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Support effects in the dissociation of CO on Rh/CeO_2(111)

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The adsorption and reaction of CO on Rh particles supported on stoichiometric and partially reduced CeO_2(111) surfaces was studied using a combination of HREELS and TPD. A fraction of the CO adsorbed on the supported Rh particles was found to undergo dissociation to produce adsorbed C and O atoms. TPD results for isotopically labeled CO demonstrated that O atoms produced by CO dissociation rapidly exchange with the oxygen in the ceria lattice. The fraction of adsorbed CO which dissociated was found to increase significantly with the extent of reduction of the CeO_2(111) surface, suggesting that oxygen vacancies on the surface of the support play a direct role in the CO dissociation reaction.

Keywords: Rh, CeO_2(111), CO dissociation

1. Introduction

TPD and steady-state rate measurements employing Rh/CeO_2 model catalysts have demonstrated that ceria can undergo reduction and supply oxygen for reaction with CO adsorbed on supported Rh particles [1–5]. For example, during TPD of CO from Rh supported on a CeO_2 thin film, Zafiris and Gorte observed that as much as 30% of the adsorbed CO could be oxidized to CO_2 [3]. This ability of ceria to donate oxygen for reaction with CO and hydrocarbons adsorbed on supported metals is thought to be central to its function as a promoter in automotive emissions control catalysts.

The transfer of oxygen from ceria to supported group VIII metals has been shown to be highly structure sensitive. During TPD the fraction of the adsorbed CO oxidized to CO_2 on Rh supported on CeO_2(111) and CeO_2(100) single-crystal surfaces is substantially less than that on polycrystalline ceria supports [2]. It has also previously been shown that reduction of the ceria surface can have a dramatic effect on the interaction of CO with supported Rh. For Rh supported on nearly stoichiometric CeO_2(111) and CeO_2(100) surfaces, during TPD CO desorbs in a single peak centered at 500 K, which is typical of the desorption of CO from bulk Rh [5]. However, upon partial reduction of the CeO_2(111) and CeO_2(100) surfaces a second CO desorption peak appears at 600 K. The intensity of this high-temperature feature correlates with the degree of reduction of the CeO_2 surface. Based on this result and comparison to FTIR studies of CO adsorbed on Rh/polycrystalline ceria [6,7], it has been postulated that the high-temperature CO desorption feature is due to CO species adsorbed at the Rh–CeO_2 interface [5]. In the work reported here we have used HREELS and TPD of isotopically labeled CO to further characterize the nature of the high-temperature CO desorption feature. The results of this study demonstrate that this feature is due to reaction of adsorbed carbon and oxygen atoms produced by dissociation of CO at lower temperatures. Oxygen vacancies on the surface of the ceria support appear to play a direct role in the CO dissociation reaction.

2. Experimental

Experiments were conducted in two separate ultrahigh vacuum surface analysis systems. One system was used primarily for temperature-programmed desorption experiments and contained a quadrupole mass spectrometer (UTI), a LEED/Auger spectrometer (Omicron) and a sputter ion gun. The second system was used for HREELS studies and contained a HREEL spectrometer (LK Technologies), a LEED/Auger spectrometer (OCI), and a sputter ion gun. Both UHV systems were also equipped with evaporative metal deposition sources.

The preparation and mounting of the CeO_2(111) sample was identical to that used previously [5]. Once in vacuum the CeO_2(111) surface was cleaned by sputtering with 500 eV Ar^+ ions for 30 min followed by annealing at 800 K in 1×10^{-7} Torr of O_2 for 1 h. This sputter/anneal cycle was repeated until a clean well-ordered, nearly stoichiometric CeO_2(111) surface was obtained as determined by LEED and AES. In order to obtain a partially reduced CeO_2(111) surface, the stoichiometric surface was sputtered for an additional 15 min with 500 eV Ar^+ ions. It has previously been shown that sputtering preferentially removes surface oxygen and reduces a portion of the surface Ce^{4+} cations to Ce^{3+} [5].

