**The Interaction of Carbon Monoxide with Rhodium
On Potassium-Modified CeO₂(111)**

David R. Mullins*

Chemical Sciences Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831-6201

This manuscript has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (<http://energy.gov/downloads/doe-public-access-plan>).

*Corresponding Author:

David R. Mullins
Oak Ridge National Laboratory
PO Box 2008, MS 6201
Oak Ridge, TN 37831-6201
e-mail: mullinsdr@ornl.gov
phone: 865-574-2796
FAX: 865-241-5252

Abstract

The adsorption and reactions of CO adsorbed on Rh particles deposited on K-covered CeO₂(111) were studied by temperature programmed desorption and photoelectron spectroscopy. K deposited on CeO₂(111) forms a KO_x over-layer by extracting O from the ceria and partially reducing some of the Ce⁴⁺ to Ce³⁺. CO does not adsorb on the KO_x / CeO_{2-x}(111) surface in the absence of Rh particles. CO adsorbed on Rh / K / CeO₂(111) adsorbs molecularly on the Rh at 200 K. As the surface is heated the CO spills-over and reacts with the KO_x to form carbonate. The carbonate decomposes at elevated temperature to produce CO and CO₂. The carbonate stabilizes the KO_x so that K desorbs at a higher temperature than it would in the absence of CO. When the Rh and K deposition are reversed so that K is deposited on both the Rh and the CeO₂(111), CO adsorbs as CO₂⁻ at 200 K. The CO₂⁻ decomposes below 350 K to produce gas phase CO and adsorbed CO₃²⁻ and CO. The CO is stabilized by the K on the Rh and desorbs above 540 K. The carbonate decomposes into gas phase CO and CO₂.

1. Introduction

The adsorption of alkali metals, and more specifically the co-adsorption of alkali metals and molecules, on surfaces has been studied extensively. Alkali metals are well-known “promoters” for catalytic reactions. In a review of alkali doping in heterogeneous catalysis Mross noted that alkalis can i) increase selectivity, ii) increase activity, and iii) prolong the lifetime of the catalyst.[1] Many fundamental surface science studies occurred in the 1980s culminating in a review by Bonzel. [2] Much of the surface science literature was devoted to the modification of CO adsorption and reaction on K-modified single crystal surfaces.[2-9] These studies were motivated by the wide-spread use of alkali promoters in Fischer-Tropsch catalysis[1,10] General observations from these studies indicated that K weakened the CO bond and strengthened the Metal-C bond.

There have been surprisingly few studies on K adsorption on well characterized metal oxide surfaces despite the increasing attention to these surfaces in recent years.[11] From a practical point of view one can assume that alkalis added to industrial catalysts will be deposited on the oxide supports as well as the supported metal nanoparticles. Therefore it is of fundamental interest to determine how the alkalis may affect molecule-support interactions as well as molecule-metal interactions. There have been reports of K adsorption on $\text{TiO}_2(100)$ [12], $\text{TiO}_2(110)$ [13,14], $\text{Cr}_2\text{O}_3(0001)$ [15,16], $\text{ZnO}(10\bar{1}0)$ [17,18], $\text{MgO}(100)$ [19,20] and $\text{NiO}(100)$. [21] These studies did not report the influence of K on molecular adsorption, however.

An additional motivation for this current work is to explore the unique behavior that CO has when adsorbed on Rh supported on single crystal $\text{CeO}_x(111)$. [22-24] When Rh is supported on fully oxidized $\text{CeO}_2(111)$, CO adsorbs and desorbs much as it would on single crystal Rh surfaces with little interaction with or influence by the oxide support. However, when the Rh sits on partially reduced $\text{CeO}_{2-x}(111)$ the CO dissociates into C(a) and O(a) which ultimately recombine at an elevated temperature to desorb as CO. On oxide and metal surfaces K has been shown to donate its valence electron to the substrate and adsorb as ionic K^+ . This behavior may mimic the interaction that may occur between reduced Ce^{3+} and a supported Rh particle. Either K^0 might donate its electron to the Rh or to Ce^{4+} to produce Ce^{3+} , in either case producing a situation which may promote CO dissociation on the Rh. If CO dissociation is observed on Rh / K / $\text{CeO}_2(111)$ this may suggest an electronic effect is responsible for CO dissociation on Rh / $\text{CeO}_{2-x}(111)$.

In a complex system such as CO / Rh / K / CeO_x(111) there is an extensive parameter space that could be investigated. In this investigation I have chosen to limit the K and Rh coverages and the CO exposure to one reproducible set. In addition only initially fully oxidized CeO₂(111) is used as the starting substrate. A systematic variation in these coverage and oxidation state parameters, in particular the K coverage, will add further insight to the results presented in this paper.

This paper is organized as follows: the adsorption of K on CeO₂(111) without Rh or CO is presented first to establish the properties of the K adsorbate and its effect on the ceria support. CO adsorption will then be considered. K has a dramatic effect on the CO adsorption on Rh therefore, for comparison, TPD and photoemission data will be presented for CO adsorption on Rh, K / Rh and Rh / CeO₂(111). There are two possible ways to deposit Rh and K on ceria; the K can be deposited first, followed the Rh (designated Rh / K / CeO₂(111)) or the Rh can be deposited first followed by the K (designated K / Rh / CeO₂(111)). Presumably the second method has a greater probability than the first for depositing K on the Rh particle in addition to K on the ceria. These two deposition orders produced strikingly different results and will be presented separately.

2. Experimental

The experiments were conducted in two different ultrahigh vacuum (UHV) chambers. Temperature programmed desorption (TPD) experiments were performed in a UHV chamber at Oak Ridge National Laboratory (ORNL). The temperature was ramped at 3 K / sec and the sample was biased -70V to prevent electrons generated by the mass spectrometer ionizer from stimulating reactions at the surface. Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) were used to determine the elemental composition of the surface and the Ce oxidation state, respectively. Ceria films were grown onto a Ru(0001) single crystal *in situ* by evaporating Ce metal under an O₂(2×10^{-7} Torr) environment[25].

