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CO Dissociation on Rh Deposited on Reduced Cerium Oxide Thin Films

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The adsorption and reaction of CO on Rh-loaded ceria was studied by soft x-ray photoelectron spectroscopy. The system was studied as a function of the degree of oxidation of the ceria and different preparations of the Rh. Molecular CO and atomic C on Rh are readily distinguished in the C 1*s* spectra. CO adsorbed directly on ceria, possibly as carbonate or carboxylate, is also observed in the C 1*s* spectra. The degree of dissociation of CO on Rh deposited on ceria (Rh/CeO$_x$) is directly dependent on the degree of oxidation of the ceria. Nearly total decomposition can occur if the ceria substrate is highly reduced. Molecular CO also persists to a higher temperature on Rh deposited on reduced ceria compared with Rh on oxidized ceria. The degree of dissociation does not depend on the amount of Rh deposited or on the annealing treatment after deposition.

Key Words: **carbon monoxide; ceria; rhodium; X-ray photoelectron spectroscopy.**

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1. INTRODUCTION

Cerium oxide is used extensively in automotive exhaust catalysts to help promote the oxidation of CO and the reduction of NO$_x$ (1, 2). One of the principal roles played by ceria in an automotive exhaust catalyst is as an oxygen storage medium (2, 3). Other beneficial effects of ceria have been proposed as well (2, 4–8). It has been suggested the ceria stabilizes the dispersion of active metals better than an alumina substrate. It has also been suggested that ceria may enhance the chemical activity of the reactant and supported metal, either by promoting certain metal morphologies that expose active sites or by changing the electronic interaction between the reactant and the metal particles.

Stubenrauch and Vohs (9, 10), expanding on the work of Bunluesin *et al.* (11, 12), have examined the adsorption of CO on Rh deposited on single-crystal cerium oxide. They observed that the thermal desorption of CO from Rh deposited on fully oxidized ceria resembled the desorption of CO from the low-index planes of single-crystal Rh. A high-temperature CO desorption state occurred, however, when the ceria substrate was partially reduced by Ar$^+$ ion sputtering prior to the deposition of Rh. They deduced through the use of isotopically labeled CO that the high-temperature state resulted from the recombination of dissociated CO.

In this work we have studied the adsorption and reaction of CO on Rh-loaded ceria by soft X-ray photoelectron spectroscopy (SXPS). Unlike previous studies, we are able to identify and quantify the surface species, i.e., molecular CO and atomic C on Rh. In addition, through the use of thin ceria films grown on Ru(0001) *in situ*, we are able to create ceria substrates with any average composition between CeO$_{1.5}$ and CeO$_2$ (13). The composition of these films is stable from 100 to 900 K. From these data, we can derive the degree of dissociation on the surface as a function of Ce oxidation state, temperature, and Rh coverage. The results indicate that the degree of dissociation of CO on the Rh is directly dependent on the oxidation state of the ceria substrate. The reactivity does not appear to be strongly influenced by the Rh coverage or particle size in the range of Rh loadings used.

2. EXPERIMENTAL

CeO$_2$(111) thin films were grown *in situ* on a Ru(0001) crystal as previously described (13). The ceria film was estimated to be ca. 5 nm thick based on the attenuation of the Ru 3*d* XPS intensity. The oxidation state of the Ce was controlled by adjusting the oxygen pressure during deposition. The oxidation state was determined from the Ce 4*d* spectra (14). In this paper the "degree of oxidation" refers to the amount of Ce^{4+} and Ce^{3+} in the oxide: "100% oxidized" therefore refers to all of the Ce present as Ce^{4+} (CeO$_2$) and "0% oxidized" refers to all of the Ce present as Ce^{3+} (CeO$_{1.5}$). The sample could be cooled by liquid nitrogen to temperatures lower than 100 K and heated resistively to 1000 K. The temperature was monitored with a Type K thermocouple spot welded to the back of the Ru.

Rh was deposited from a resistively heated evaporative source while the sample was maintained at 300 K. The relative exposure of Rh was determined with a quadrupole mass spectrometer. CO (Matheson, 99.99%) was adsorbed from a directional doser (15). All exposures were sufficient to saturate the surface with CO and were on the order of 20 L.