Rhodium was deposited onto both the nearly stoichiometric and partially reduced CeO_2(111) surfaces using an evaporative metal source. The metal source was operated with a Rh flux of 3.5×10^{12} atoms/cm^2 as measured by a quartz crystal film thickness monitor. Rh coverages were measured in monolayers (ML) where one monolayer was assumed to be 1.6×10^{15} atoms/cm^2, the density of atoms in a close-packed plane of Rh. All metal depositions were carried out with the sample at 300 K. It has previously been shown that Rh films grow via the formation of three-dimensional particles on the $CeO_2(111)$ surface [5,8]. The average Rh particle size for a 1.5 ML Rh film on $CeO_2(111)$ has been estimated to be 20 Å [5,8].

Carbon monoxide source gases were contained in lecture bottles that were attached to dosing manifolds that were in turn connected to the UHV systems via variable leak valves. Isotopically labeled $^{13}C^{18}O$ (Isotec Inc., 99.03 at% ^{13}C, 97.3 at% ^{18}O) was used in the CO TPD experiments, while $^{12}C^{16}O$ (Matheson, 99.99%) was used in the HREELS experiments. TPD was performed with a heating rate of 4 K/s.

HREEL spectra were collected using a 4.0 eV electron beam directed 60° from the surface normal with detection in the specular direction. HREEL spectra of the $CeO_2(111)$ surface before and after deposition of 3 ML of Rh are displayed in figure 1. The spectrum of the clean surface (curve a) contains a large peak centered at 542 cm^{-1} which is due to excitation of the surface optical phonon mode of the ceria lattice. The series of smaller losses appearing at integer multiples of the phonon energy are due to multiple excitation of the phonon mode by a single incident electron. The spectrum of the Rh-covered surface (curve b, figure 1) was similar to that of the clean surface except for a 35% decrease in the intensity of the phonon loss due to shielding by the metal overlayer. The lack of complete shielding of the phonon mode demonstrates that the metal film does not completely cover the surface and that the Rh layer grows via particle formation [9,10].

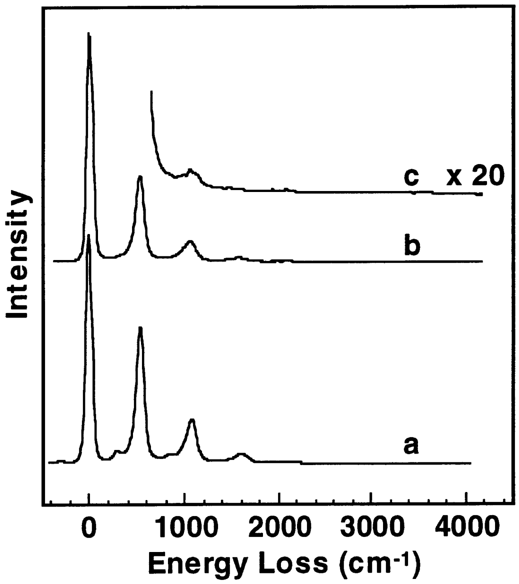

Figure 1. HREEL spectra of $CeO_2(111)$: (a) clean surface, (b) following deposition of 3 ML of Rh, and (c) spectrum in (b) following deconvolution.

Unfortunately, the peaks due to sequential excitation of the substrate phonon mode in the HREEL spectrum of the Rh-covered $CeO_2(111)$ surface obscured the relatively small peaks due to the vibrational modes of adsorbed CO. In order to detect the ν(CO) mode of adsorbed CO, it was therefore necessary to remove the multiple phonon losses from the spectrum. This was done using a Fourier deconvolution procedure that has been previously described in detail [11–15]. Curve c in figure 1 displays the HREEL spectrum of the $CeO_2(111)$ surface covered with 3 ML of Rh following deconvolution.

3. Results and discussion

TPD spectra obtained from a 1.5 ML Rh film supported on the annealed $CeO_2(111)$ surface following exposure to a saturation dose of $^{13}C^{18}O$ at 300 K are displayed in the lower portion of figure 2. The various curves correspond to the desorption spectra for $^{13}C^{18}O$, $^{13}C^{16}O$, $^{12}C^{18}O$, and $^{12}C^{16}O$. As would be expected, the primary gaseous product was $^{13}C^{18}O$ which desorbed in