The K was evaporated onto the ceria film from an SAES getter source. A multilayer coverage of K was evaporated onto the sample at 200 K and then the sample was annealed to 350 K to remove multilayer K (see below). This procedure resulted in reproducible K coverages for all experiments. Rh was deposited from a resistively heated evaporative source while the sample was maintained at 300 K. The Rh coverage was $8 \pm 1 \text{ nm}^{-2}$.

The samples were exposed to $^{13}\text{C}^{16}\text{O}$ (Cambridge Isotope Labs) through a directional doser.[26] The CO contained ca. 10% $^{13}\text{C}^{18}\text{O}$ and the precise ratio of $^{13}\text{C}^{16}\text{O}$ to $^{13}\text{C}^{18}\text{O}$ was determined to be 11:1 by recording a TPD of the mixture from Ru(0001) before ceria was deposited. $^{12}\text{C}^{16}\text{O}$ (Matheson) was used in the sXPS experiments. The gases were dosed to ensure saturation, i.e. further exposure resulted in no changes in the sXPS or TPD spectra. The typical exposure was approximately equal to 20 L.

Soft-X-ray photoelectron spectroscopy (sXPS) was performed at beamline U12a at the National Synchrotron Light Source (NSLS). The experimental setup for these studies has also been previously described[27,28]. Ceria films, K and Rh were deposited as described above. The C 1s and K 2p spectra were recorded using 410 eV and O 1s using 600 eV photon excitation energies ($h\nu$). The total instrumental resolution is less than 0.5 eV. On the ceria films the binding energies were calibrated relative to the Ce 4d spectra ($X''' - 122.3$ eV) at the different photon energies.[29] In the absence of ceria the binding energies were referenced to the metallic Fermi edge. The Ce oxidation state was determined using the Ce 4d spectra.[30]

3. Results

3.1 Deposition of K on $\text{CeO}_2(111)$

Figure 1 shows the TPD (Mass 39) of K on Ru(0001) (black curve) and $\text{CeO}_2(111)$ (red curve). The prominent peak near 330 K on both surfaces results from the desorption of multilayer K. On metal surfaces the desorption of K is relatively structure-less and desorbs in a broad plateau from just above the multilayer peak to ca. 1000 K.[31] The onset temperature decreases monotonically with K coverage. The progressively decreasing adsorption energy has been related to repulsion between K atoms in the first layer.[31] A small feature labeled α has previously been reported between 550 K and 600 K. A similar peak is evident in Figure 1. The sharper feature near 640 K is associated with co-adsorbed CO that adsorbed on the surface during the K deposition.[5] The first monolayer coverage of K on Ru(0001) has been determined to be 0.36 ML relative to the Ru(0001) surface density or 5.7 nm^{-2} . [5,31]

The TPD of K from $\text{CeO}_2(111)$ (Figure 1 – red curve) displays a series of intense peaks at ca. 450 K, 630 K and 730 K. The peak at 630 K and 450 K may be associated with the desorption of first and second layer K, respectively, as reported for K desorption on $\text{Cr}_2\text{O}_3(0001)$. [16] The high temperature peak near 730 K may be related to the decomposition of

KO_x as has been reported for oxidized K films on Ru(0001).[32] It is clear from a visual comparison of Figure 1a and 1b that a larger amount of K desorbs from $\text{CeO}_2(111)$ than from Ru(0001) above the multilayer desorption temperature.

Figure 1 – K TPD following K deposition on Ru(0001) (black) and $\text{CeO}_2(111)$ (red) at 200 K.

Figures 2a and 2b show the K 2p core-level spectra for K deposited on a) Ru(0001) and b) $\text{CeO}_2(111)$ at 200 K and annealed as indicated. A Shirley background has been subtracted from all of the spectra.[33] The most prominent peaks in the K 2p spectra on Ru(0001) consist of a spin-orbit split doublet with K $2p_{3/2}$ at 293.8 eV and K $2p_{1/2}$ at 296.6 eV. At 200 K and 300 K the peaks have small additional peaks at 0.9 eV higher binding energies and broad asymmetric tails toward higher binding energies. The satellite peaks have been assigned to K in the second monolayer.[6] The tail has been interpreted as an indication of metallic character resulting from plasmons in the K.[34] When the sample was annealed to 400 K, which is above the multilayer desorption temperature, the satellite peaks and the asymmetric tail largely disappear. As the sample is annealed to higher temperatures the intensity decreases as K desorbs and the peak positions shift to higher binding energies.[6]

Figure 2 – K 2p spectra following K deposition on A) Ru(0001) and B) CeO₂(111) at 200 K and then annealed as indicated.

Following K deposition at 200 K on CeO₂(111) the K 2p spectrum (Figure 2b) has the asymmetric tail indicating metallic K. The peaks are relatively broad and any satellite peaks are not readily evident in the spectra. When the sample was annealed to 350 K the asymmetric tail disappears however the peak heights actually increase and the integrated intensity remains constant. This behavior suggests a change in the state of the K, perhaps indicating an activated interaction with the CeO₂ substrate. Note the difference in the vertical scale in Figures 2a and 2b that indicates that the intensity is greater on CeO₂(111) compared to Ru(0001). At 350 K the K

$2p_{3/2}$ and K $2p_{1/2}$ peaks are at 294.4 eV and 297.2 eV, respectively. These peak positions stay fairly constant as the sample is annealed and K desorbs. At 700 K the peaks become distinctly asymmetric on the low binding energy side and at 1000 K the peak position has shifted to 294.0 eV. The K 2p peaks on $\text{CeO}_2(111)$ are broader than the K 2p peaks on Ru(0001) suggesting greater heterogeneity in the K on $\text{CeO}_2(111)$. In addition, the K 2p peaks on $\text{CeO}_2(111)$ have a higher binding energy, K $2p_{3/2}$ at 294.4 eV vs. 293.8 eV, suggesting a higher oxidation state for the K on $\text{CeO}_2(111)$.

The K coverage on Ru(0001) and $\text{CeO}_2(111)$ are plotted as a function of temperature in Figure 3. The coverages were determined from the integrated K 2p core level spectra intensities. The K coverage in the first monolayer on Ru(0001) is 5.7 nm^{-2} . [5] This coverage occurs after the multilayer desorbs at 400 K. The K coverage at 350 K – 400 K on $\text{CeO}_2(111)$ is $13 \text{ nm}^{-2} - 14 \text{ nm}^{-2}$ or roughly twice the coverage on Ru(0001). In addition, whereas the coverage decays nearly linearly on Ru(0001) as the temperature is increased the coverage on $\text{CeO}_2(111)$ displays some discontinuous decreases consistent with desorption peaks in Figure 1.