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Soft X-ray photoelectron spectra were collected using a multichannel hemispherical analyzer on beamline X1b at the National Synchrotron Light Source. C 1*s* and Rh 3*d* spectra were collected using 530- and 500-eV excitation, respectively. Binding energies are referenced to the X'''-peak in the Ce 4*d* spectra at 122.8 eV (14).

3. RESULTS

3.1. Analysis of C 1s Spectra

Figure 1 shows a typical set of C 1*s* spectra for CO adsorbed on Rh-loaded CeO$_x$. A broad feature near 290 eV occurred in all spectra that is assigned to the Ce 4*s* core level (16). A background spectrum, recorded before the surface was exposed to CO, has been subtracted from the spectra shown in Fig. 1. The peak at 291 eV results from CO adsorption on the ceria surface and is evident with or without Rh. The peak near 287 eV occurs only if CO is exposed to a surface with Rh present and its intensity increases with the amount of Rh deposited. This feature is assigned to molecular CO on Rh. The intensity of this peak correlates with that of a peak in the O 1*s* spectra at 533.1 eV (not shown). A third peak near 285 eV appears at elevated temperatures and occurs only if the ceria substrate is reduced and Rh is present. This peak is assigned to atomic C on Rh. After the disappearance of the C 1*s* peak at 287 eV, the only peak in the O 1*s* spectrum is the lattice oxygen peak at 530.7 eV (14).

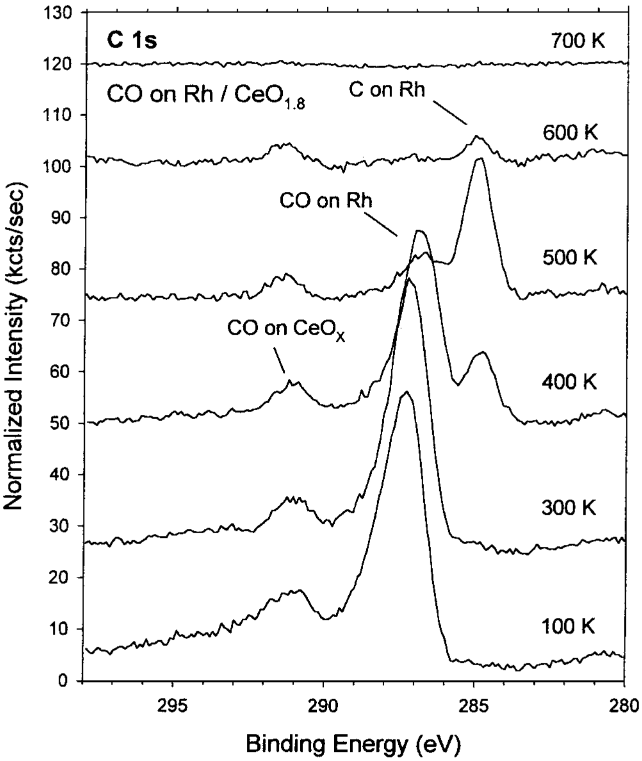

FIG. 1. C 1*s* soft X-ray photoelectron spectra for CO adsorbed on Rh deposited on partially reduced CeO$_{1.8}$. The CO was adsorbed at 100 K and each spectrum was recorded sequentially after annealing for 1 min at the indicated temperatures. A background spectrum recorded before CO adsorption has been subtracted from each spectrum.

3.2. Effect of Ce Oxidation State

The effect of the ceria oxidation state on the dissociation of CO on Rh is shown in Fig. 2. The intensities of the C 1*s* peak heights from CO and C on Rh are shown in Figs. 2a and 2b, respectively, for three different degrees of ceria oxidation. Equivalent amounts of Rh were deposited onto each substrate. The intensities are normalized to the CO peak height at 100 K. The amount of CO is essentially unchanged between 100 and 300 K, regardless of the oxidation state of the ceria (Fig. 2a). Annealing above 300 K causes a precipitous decrease in the CO peak intensity due in part to CO desorption. On the reduced surfaces, the CO decrease is balanced by an increase in the atomic C. The total CO + C is virtually unchanged up to 500 K on CeO$_{1.57}$, indicating dissociation of adsorbed CO is favored over desorption. In contrast, on the oxidized surface the CO desorbs completely by 500 K without dissociation. For the intermediately reduced surface (CeO$_{1.8}$), 50% of the CO desorbs and 35% dissociates by 500 K. By 600 K, no CO remains on any surface and atomic C decreases on the partially reduced surface. Based on the thermal desorption of isotopically labeled CO (10), all of the C loss above 550 K results from the recombination of dissociated CO.