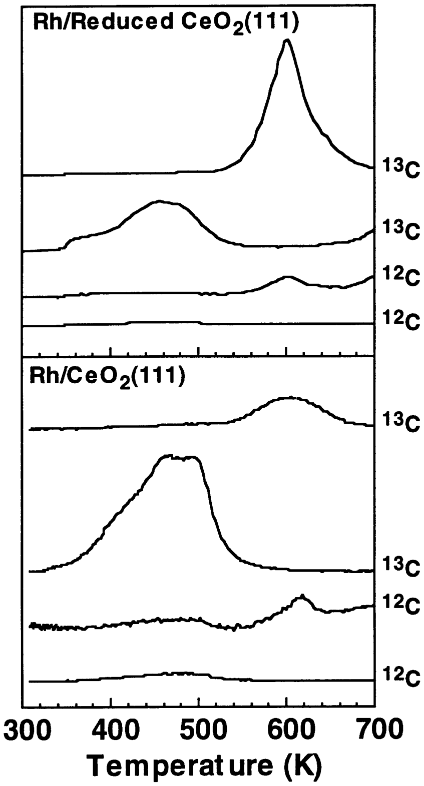

Figure 2. TPD spectra obtained after exposing Rh particles supported on nearly stoichiometric $CeO_2(111)$ (lower panel) and partially reduced $CeO_2(111)$ (upper panel) to a saturation dose of $^{13}C^{18}O$.

a broad peak centered at 480 K. This result is consistent with that reported in our previous study and can be attributed to the desorption of CO from the supported Rh particles. Note that it has been shown that CO does not adsorb on $CeO_2(111)$ under UHV conditions at temperatures above 120 K [5,8]. In addition to the $^{13}C^{18}O$ peak, small peaks for $^{13}C^{16}O$ and $^{12}C^{16}O$ were observed at 600 K. Since $^{13}C^{16}O$ and $^{12}C^{16}O$ desorption did not accompany $^{13}C^{18}O$ desorption at 480 K, these products cannot be attributed to impurities in the $^{13}C^{18}O$ source gas. Thus, the production of $^{13}C^{16}O$ indicates that a small fraction of the adsorbed CO dissociates at low temperature. The resulting adsorbed ^{13}C atoms are apparently reoxidized by ^{16}O from the $CeO_2(111)$ surface at 600 K and then rapidly desorb. The $^{12}C^{16}O$ peak can be assigned to oxidation of a small amount of ^{12}C impurity present on the sample prior to exposure to $^{13}C^{18}O$. In addition to CO, a small amount of CO_2 desorbed during the TPD experiment at temperatures between 400 and 600 K. The fraction of the adsorbed CO which was oxidized to CO_2 was less than 2% which is consistent with our previously reported results [5].

CO TPD results obtained from Rh supported on a partially reduced $CeO_2(111)$ substrate are displayed in the upper portion of figure 2. As was the case for the nearly stoichiometric support, for the partially reduced $CeO_2(111)$ support, $^{13}C^{18}O$ desorbed in a broad peak at 480 K, while $^{13}C^{16}O$ and $^{12}C^{16}O$ desorbed at 600 K. The intensity of the $^{13}C^{16}O$ peak relative to that of the $^{13}C^{18}O$ peak was significantly greater, however, in the TPD data from the reduced $CeO_2(111)$ support. The ratio of the areas of the $^{13}C^{18}O$ peak to that of the $^{13}C^{16}O$ peak was 6.1 for Rh/$CeO_2(111)$ and 0.6 for Rh/reduced-$CeO_2(111)$. The production of $^{13}C^{16}O$ again demonstrates dissociation of CO adsorbed on Rh supported on $CeO_2(111)$. The carbon atoms produced by CO dissociation are reoxidized by oxygen supplied from the CeO_2 lattice upon heating to 600 K.