Figure 3 – K coverage following K deposition on Ru(0001) (black) and $\text{CeO}_2(111)$ (red) at 200 K and then annealed to progressively higher temperatures.

Ce 3d core-level spectra, excited by a Mg $k\alpha$ laboratory source, are shown in Figure 4 as a function of annealing temperature after K deposition at 100 K. The K over-layer attenuates the Ce photoemission by 35%. To facilitate a comparison of these spectra a Shirley background was subtracted from the raw data and then the spectra were normalized to a constant total integrated

intensity. Before K deposition the Ce 3d spectrum from fully oxidized $\text{CeO}_2(111)$ (black curve) consists of six peaks assigned to the Ce $3d_{5/2}$ and Ce $3d_{3/2}$ spin-orbit doublet and associated satellite features.[30] After K deposition the peaks at 916.7 eV, 907.5 eV and 889.0 eV decrease in intensity while the valleys near 904 eV and 885 eV increase in intensity and a low binding energy shoulder emerges near 880 eV (red curve). This behavior is indicative of the reduction of Ce^{4+} to Ce^{3+} .[30] Based on the intensity decrease of the isolated Ce^{4+} peak at 916.7 eV the degree of reduction is estimated to be 65% Ce^{4+} or $\text{CeO}_{1.83}(111)$. After the sample is annealed to 350 K to remove the K multilayer the Ce re-oxidizes slightly to 75% Ce^{4+} (blue curve). After annealing to 900 K to remove most of the K the Ce 3d spectrum (green curve) looks virtually identical to the spectrum from the surface before K deposition.

Figure 4 – Ce 3d spectra following K deposition on $\text{CeO}_2(111)$ at 100 K and then annealed as indicated. A Shirley background has been subtracted from all spectra and the spectra have been scaled to a constant integrated intensity to compensate for attenuation by the K overlayer.

The Ce 3d spectra indicate that the K reacts with the $\text{CeO}_2(111)$ surface to produce KO_x and CeO_{2-x} . This reaction occurs even at 100 K. When the sample was annealed to 350 K to desorb multilayer K the Ce is slightly re-oxidized. This suggests that K is oxidized into the multilayer at lower temperatures. The decomposition of KO_x in the multilayer results in

desorption of K and return of O to the CeO_{2-x} substrate. An alternative interpretation of the apparent re-oxidation of Ce is that the Ce 3d spectra at 100 K and 350 K reflect the distribution of Ce^{3+} as a function of depth within the $\text{CeO}_{2-x}(111)$ substrate. The K over-layer limits the depth from which Ce 3d electrons can escape. The thicker over-layer at 100 K results in more sensitivity to Ce near the K / $\text{CeO}_{2-x}(111)$ interface. After desorption of K at 350 K the Ce 3d XPS probes deeper into the ceria substrate. If Ce reduction is localized near the surface the average concentration of Ce^{4+} will increase as deeper layers are included in the spectra.

Figure 5 – O 1s spectra following K deposition on $\text{CeO}_2(111)$ at 200 K and then annealed as indicated.

Figure 5 shows the O 1s spectra from clean $\text{CeO}_2(111)$ (black curve) and from K-covered $\text{CeO}_2(111)$ annealed to various temperatures. The clean surface has a single O 1s peak at 530.1 eV. When K is adsorbed and annealed to 350 K (red curve) two new peaks appear at 532.7 eV and 528.5 eV. The peak at 532.7 eV shifts to 532.3 eV when the sample is annealed from 350 K to 500 K and the peak at 528.5 eV disappears. Lamontagne et al assigned O 1s peaks near 527 eV – 528 eV to K_2O , peaks near 531 eV to K_2O_2 , peaks near 532 eV to K_2O_3 and peaks near 534 eV to K_2O_3 . [35] Therefore peaks above the CeO_2 peak at 530.1 eV are assigned to a mixture of K_2O_3 and K_2O_2 while the peak at 528.5 eV is assigned to K_2O . When the sample is annealed to

700 K (green curve) the K_2O_3 / K_2O_2 peak is diminished and the CeO_2 peak grows consistent with the desorption of K.

Both the Ce 3d and O 1s spectra indicate that adsorbed K reacts with the $CeO_2(111)$ surface to form KO_x . The removal of O from the ceria, and the transfer of an electron from K to Ce, reduces Ce^{4+} to Ce^{3+} .

3.2 CO adsorption on K/Rh

CO was adsorbed on Rh/Ru(0001) and on K/Rh/Ru(0001) for comparisons to what is observed when Rh is supported on $CeO_2(111)$. As noted below, the results are consistent with what has been reported for CO/Rh(111) and CO/K/Rh(111).[4]

A thick film of Rh was deposited on Ru(0001) at 300 K and then annealed to 900 K. Based on the attenuation of the Ru AES and Ru 2p XPS signals the Rh over-layer was estimated to be greater than 4 nm.[36,37] Figure 6a shows the desorption of $^{13}C^{16}O$ and $^{13}C^{18}O$ following exposure at 200 K. The $^{13}C^{18}O$ has been scaled so that it matches the desorption of the $^{13}C^{16}O$ and reflects their relative compositions in the CO source. The CO desorbs in a broad peak with a peak maximum at ca. 455 K. K was then deposited on the Rh film at 200 K and then annealed to 500 K. Assuming the K over-layer behaves similarly on Ru and Rh, i.e. the monolayer coverages are similar on the two surfaces,[4,5] the K coverage was ca. 4 nm^{-2} (Figure 3). The K/Rh film was then exposed to CO at 200 K. The CO desorption was delayed until higher temperature compared to CO on the clean Rh film (Figure 6a and 6b). A prominent peak occurred at ca. 660 K with a shoulder at ca. 580 K. The K desorption coincided with the high temperature CO desorption at 660 K. Note that the K desorption is also delayed compared to K/Rh without CO where the desorption would have started at 500 K, i.e. the annealing temperature before CO exposure. The desorption behavior of CO on clean and K-covered Rh is completely consistent with the results reported by Crowell and Somorjai on Rh(111).[4] Note in Figure 6b that the $^{13}C^{16}O$ desorption and the $^{13}C^{18}O$ desorption scaled as in Figure 6a again overlap perfectly. In subsequent results a decrease in the relative intensity of the $^{13}C^{18}O$ compared to $^{13}C^{16}O$ will indicate an exchange of O between the CO adsorbate and the oxide substrate.