3.3. Effect of Rh Coverage and Morphology

The amount of Rh and possible changes in the Rh morphology do not affect the CO dissociation activity. C 1*s* peak intensities from CO and atomic C on Rh are shown in Figs. 3a and 3b, respectively, for three different Rh treatments. In all cases the ceria substrate is less than 15% oxidized. The results in the first data set (Rh #1) are the same as were shown in Fig. 2 for the highly reduced surface except that the C 1*s* intensities are not normalized to the CO intensity at 100 K. The amount of Rh deposited was estimated to be 5×10^{14} cm^{-2} (±50%) based on the Rh 3*d* SXPS intensity compared with the Ru 3*d* SXPS intensity for clean Ru, the attenuation of the Ce 4*d* intensity after Rh deposition, and the O 1*s* intensity for CO on the deposited Rh compared with CO on clean Ru. The second data set (Rh #2) shows the results for a Rh coverage twice that used in Rh #1. The Rh 3*d* intensity is 65% larger in Rh #2 than in Rh #1. The last data set (Annealed Rh #2) contains the results when CO is reexposed to the Rh #2 surface after the surface was annealed to 700 K. The Rh 3*d* intensity decreases by 60% after annealing Rh #2 to 700 K.

CO dissociation activity is essentially unaffected by changes in the Rh particles. The shapes of the curves in

