and H₂ increase correspondingly. As expected the CO/H₂ production from methoxy on the ceria decreases with the increase of Rh coverage.

5. Conclusions

Methanol reacts with Rh supported on thin-film cerium oxide to produce methoxy on the ceria and CO and H on the Rh. When the ceria substrate is fully oxidized, the H recombines and the CO desorbs from the Rh in a manner similar to what is observed for methanol on Rh single-crystal surfaces. If the ceria substrate is reduced, the CO further decomposes on the Rh into C and O. The methoxy on the ceria reacts at the Rh/ceria interface to produce H₂ and CO. All of the methoxy on the ceria diffuses to the Rh particle to react, and the desorption kinetics are determined by the methoxy decomposition at the interface. Capture zone behavior is indicated in that at low methanol exposures all of the methanol that impinges on the surface adsorbs and reacts on the Rh particles.

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