Figure 6 – TPD following CO adsorption at 200 K on A) Rh / Ru(0001) and B) K / Rh / Ru(0001).

Figure 7 shows the C 1s XPS for CO on the clean Rh film and CO on K/Rh. On the clean Rh film the CO produces a single peak at 286.4 eV. Note that the Ru 3d_{3/2} peak is visible from the buried substrate but has been attenuated ca. 500x compared to clean Ru(0001). The CO was flashed off, K was evaporated on to the Rh surface at 200 K which was then annealed to 500 K and then CO re-exposed onto the K / Rh surface. The CO peak position shifted to 285.1 eV. This is consistent with the C 1s XPS results reported by Strisland et al for CO/K/Rh(111).[38] They assigned the CO at the higher binding energy, that occurred in the absence of K, to CO adsorbed in an atop site and the CO at the lower binding energy, that occurred when K was present, to CO adsorbed in a hollow site.

Figure 7 – C 1s spectra following CO adsorption on A) Rh / Ru(0001) and B) K / Rh / Ru(0001) at 200 K then annealed as indicated.

The CO was completely removed from the K-free surface after annealing to 500 K (Figure 7a) while the CO remained on the surface at 500 K when K was present (Figure 7b). This is consistent with the delayed CO desorption observed in the TPD (Figure 6b) due to CO – K interaction. A new feature appeared near 290 eV at higher temperatures on the CO / K / Rh surface. This is assigned to carbonate, CO_3^{2-} , that presumably formed from a reaction between CO and O that adsorbed on the surface during K deposition.

3.3 CO adsorption on Rh/K/CeO₂(111)

TPD and C 1s core-level photoemission indicated that CO did not adsorb on Rh-free CeO₂(111), with or without the presence of K. Therefore a metal particle is necessary for CO adsorption.[22,28] The desorption of CO from Rh/CeO₂(111) is essentially the same as has been reported for CO on Rh(111).[4] As shown in Figure 8a after exposure at 200 K the CO desorbs from the Rh in a broad doublet between ca. 300 K and 550 K. The ¹³C¹⁶O and scaled ¹³C¹⁸O signals no longer match which indicates a small loss of ¹⁸O from the ¹³C¹⁸O adsorbate due to exchange with the Ce¹⁶O₂ substrate. There is also some ¹³C¹⁶O₂ formed through reaction of ¹³C¹⁶O with the Ce¹⁶O₂.

Figure 8 – TPD following CO adsorption at 200 K on A) Rh / CeO₂(111) and B) Rh / K / CeO₂(111).

K was evaporated onto the CeO₂(111) at 200 K and then annealed to 400 K to remove the K multilayer and leave a K coverage of 13 nm⁻² – 14 nm⁻² (Figure 3). Rh was then deposited on the K/CeO₂(111) substrate at 300 K followed by CO exposure at 200 K. The resulting TPD (Figure 8b) is totally different from either CO on Rh / CeO₂(111) (Figure 8a) or CO on K / Rh (Figure 6b). K desorption is again delayed until ca. 700 K, as on the CO / K / Rh surface, but instead of the K desorption coinciding with CO it desorbs in a peak coincident with CO₂. In addition to the peak at 700 K, CO₂ desorbs in a broad feature that starts near 320 K. ¹³C¹⁶O has a prominent peak near 620 K as well as broad shoulders on both the low and high temperature sides. There is an almost total loss of ¹³C¹⁸O which, along with the production of CO₂, indicates a strong interaction of the CO with the O in the substrate.

The C 1s core-level spectra for CO on Rh / CeO₂(111) are shown in Figure 9a. Following exposure at 200 K the spectrum is dominated by a peak at 286 eV with a small peak near 290 eV. The peak at 286 eV is assigned to CO adsorbed in an atop site on the Rh particle.[38] The peak at 290 eV is assigned to carbonate, CO₃²⁻. [39] The intensity from these species diminishes significantly after the sample is annealed to 500 K as most of the CO has desorbed (Figure 8a). All of the C-containing species are removed from the surface at 700 K.

The C 1s spectra for the CO / Rh / K / CeO₂(111) surface, prepared the same way as for the TPD spectra in Figure 8b, are shown in Figure 9b. At 350 K the spectrum is similar to the spectrum for CO on Rh / CeO₂(111) (Figure 9a) with peaks at 286 eV and 290.3 eV. The carbonate peak is somewhat more prominent on the K-modified surface. Note that there is a change in scale between Figures 9a and 9b and the intensity of the CO-related peak at 286 eV is about the same in both spectra.

As the sample is annealed the CO peak diminishes but the carbonate peak increases and reaches a maximum intensity near 600 K. Comparing the C 1s spectra with the TPD spectra it appears that carbonate decomposes into both CO and CO₂ at high temperature. CO apparently contributes to the CO₂ desorption but it isn't clear whether it proceeds to CO₂ through a carbonate intermediate or through direct reaction with O in the substrate. The total integrated C 1s intensity *increases* as the sample is annealed from 350 K to 600 K despite the desorption of CO and CO₂ in this temperature range. One possible explanation is that the intensity of the carbonate peak was affected by diffraction effects. Another possible explanation is that the

carbonate was initially formed subsurface and later emerged to the surface as the sample was heated. This anomalous behavior of the C 1s intensity was not explored further.

Figure 9 – C 1s spectra following CO adsorption on A) Rh / CeO₂(111) and B) Rh / K / CeO₂(111) at 200 K and then annealed as indicated.

3.4 CO on K/Rh/CeO₂(111)

The deposition order of K and Rh was reversed, i.e. Rh was first evaporated onto the CeO₂(111) surface then K was deposited onto Rh / CeO₂(111) and annealed to 400 K. This presumably produced the same coverages of Rh and K on the ceria as in Section 3.3 but K was deposited on both the Rh and the CeO₂(111). The resulting TPD after CO exposure is shown in Figure 10.