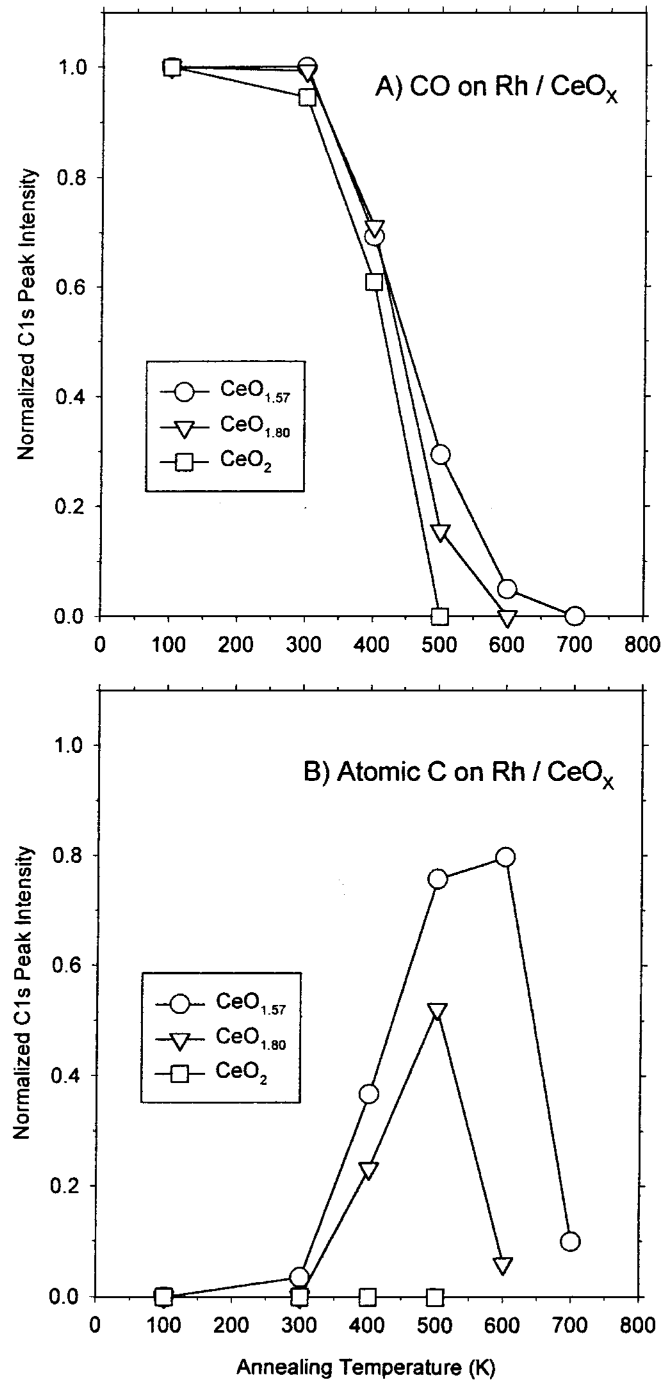

FIG. 2. C 1*s* SXPS peak intensity for (A) CO on Rh/CeO$_x$ and (B) atomic C on Rh/CeO$_x$ following CO adsorption at 100 K on Rh deposited on fully oxidized, partially reduced, and highly reduced CeO$_x$ versus annealing temperature. The C 1*s* intensity was normalized to the CO peak intensity at 100 K.

Fig. 3 are the same. In all cases, dissociation starts at 300 K and the maximum degree of dissociation occurs near 600 K; the maximum degree of dissociation is greater than 80%. Only total CO uptake is significantly affected by Rh coverage or particle morphology. The amount of CO that adsorbs on the Rh increases by 40% when the Rh coverage is doubled. Rh particles are therefore growing three-dimensionally since the surface area, as indicated by CO uptake, is not increasing linearly with the amount of Rh deposited. The amount of CO adsorbed would be directly