HREELS was used to characterize the bonding of CO to the supported Rh particles. Figure 3 displays HREEL spectra of the CO-dosed Rh/reduced-$CeO_2(111)$ sample as a function of annealing temperature. As noted above, in order to facilitate the observation of the C–O stretching modes, peaks due to sequential excitation of the phonon mode of the CeO_2 lattice were removed from the spectra using a Fourier deconvolution procedure. Curve a in this figure was obtained immediately following exposure of the sample to a saturation dose of CO at 300 K. This spectrum contains peaks centered at 542 (not shown in the figure), 1080, 1895 and 2020 cm^{-1}. The peak at 542 cm^{-1} is due to the phonon mode of the CeO_2 lattice. The small peak at 1080 cm^{-1} can be attributed to incomplete removal of the double phonon loss during deconvolution. The peaks at 1895 and 2020 cm^{-1} can be assigned to the ν(CO) modes of CO adsorbed in twofold bridging and linear on-top configurations, respectively. These peak positions are in relatively good agreement with those reported for CO adsorbed on single-crystal Rh surfaces [16,17] as well as Rh supported on Al_2O_3 [18,19] and SiO_2 [19]. Note that the presence of the intense phonon loss at 542 cm^{-1} precluded the detection of the low-energy Rh–C stretching mode of the adsorbed CO molecules. Vibrational spectra for CO adsorbed on the Rh/stoichiometric $CeO_2(111)$ sample were nearly identical to those in figure 3.

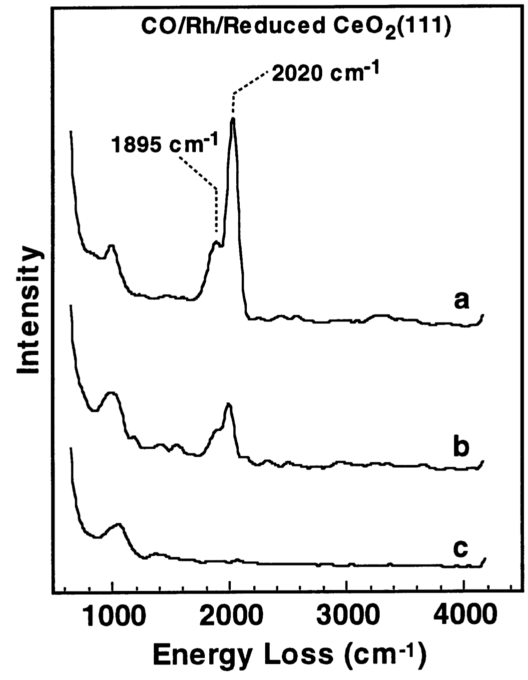

Figure 3. Deconvoluted HREEL spectra of CO-dosed Rh particles supported on partially reduced $CeO_2(111)$ as a function of temperature: (a) 300 K, (b) 450 K, and (c) 580 K.

Spectrum b in figure 3 was obtained after heating the CO-dosed Rh/reduced-$CeO_2(111)$ sample to 450 K. This temperature corresponds to the center of the low-temperature CO desorption feature in the TPD spectrum. Note the decrease in the intensity of the ν(CO) peaks of the bridging and linear CO species, indicating desorption of CO from the surface. Heating the sample to 550 K resulted in the complete disappearance of the C–O stretching modes as shown in spectrum c in figure 3. This temperature falls midway between the low- and high-temperature CO desorption features in the TPD spectra. The lack of a discernible CO stretching mode demonstrates that CO molecules are not present on the surface at this temperature. This result is consistent with the TPD results which indicated that the high-temperature CO desorption feature is due to oxidation of carbon atoms produced by CO dissociation and not due to decomposition of some other surface species such as carbonate. Unfortunately, due to overlap with the phonon peak at 542 cm^{-1}, Rh–O and Rh–C stretching modes could not be observed. Thus, from the HREELS results it is not clear whether the C and O atoms remain on the Rh particles or migrate onto the oxide following CO dissociation.

It is useful to compare the results obtained in the present study with those reported previously for the interaction of CO with both Rh single crystals and supported Rh particles. Although there is some controversy in the literature, it is generally accepted that CO does not dissociate on the low index planes of Rh [16,17,20–23]. In contrast, CO dissociation has been reported for highly stepped Rh surfaces [24–26]. TPD results obtained from these surfaces are similar to those reported here for Rh supported on the nearly stoichiometric $CeO_2(111)$ surface. For example, upon heating CO-dosed Rh(210), the primary CO desorption peak occurs near 450 K, with a much smaller CO peak at 580 K [25]. Based on SIMS analysis, the high-temperature CO desorption feature has been attributed to reaction of adsorbed carbon and oxygen atoms produced by CO dissociation at lower temperatures. Similar SIMS and TPD results have been obtained for the interaction of CO with small Rh particles supported on both MgO and Al_2O_3 [27–29].