Figure 10 – TPD following CO adsorption at 200 K on K / Rh / CeO₂(111).

Again the TPD is dramatically different from the Rh / CeO₂(111) surface without K (Figure 8a) but is also very different from the Rh / K / CeO₂(111) surface (Figure 8b). The CO desorption splits into two regions, a single peak between 200 K and 300 K and a doublet between 500 K and 700 K. The high temperature region between 500 K and 700 K is similar to the CO desorption that occurred on CO / K / Rh (Figure 6b). The CO₂ desorption is diminished compared to the case of CO / Rh / K / CeO₂ (Figure 8b). Only a small CO₂ peak is evident coincident with the K and CO peaks near 660 K. Compared to the K desorption from CO / K / Rh (Figure 6b) the K desorbs between 500 K and 600 K in addition to the peak coincident with CO at 660 K. This may be K that is not interacting with the CO, such as K on the CeO₂. Finally the CO between 200 K and 300 K is unique to this surface. An analogous weakly bound CO species was not observed in any of the other permutations of CO / K / Rh / CeO₂(111).

Figure 11 – C 1s spectra following CO adsorption on K / Rh / CeO₂(111) at 200 K and then annealed as indicated.

The C 1s spectra for this system, CO / K / Rh / CeO₂(111), are shown in Figure 11. Upon adsorption of CO at 200 K a new feature that wasn't observed in any of the other spectra is evident at 288 eV. This binding energy indicates a species with C having an oxidation state that lies between CO (+2) and CO₃²⁻ (+4). A likely candidate is CO₂⁻ which has been identified as a surface intermediate following CO₂ adsorption on several K-covered metals surfaces.[40-43] Oxalate, (C₂O₄)²⁻, would also be consistent with this binding energy since the C has the same nominal oxidation state as in CO₂⁻. The XPS data cannot differentiate between these two species. The C 1s feature at 288 eV appears to be associated with the low temperature CO desorption from CO / K / Rh / CeO₂(111) (Figure 10). After annealing to 500 K this feature disappears and is replaced by CO at 285.6 eV and carbonate at 291 eV. The CO binding energy is lower than the binding energy for CO / Rh / CeO₂(111) however the shift is not as great as between CO / Rh and CO / K / Rh (Figure 7) and therefore may not be definitive of a change in adsorption site. Note that the relative intensity of CO₃²⁻ to CO is smaller on K / Rh / CeO₂(111) compared to Rh / K / CeO₂(111) (Figure 9b) at 500 K. This indicates that less of the adsorbed CO interacts with the KO_x to form carbonate at this temperature. At 600 K, after the lower temperature shoulders of

CO and K have desorbed, most of the remaining CO has reacted with the KO_x and formed CO_3^{2-} . Consistent with the TPD, all of the C is removed from the surface at 700 K.

Discussion

The interaction of CO with Rh on K-covered $\text{CeO}_2(111)$ results from the adsorption of CO on the Rh which then spills-over and reacts with KO_x on the ceria. As described in Section 3.1, K reacts with $\text{CeO}_2(111)$ to produce KO_x . This is evident from the K 2p spectra (Figure 2) where the peak positions and line shapes indicate that the K is ionic and not metallic.[6,34] The O 1s spectra (Figure 5) indicate the formation of a new oxide, i.e. one that differs from CeO_2 , and the Ce 3d spectra (Figure 4) indicate that the Ce is reduced, presumably because the K extracts O from the ceria to form KO_x .

The precise stoichiometry of the KO_x is not clear; however the O 1s spectra indicate that only a small amount of K_2O is formed and the O 1s peak at a higher binding energy than CeO_2 is similar to that from K_2O_3 and K_2O_2 . [35] It isn't known whether the KO_x exists as a pure overlayer or whether a mixed oxide, $\text{Ce}_a\text{K}_b\text{O}_2$, might be formed. It also isn't known whether the KO_x forms continuous layers on the ceria or whether it forms islands. No ordered structure was observed in the LEED following K deposition or after annealing at various temperatures to lower the K coverage. Previous experiments have also indicated that the O mobility between the surface and the bulk in the ceria does not occur until above 500 K. [27] Therefore the ceria reduction is probably confined to the surface layers since the K / CeO_2 film is only annealed to 350 K – 400 K before exposure to CO. In the TPD spectra, where the surface is heated to 900 K, presumably O mobility from the bulk plays a role.

CO did not adsorb on KO_x / $\text{CeO}_{2-x}(111)$. Rh particles were needed to provide initial adsorption sites for the CO. When CO is adsorbed on Rh / $\text{CeO}_2(111)$, in the absence of K, the CO demonstrates very little interaction with the $\text{CeO}_2(111)$ support and simply desorbs from the Rh by 600 K (Figure 8a) in a manner similar to CO on Rh(111). When K is deposited before the Rh the C 1s spectra indicate that at 350 K CO on Rh / K / $\text{CeO}_2(111)$ is largely the same as CO on Rh / $\text{CeO}_2(111)$ with CO adsorbed molecularly on the Rh. More CO_3^{2-} is formed on the oxide

due to spillover from the Rh to the oxide when K is present than when it's absent (compare Figure 9a and 9b). However, as the sample is heated additional CO spills-over from the Rh to the KO_x to form carbonate, and CO and CO_2 desorb between 350 K and 550 K. Presumably some of the desorbed CO results from molecular desorption directly from the Rh particle. This is suggested by the overlap of this desorption with the CO that desorbed from Rh / $\text{CeO}_2(111)$ in the absence of K (compare Figures 8a and 8b). The relative amount of $^{13}\text{C}^{18}\text{O}$ to $^{13}\text{C}^{16}\text{O}$ in this temperature range also indicates little loss of ^{18}O in the CO and therefore little interaction with the oxide. However, a large amount of CO_2 is also formed in this temperature range which could only have resulted from a reaction between the CO and the oxide. It isn't known whether this CO_2 formed from a direct reaction between the CO and the oxide or whether it went through a CO_3^{2-} intermediate that then decomposed to CO_2 .