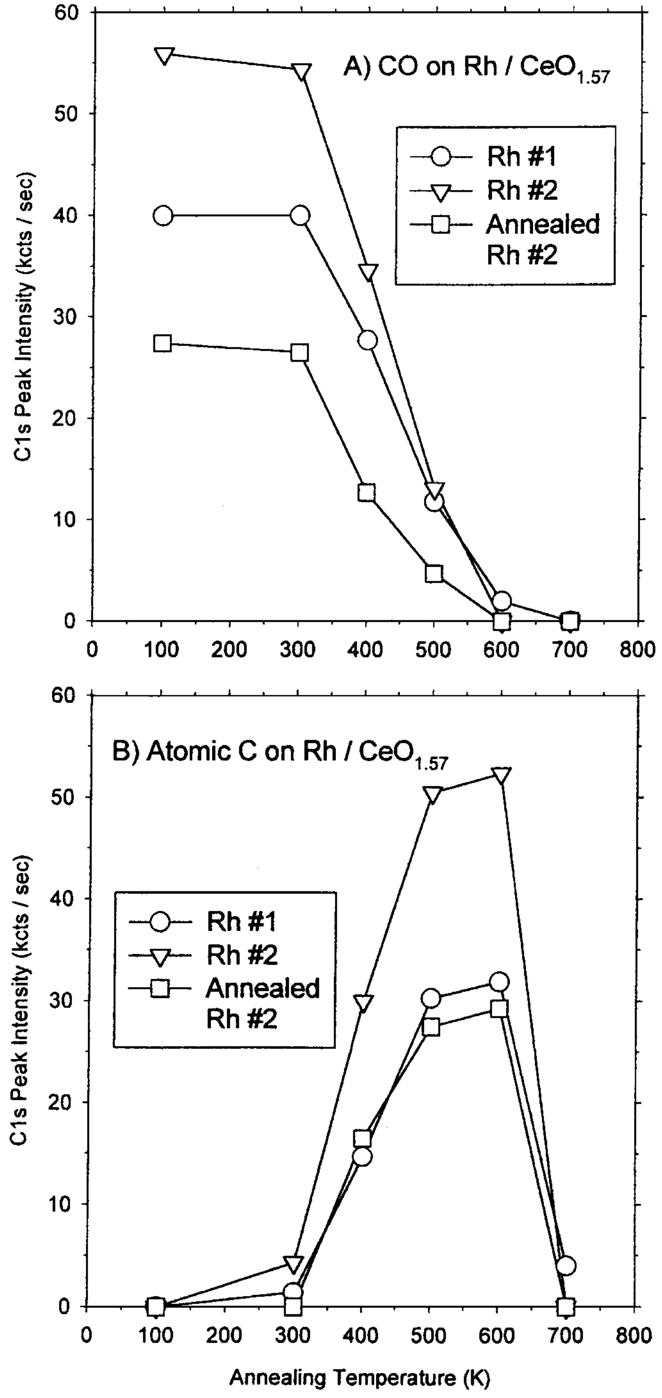

FIG. 3. C 1*s* SXPS peak intensity for (A) CO on Rh/CeO$_{1.57}$ and (B) atomic C on Rh on CeO$_{1.57}$ following CO adsorption at 100 K for two different Rh coverages, and annealed Rh, versus annealing temperature. The Rh #2 coverage is ca. two times greater than the Rh #1 coverage.

proportional to the amount of Rh deposited if the particles were growing as monolayer islands on the oxide surface. The 50% decrease in CO uptake, induced by annealing, is consistent with the 60% decrease in Rh 3*d* intensity and indicates a thickening of the Rh particles on the surface.

3.4. *Effect of CO Dissociation on CeO$_x$ and Rh*

No oxidation of the ceria is evident following the decomposition of CO. Ce 4*d* spectra were recorded to determine the oxidation state of the Ce substrate following adsorption and decomposition of CO (not shown). After adjusting for the attenuation of the Ce spectra due to the adsorption of Rh and CO, all of the Ce 4*d* spectra are virtually identical.

The Rh 3*d* spectra were recorded before CO exposure and then after the CO was annealed to different temperatures. The Rh $3d_{5/2}$ for CO on Rh on $CeO_{1.6}$ are shown in Fig. 4. The Rh $3d_{5/2}$ peak before the CO is adsorbed is relatively broad and is centered at ∼307.9 eV. After the CO is adsorbed the peak sharpens and shifts to 308.1 eV. Except for changes in intensity, the peak shape and position remain the same after annealing at all temperatures up to 600 K. The peak after annealing to 700 K is the same as the peak before CO exposure.

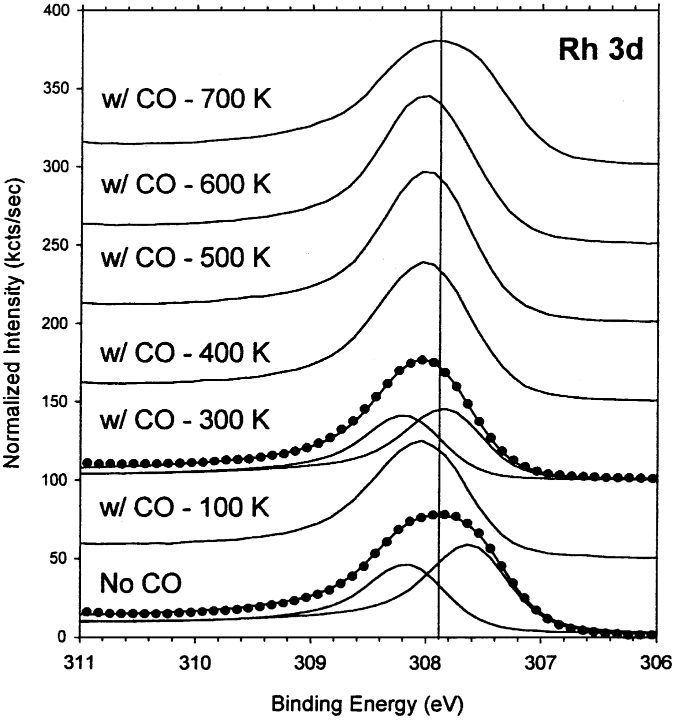

FIG. 4. Rh $3d_{5/2}$ spectra for Rh on $CeO_{1.6}$ before and after CO was adsorbed at 100 K and then annealed as indicated. The Rh was annealed to 800 K after it was deposited. Spectral fits using two components are shown for the spectra without CO and with CO annealed to 300 K.