The TPD results obtained in the present study provide conclusive evidence for the partial dissociation of CO adsorbed on Rh supported on $CeO_2(111)$. The amount of adsorbed CO which dissociated was 14% for Rh particles supported on the nearly stoichiometric $CeO_2(111)$ surface. This is similar to that reported for the interaction of CO with both stepped Rh single-crystal surfaces [24–26] and Rh supported on MgO and Al_2O_3 [27–29] and suggests that the surface of the $CeO_2(111)$-supported Rh particles have a high concentration of step and defect sites. Furthermore, the isotopic composition of the high-temperature recombinative CO desorption peak demonstrates that following CO dissociation on $Rh/CeO_2(111)$ there is facile exchange of O atoms between the Rh particles and the support. This observation is consistent with previous studies of CO oxidation on Rh/CeO_2 model catalysts which have also demonstrated the transfer of oxygen from ceria to supported Rh particles [1–4]. It has been suggested that this oxygen exchange process may be an important factor in the use of ceria for oxygen storage in automotive emissions control catalysts.

The most interesting result of this study was the dramatic effect that partial reduction of the $CeO_2(111)$ support had on the extent of dissociation of adsorbed CO. For the reduced support, the high-temperature CO desorption peak near 600 K which results from reaction of adsorbed C and O atoms was larger than the low-temperature molecular CO desorption peak at 480 K. Based on the TPD peak areas, for the reduced support 62% of the adsorbed CO underwent dissociation while only 14% underwent dissociation on the oxidized support. There are several possible explanations for this support effect. First, the structure of the Rh particles may depend on the extent of reduction of the $CeO_2(111)$ surface, with those on the reduced surface having a much higher concentration of step and/or defect sites. The available data suggests, however, that this is probably not the case. The total areas of the CO desorption features, obtained from the Rh particles produced by depositing equivalent amounts of Rh on the stoichiometric and reduced $CeO_2(111)$ surfaces were nearly identical. This result demonstrates that the surface area of the Rh particles did not vary significantly with the extent of reduction of the support and implies that the Rh particles had similar morphologies on both the stoichiometric and reduced supports.

The large increase in the extent of CO dissociation upon partial reduction of the $CeO_2(111)$ surface suggests a more direct involvement of the support in this process. It is possible that transfer of oxygen from the supported Rh particles to the $CeO_2(111)$ surface is facilitated by the presence of surface oxygen vacancies. Adsorbed oxygen atoms on the Rh particles produced by dissociation of CO at step sites may diffuse onto the $CeO_2(111)$ surface in order to fill these vacancies. It is also possible that the oxygen vacancies actually comprise part of the active site for CO dissociation. FTIR studies of the interaction of CO on Rh supported on reduced CeO_2 powders have provided evidence for adsorbed CO species that bridge across the Rh–CeO_2 interface [6,7]. In this bonding configuration the carbon end of the molecule is bonded to Rh, while the oxygen end is bonded to Ce^{3+} cations (i.e. oxygen vacancy sites) on the support. The carbon–oxygen bond in these bridging CO species is considerably weaker than that in CO adsorbed exclusively on the metal surface as evidenced by an unusually low C–O stretching frequency of 1695 cm^{-1} [6]. This frequency is in the range characteristic of a carbon–oxygen double bond. The reduction in the CO bond order makes these bridging species prime candidates for dissociation. Note that the HREELS experiments in the present study did not provide any evidence for CO adsorbed at the Rh–CeO_2 interface. Such species may be transient in nature, however, rendering them difficult to observe using HREELS.

4. Conclusions

The results of this study demonstrate that adsorbed CO partially dissociates on Rh supported on $CeO_2(111)$. The fraction of the adsorbed CO which undergoes dissociation was found to vary significantly with the degree of reduction of the $CeO_2(111)$ surface, suggesting that oxygen vacancies on the surface of the support are directly involved in the dissociation reaction. Isotopic labeling studies demonstrated that oxygen atoms produced by dissociation of CO rapidly exchange with the oxygen in the ceria lattice. During TPD adsorbed carbon atoms are reoxidized to CO at 600 K.

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