The large CO desorption peak that occurs near 620 K results from the decomposition of carbonate since, based on the C 1s spectra (Figure 9), there is only a small amount of CO present at 500 K and at 600 K carbonate is the only C-containing species on the surface. Interestingly this CO desorbs before the K (Figure 8). This is very different from CO co-adsorbed with K on Rh / Ru(0001) in (Figure 6b) where CO and K stabilize each other and desorbed together at a temperature that is higher than either adsorbed on Rh separately. In the case of CO adsorbed on Rh / KO_x / $\text{CeO}_{2-x}(111)$ the K desorbs at the same temperature as CO_2 . The potassium carbonate therefore appears to decompose in two steps; the first liberates CO leaving KO_x on the surface, the second produces $\text{CO}_2(\text{g})$ and $\text{K}(\text{g})$.

Above the CO_2 desorption peak near 700 K there is no C remaining on the surface but KO_x continues to decompose producing $\text{K}(\text{g})$. In this respect CO / Rh / K / $\text{CeO}_2(111)$ is similar to CO / K / Rh(111). The CO and the K or KO_x form complexes which stabilizes each of them, but when the CO or CO_2 is gone some K remains behind which is then desorbed at higher temperatures.

The formation of CO_2 requires a reaction between CO and the oxidized substrate. Presumably this should reduce Ce^{4+} to Ce^{3+} . No Ce^{3+} was detected in either the Ce 3d or Ce 4d spectra recorded after CO / Rh / K / $\text{CeO}_2(111)$ was annealed to 900 K (data not shown). This observation can be rationalized as resulting from the diffusion of O from deeper layers in the $\text{CeO}_{2-x}(111)$ film which dilutes the Ce^{3+} in the near-surface layers which are sampled by XPS. Similar results have been observed for methanol on oxidized $\text{CeO}_2(111)$ [29] and water on

reduced CeO_{2-x}(111)[27] where single adsorption / desorption cycles do not alter the apparent oxidation state of the Ce despite reactions that remove or deposit O.

The CO reaction and desorption behavior changes dramatically if the K is deposited after the Rh rather than before. When K is deposited after the Rh we assume that the K adheres to both the Rh and the CeO₂ although we don't know if some of the K might have spilled over from the Rh to the ceria. There are two prominent differences in the adsorption and reaction of CO adsorbed on K / Rh / CeO₂(111) (Figure 10) and CO adsorbed on Rh / K / CeO₂(111) (Figure 8b). The CO₂ desorption between 500 K and 700 K is considerably reduced and is replaced by CO desorption. In this way the CO desorption is more similar to CO on K / Rh (Figure 6b). The peak in the CO desorption is closer to the peak in the K desorption although it still precedes it by about ten degrees. Note, however, that the K desorption (blue line) is broad and actually precedes the CO desorption at the lower end.

The second major difference between CO on K / Rh / CeO₂(111) and CO on Rh / K / CeO₂(111) is the low temperature CO desorption that occurs between 200 K and 340 K. This desorption is associated with the C 1s peak at 288 eV (Figure 11) and has been assigned to CO₂⁻. CO₂⁻ has been reported following CO₂ adsorption on K / Cu(110)[41], K / Pd(110)[40], K / Pt(111)[42] and K / Rh (111).[43] The most commonly proposed mechanisms for CO₂⁻ formation involve the transfer of an electron from K to CO₂.

As the surface is heated the CO₂⁻ disproportionates into CO and CO₃²⁻.

The disproportionation is evident in the C 1s spectra (Figure 11) where CO₂⁻ at 200 K is replaced by CO and CO₃²⁻ at 500 K. Following this disproportionation some of the CO immediately desorbs and some remains on the surface to desorb later. The carbonate remains on the surface and decomposes at a higher temperature. Only in the case of CO₂ adsorbed on K / Cu(110) was a new, low temperature CO desorption state near 200 K observed.

In the case of CO adsorbed on K / Rh / CeO₂(111) it appears that the CO reacts with O from the substrate to produce CO₂⁻ upon exposure at 200 K. Two possible mechanisms are that the CO reacts with the substrate to form CO₂ which then binds to K on the Rh to stabilize K⁺CO₂⁻, or that O from the substrate initially reacts with K on the Rh to form KO_x which then reacts with CO to form K⁺CO₂⁻. The current data does not support one mechanism over the other. However, almost all of the CO forms CO₂⁻ upon adsorption on K / Rh / CeO₂(111) at 200 K. Contrast this with CO adsorption on Rh / CeO₂ (Figure 9a) or Rh / K / CeO₂(111) (Figure 9b) where there is no evidence of CO₂ or CO₂⁻ formation. This suggests that CO is reacting with K and O *on* the Rh particle rather than with O still in the substrate at the periphery of the particle.

Note that the weighted ¹³C¹⁸O at 300 K is roughly half the intensity relative to the ¹³C¹⁶O compared to isotopically labeled CO on Rh, K / Rh (Figure 6) or Rh / CeO₂(111) (Figure 8a). This is consistent with the decomposition of (¹⁸O ¹³C¹⁶O)⁻ where half of the ¹⁸O would be lost after random decomposition. In the CO that desorbs at higher temperature the relative amount of ¹³C¹⁸O is even smaller reflecting the dilution of ¹⁸O in (¹³C¹⁸O¹⁶O₂)²⁻.

A remaining question is why CO desorption increases while CO₂ desorption decreases at higher temperature on K / Rh / CeO₂(111) compared to Rh / K / CeO₂(111). This is partly explained by the persistence of molecular CO at 500 K and 600 K (Figure 11) which desorbs directly as CO. In addition, some or all of the carbonate that is formed following the disproportionation of CO₂⁻ may persist on the Rh rather than spill-over onto the KO_x / CeO₂(111). The decomposition of this carbonate may favor CO formation rather than CO₂ formation. Also note that the K desorption isn't completely stabilized by the CO adsorbate (Figure 10). It starts to desorb near 500 K before the CO and CO₂. This may result from KO_x on the ceria that hasn't reacted with CO. Because of the K on the Rh the CO that adsorbs on the Rh stays on the Rh rather spilling over onto the KO_x.