4. DISCUSSION

Three C-containing species are observed in the C 1*s* soft X-ray photoelectron spectra from CO adsorbed on Rh deposited on reduced cerium oxide. The feature at 290.5 eV results from the direct interaction of CO with the cerium oxide. This peak occurs in the presence or absence of Rh. Several species have been identified by IR spectroscopy following CO exposure on ceria powder at high pressures (17, 18). Linearly bonded CO was weakly adsorbed and only observed at room temperature when the pressure was maintained above 20 Torr. Undoubtedly this species is absent in the present UHV experiments. Several other IR bands were observed and were assigned to surface species that were stable to higher temperatures. CO bonded to anion sites formed different carbonate species depending on the coordination of the CO to the surface. CO bonded at cation sites formed inorganic carboxylate. The different types of carbonate and carboxylate are not readily distinguishable in the present soft X-ray photoelectron spectra; however, the species at 290.5 eV is more stable on the reduced ceria surface and is presumably related to bonding at Ce sites that are exposed on the reduced surface (13).

The peak at 287 eV is observed only when Rh is present. The peak position is similar to the values of 286–287 eV that have been reported for molecular CO adsorbed on Rh deposited on Al_2O_3 (19, 20). The binding energies for CO adsorbed in atop and threefold sites on single-crystal Rh(111) were 286.0 and 285.4 eV, respectively (21). The increase in binding energy for CO on Rh particles on the oxides results from a reduction in the final state screening on the small metal particles. Stubenrauch and Vohs have observed molecular CO in atop and bridge sites on Rh deposited on ceria at 300 K by EELS (10). The EELS results further support the assignment of the C 1*s* peak at 287 eV to molecular CO on Rh.

The peak at 284.5–284.9 eV is assigned to atomic C on Rh. Atomic C on Rh deposited on Al_2O_3 had a binding energy of 284.0 eV (19, 20). The difference between the CO and C binding energies for Rh/Al_2O_3, 2 to 3 eV, is the same as the difference between the peaks assigned to CO and C on Rh/CeO$_x$. The slight differences in absolute binding energies are probably due to differences in how the binding energies are referenced on the two oxides. Similar XPS peaks, assigned to CO and C on Rh, were reported by Putna *et al.* for CO on Rh on reduced ceria (16).

No CO decomposition occurs on Rh on a fully oxidized ceria substrate and the CO completely desorbs by 500 K. Partial decomposition occurs on the Rh when the ceria substrate is 60% oxidized. The maximum C 1*s* intensity from atomic C is less than the CO intensity before decomposition occurs (Fig. 2). These observations are consistent with the TPD spectra of CO from Rh deposited on oxidized and sputtered CeO_2(111) reported by Stubenrauch and Vohs (9, 10). They observed 14% dissociation on a fully oxidized surface and 62% dissociation on the partially reduced surface. In their case, they estimated that a sputtered $CeO_2(111)$ surface was ca. 50% oxidized ($CeO_{1.75}$) (9). The small amount of dissociation on the oxidized surface, as opposed to no dissociation in the current experiment, may have been due to the different numbers of defects present in the two experiments.

Nearly total CO decomposition occurs on Rh deposited on a highly reduced ceria substrate ($<15\%$ Ce^{4+}). This is evident from the observation that the C 1*s* signal from atomic C becomes nearly as intense as the CO signal before decomposition (Fig. 2). The molecular CO is also slightly stabilized on the reduced surfaces. The CO is completely removed at 500 K on the fully oxidized surface and is still evident at 500 K on the reduced surfaces (Fig. 2).

Several studies have indicated that CO dissociation activity on metal particles adsorbed on oxide surfaces is related to the morphology of the metal particles (19, 20, 22). In the present study there is no clear relationship between CO dissociation activity and Rh morphology. The structure of the Rh particles on CeO_x is not known. However, we have attempted to change Rh morphology by altering Rh coverage and annealing temperature. Campbell (23) and Henry (22) have discussed the growth of metal particles on other oxide surfaces. In general, the morphology of metal particles is affected by the amount of metal deposited and the temperature to which it is annealed. In our results, the extent of CO decomposition and the temperature of CO desorption did not vary as a function of the amount of Rh deposited on the surface or whether the Rh was annealed to a higher temperature after deposition (Fig. 3). Changes in structure, either with the amount of Rh or with annealing temperature, do not appear to affect the dissociation activity of CO on Rh deposited on reduced CeO_x.