Finally, there is no indication of atomic C produced by CO dissociation in any of the C 1s data. Therefore the mere presence of Ce³⁺ was not sufficient to induce dissociation in the CO adsorbed on the Rh particle. However there are too many other interactions occurring in the present systems that preclude drawing any conclusions as to the role of Ce³⁺ in the dissociation of CO on Rh / CeO_{2-x}(111). The K coverage studied in this work was relatively high therefore the Rh may not have been in contact with the ceria, nor might there have been any ceria exposed at the Rh / oxide interface. Further the interactions between CO / KO_x or CO / K may have been

stronger than any possible interactions between CO / Rh / Ce³⁺. However, there is one significant similarity between CO / Rh / K / CeO₂(111) and CO / Rh / CeO_{2-x}(111). In both cases it was possible for the oxide to affect *all* of the CO adsorbed on the Rh particle. In the case of CO / Rh / K / CeO₂(111) all of the CO forms CO₃²⁻ upon annealing. On Rh / CeO_{2-x}(111) it was possible to dissociate all of the CO, provided the ceria was highly reduced.[24] The formation of CO₃²⁻ can only occur at the periphery of the particles since it requires reaction with O from the substrate. Therefore even the CO that is adsorbed away from the edge can migrate to the edge to react, and the CO that was initially at the edge doesn't block this reaction after it forms CO₃²⁻. This suggests that CO dissociation on Rh / CeO_{2-x}(111) may similarly be an "edge effect" where CO at the periphery reacts with Ce³⁺, or an O vacancy, in the substrate.

Conclusions

K deposited on CeO₂(111) forms a KO_x over-layer by extracting O from the ceria and partially reducing some of the Ce⁴⁺ to Ce³⁺. This surface does not form an ordered structure as detected by LEED. Approximately 13 nm⁻² of KO_x forms before the K no longer reacts with the ceria and multilayer metallic K is deposited. CO does not adsorb on the KO_x / CeO_{2-x}(111) surface without Rh. CO adsorbed on Rh / K / CeO₂(111) adsorbs molecularly on the Rh at 200 K. As the surface is heated the CO spills-over and reacts with the KO_x to form carbonate. The carbonate decomposes at elevated temperature to produce CO and CO₂. The carbonate stabilizes the KO_x so that it desorbs at a higher temperature than it would in the absence of CO. When the Rh and K deposition are reversed so that K is deposited on both Rh and CeO₂(111), CO adsorbs as CO₂⁻ at 200 K. The CO₂⁻ decomposes below 350 K to produce gas phase CO and adsorbed CO₃²⁻ and CO. The CO is stabilized by the K on the Rh and desorbs above 540 K. The carbonate decomposes into gas phase CO and CO₂. The K deposited directly onto the Rh prevents some of the CO from spilling over onto the KO_x. This leaves some of the K on the ceria is unaffected by the CO and enables it to desorb before the C-containing products.

Acknowledgements

This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division. Research carried out in part at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract DEAC02-98CH10886.

References

- [1] W.D. Mross, Alkali Doping in Heterogeneous Catalysis, *Catalysis Reviews-Science and Engineering* 25 (1983) 591-637.
- [2] H.P. Bonzel, Alkali-Metal-Affected Adsorption of Molecules on Metal-Surfaces, *Surface Science Reports* 8 (1988) 43-125.
- [3] J. Kiss, G. Klivenyi, K. Revesz, F. Solymosi, Photoelectron Spectroscopic Studies on the Dissociation of CO on Potassium-Dosed Rh(111) Surface, *Surface Science* 223 (1989) 551-568.
- [4] J.E. Crowell, G.A. Somorjai, The Effect of Potassium on the Chemisorption of Carbon-Monoxide on the Rh(111) Crystal-Face, *Applied Surface Science* 19 (1984) 73-91.
- [5] J.J. Weimer, E. Umbach, D. Menzel, The Properties of K and Coadsorbed CO + K on Ru(001) .1. Adsorption, Desorption, and Structure, *Surface Science* 155 (1985) 132-152.
- [6] J.J. Weimer, E. Umbach, D. Menzel, The Properties of K and Coadsorbed CO + K on Ru (001) .2. Electronic-Structure, *Surface Science* 159 (1985) 83-107.
- [7] J.E. Crowell, W.T. Tysse, G.A. Somorjai, Potassium Coadsorption Induced Dissociation of CO on the Rh(111) Crystal-Surface - an Isotope Mixing Study, *Journal of Physical Chemistry* 89 (1985) 1598-1601.
- [8] M.P. Kiskinova, CO Adsorption on Alkali-Metal Covered Ni(100), *Surface Science* 111 (1981) 584-594.
- [9] L.J. Whitman, W. Ho, The Effects of Surface Geometry and Island Formation on Alkali-Promoted Surfaces - the Coadsorption of CO and K on Ni(110), *Journal of Chemical Physics* 83 (1985) 4808-4816.
- [10] A.T. Bell, Catalytic Synthesis of Hydrocarbons over Group-VIII Metals - a Discussion of the Reaction-Mechanism, *Catalysis Reviews-Science and Engineering* 23 (1981) 203-232.
- [11] M.A. Barteau, Organic reactions at well-defined oxide surfaces, *Chemical Reviews* 96 (1996) 1413-1430.
- [12] R. Lindsay, E. Michelangeli, B.G. Daniels, M. Polcik, A. Verdini, L. Floreano, A. Morgante, J. Muscat, N.M. Harrison, G. Thornton, Surface to bulk charge transfer at an alkali metal/metal oxide interface, *Surface Science* 547 (2003) L859-L864.
- [13] B.E. Hayden, G.P. Nicholson, An Ellipsometric Study of Potassium Adsorption of TiO₂(110), *Surface Science* 274 (1992) 277-286.
- [14] R. Heise, R. Courths, A Photoemission Investigation of the Adsorption of Potassium on Perfect and Defective TiO₂(110) Surfaces, *Surface Science* 331 (1995) 1460-1466.
- [15] M. Wilde, I. Beauport, F. Stuhl, K. Al-Shamery, H.J. Freund, Adsorption of potassium on Cr₂O₃(0001) at ionic and metallic coverages and uv-laser-induced desorption, *Physical Review B* 59 (1999) 13401-13412.
- [16] W. Zhao, G. Kerner, M. Asscher, X.M. Wilde, K. Al-Shamery, H.J. Freund, V. Staemmler, M. Wieszowska, Interaction and diffusion of potassium on Cr₂O₃(0001)/Cr(110), *Physical Review B* 62 (2000) 7527-7534.
- [17] K. Ozawa, K. Edamoto, Photoelectron spectroscopy study of K adsorption on ZnO(1 0 (1)over-bar 0), *Surface Science* 524 (2003) 78-88.
- [18] K. Ozawa, K. Edamoto, Photoelectron spectroscopy study of the K-covered ZnO(1 0 (1)over-bar 0) surface; annealing-induced changes in the electronic structure and the chemical composition, *Surface Science* 547 (2003) 257-267.
- [19] H.H. Huang, X. Jiang, Z. Zou, W.S. Chin, G.Q. Xu, W.L. Dai, K.N. Fan, J.F. Deng, Potassium adsorption and reaction with water on MgO(100), *Surface Science* 412-13 (1998) 555-561.

- [20] H.H. Huang, X. Jiang, Z. Zou, G.Q. Xu, Interaction of atomic hydrogen with potassium on MgO(100), *Surface Science* 376 (1997) 245-253.
- [21] M. Schulze, R. Reissner, Reaction of potassium with thin epitaxial NiO(100) films, *Surface Science* 507 (2002) 851-858.
- [22] J. Stubenrauch, J.M. Vohs, Interaction of CO with Rh supported on stoichiometric and reduced CeO₂(111) and CeO₂(100) surfaces, *Journal of Catalysis* 159 (1996) 50-57.
- [23] J. Stubenrauch, J.M. Vohs, Support effects in the dissociation of CO on Rh/CeO₂(111), *Catalysis Letters* 47 (1997) 21-25.
- [24] D.R. Mullins, S.H. Overbury, CO dissociation on Rh deposited on reduced cerium oxide thin films, *Journal of Catalysis* 188 (1999) 340-345.
- [25] D.R. Mullins, P.V. Radulovic, S.H. Overbury, Ordered cerium oxide thin films grown on Ru(0001) and Ni(111), *Surface Science* 429 (1999) 186-198.
- [26] P.L. Hagans, B.M. Dekoven, J.L. Womack, A Laser Drilled Aperture for Use in an Ultrahigh-Vacuum Gas Doser, *Journal of Vacuum Science & Technology a-Vacuum Surfaces and Films* 7 (1989) 3375-3377.
- [27] L. Kundakovic, D.R. Mullins, S.H. Overbury, Adsorption and reaction of H₂O and CO on oxidized and reduced Rh/CeO_x(111) surfaces, *Surface Science* 457 (2000) 51-62.
- [28] D.R. Mullins, K.Z. Zhang, Metal-support interactions between Pt and thin film cerium oxide, *Surface Science* 513 (2002) 163-173.
- [29] D.R. Mullins, M.D. Robbins, J. Zhou, Adsorption and reaction of methanol on thin-film cerium oxide, *Surface Science* 600 (2006) 1547-1558.
- [30] D.R. Mullins, S.H. Overbury, D.R. Huntley, Electron spectroscopy of single crystal and polycrystalline cerium oxide surfaces, *Surface Science* 409 (1998) 307-319.
- [31] J. Hrbek, M.L. Shek, T.K. Sham, G.Q. Xu, Layer Resolved Spectroscopy of Potassium Adsorbed on a Ru(001) Surface - Photoemission and Thermal-Desorption Study, *Journal of Chemical Physics* 91 (1989) 5786-5792.
- [32] G.H. Rocker, C. Huang, C.L. Cobb, J.D. Redding, H. Metiu, R.M. Martin, The Interaction of Oxygen and Potassium on the Ru(001) Surface, *Surface Science* 250 (1991) 33-50.
- [33] D.A. Shirley, High-Resolution X-Ray Photoemission Spectrum of Valence Bands of Gold, *Physical Review B* 5 (1972) 4709-&.
- [34] G. Pirug, A. Winkler, H.P. Bonzel, Multilayer Growth of Potassium on a Pt(111) Surface, *Surface Science* 163 (1985) 153-171.
- [35] B. Lamontagne, F. Semond, D. Roy, K Overlayer Oxidation Studied by XPS - the Effects of the Adsorption and Oxidation Conditions, *Surface Science* 327 (1995) 371-378.
- [36] M.P. Seah, W.A. Dench, Quantitative electron spectroscopy of surfaces: A standard data base for electron inelastic mean free paths in solids, *Surface and Interface Analysis* 1 (1979) 2-11.
- [37] C.J. Powell, A. Jablonski, I.S. Tilinin, S. Tanuma, D.R. Penn, Surface sensitivity of Auger-electron spectroscopy and X-ray photoelectron spectroscopy, *Journal of Electron Spectroscopy and Related Phenomena* 98 (1999) 1-15.
- [38] F. Strisland, A. Beutler, A.J. Jaworowski, R. Nyholm, B. Setlik, D. Heskett, J.N. Andersen, Adsorption sites in coadsorption systems determined by photoemission spectroscopy: K and CO coadsorbed on Rh(111), *Surface Science* 410 (1998) 330-343.
- [39] P.M. Albrecht, D.E. Jiang, D.R. Mullins, CO₂ Adsorption As a Flat-Lying, Tridentate Carbonate on CeO₂(100), *Journal of Physical Chemistry C* 118 (2014) 9042-9050.

- [40] S.J. Pratt, D.A. King, Coverage dependent promoter action: K coadsorption and reactions with CO and CO₂ on Pd{110}, Surface Science 540 (2003) 185-206.
- [41] E.V. Thomsen, B. Jorgensen, J. Onsgaard, Adsorption and Reactivity of CO₂ on the K/Cu(110) Interface and the Effect of Photon Irradiation, Surface Science 304 (1994) 85-97.
- [42] Z.M. Liu, Y. Zhou, F. Solymosi, J.M. White, Spectroscopic Study of K-Induced Activation of CO₂ on Pt(111), Surface Science 245 (1991) 289-304.
- [43] J. Kiss, K. Revesz, F. Solymosi, Photoelectron Spectroscopic Studies of the Adsorption of CO₂ on Potassium-Promoted Rh(111) Surface, Surface Science 207 (1988) 36-54.

CO / Rh / K / CeO₂(111)

CO / K / Rh / CeO₂(111)