The present results on an annealed surface are different from the observations of Stubenrauch and Vohs (9). They observed a loss of dissociation activity after annealing the sample to successively higher temperatures whereas we observed no change in activity after annealing. They suggested that the loss of activity was because of reoxidation of the sputter-reduced surface through diffusion of oxygen from the bulk. The oxidation state of the thin films used in the present study is stable up to 1000 K. The present results decouple changes in the oxide from changes in the Rh and demonstrate that the oxidation state of the ceria is the determining factor.

The Rh 3*d* spectra also indicate that CO adsorbs on the Rh and that decomposition products remain on the Rh. The broad Rh $3d_{5/2}$ peak shown at the bottom of Fig. 4 can be analyzed in terms of two peaks associated with bulk Rh and a surface core-level shifted peak (21, 24). The two peaks are not resolved in Fig. 4; however, the spectra can be fit as shown on the clean Rh and with CO at 300 K using parameters determined in earlier work (21, 24). The peak at 308.2 eV is the component resulting from bulk Rh. The peak at 307.6 eV in the bottom spectrum results from surface Rh atoms. When CO is adsorbed on Rh particles, the lower-binding-energy peak shifts to 307.8 eV. The separation between the bulk and the clean surface peak and the magnitude of the shift that results from CO adsorption are consistent with what has been seen for CO on Rh(111) (21). The key feature of these data is that the Rh spectra shift in response to CO adsorption and remain shifted until all of the CO is desorbed above 600 K. This indicates that CO and at least some of its dissociation products are on the Rh.

The Ce 4*d* spectra indicate that Ce is not oxidized after CO is fully dissociated at 600 K. Our earlier results with NO on CeO_x demonstrated that we are sensitive to a change in surface oxidation of less than 0.1 ML (25). This, combined with the Rh 3*d* data, suggests that the O remains on the Rh. However, the isotope exchange results of Stubenrauch and Vohs (10), combined with the well-known thermodynamic affinity of reduced ceria for oxygen, strongly support the view that the O is transported to the ceria. Although we cannot say where the O is for certain, the most likely scenario that is consistent with all of the data is that the O moves from the Rh to the Ce following CO dissociation. The O is then rapidly transported throughout the ceria film at 600 K (14, 25) so that the net change in oxidation that is observable by SXPS is negligible. The C remains on the Rh, which leads to the shifted Rh 3*d* spectra.

The ability of Rh deposited on reduced cerium oxide to dissociate CO is directly related to the oxidation state of the cerium oxide. However, the Rh 3*d* intensities from similar exposures of Rh on ceria with different degrees of Ce oxidation are similar, indicating that the Ce oxidation state does not significantly alter the dispersion of the Rh. Further, the Rh coverage dependence and Rh annealing experiments also indicate that CO dissociation is not significantly affected by Rh morphology, at least for the Rh coverages examined in this study.

An alternative explanation for the increase in CO dissociation is an electronic interaction between ceria, Rh, and CO. A commonly proposed mechanism for the dissociation of CO is through weakening of the C–O bond through the donation of electrons into the π^* antibonding orbital (26). Such a donation could occur if the CO were bound to an electron-rich, Lewis base site. Such a site may exist for Rh adsorbed on reduced ceria. The Rh particles could withdraw charge from relatively electron-rich Ce^{3+} sites. This leaves the Rh slightly anionic. Another result of the Blyholder model is an increase in the CO–metal bond strength (26). This is consistent with the observation of molecular CO at 500 K on Rh deposited on reduced ceria but not on oxidized ceria. Such a charge transfer mechanism should vary, however, with Rh coverage as the available charge is diluted through larger particles. This is not the case. Clearly, further experiments to elucidate the structure of Rh on CeO_x are necessary.

5. CONCLUSIONS

The degree of dissociation of CO on Rh deposited on ceria is directly dependent on the degree of reduction of the ceria. Nearly total decomposition can occur on a highly reduced ceria substrate. Molecular CO also persists to a higher temperature on Rh deposited on reduced ceria compared with Rh on oxidized ceria. The degree of dissociation does not depend on the amount of Rh or on its morphology.

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