Isolation and Characterization of Formates on $\text{CeO}_x\text{-Cu}_y\text{O/Cu(111)}$

Kumudu Mudiyanse^{1,2}, Ashleigh E. Baber¹, Zongyuan Liu³, Sanjaya D. Senanayake¹,

Darío J. Stacchiola^{1*}

¹Chemistry Department, Brookhaven National Laboratory Upton, NY 11973

²Department of Science, BMCC-CUNY, New York, NY 10007 (USA)

³Department of Chemistry, University of Stony Brook, Stony Brook, New York 11794

Abstract

Formate species have been proposed to be either critical intermediates or spectators in the water-gas shift (WGS) and methanol synthesis processes. $\text{CeO}_x\text{-Cu}_y\text{O/Cu(111)}$ has been shown to be a very active inverse catalyst for the WGS reaction. We present here the study of formate species obtained from the deprotonation of formic acid (HCOOH) on the inverse catalysts. Exposure of $\text{CeO}_x\text{-Cu}_y\text{O/Cu(111)}$ to HCOOH at 300 K leads to the formation of formates on both ceria and Cu sites. The formates isolated on $\text{CeO}_x\text{-Cu}_y\text{O/Cu(111)}$ systems cannot be hydrogenated even at a pressure of 200 Torr H_2 at 300-350 K. The formate species localized on ceria sites are thermally more stable than those on Cu sites, and the thermal decomposition of all of the formates occurs by dehydrogenation releasing CO_2 and H_2 . Evidence of reverse spillover of formates from the oxide to the metal was observed on $\text{CeO}_{2-x}/\text{Cu(111)}$ inverse catalysts.

*Corresponding author E-mail: djs@bnl.gov

1. Introduction

The isolation and detailed study of surface species involved in catalytic processes is essential for unraveling the mechanism of catalytic reactions. Formate species (HCOO^-) have been associated with both the water-gas shift (WGS) reaction and methanol synthesis. There is continuing debate over the role of formates in these processes based on both experimental and computational results. Experimental and theoretical studies have shown that formate can be either an intermediate or a spectator in the WGS reaction and methanol synthesis[1-7]. A recent review article described that many studies have reported evidence for and against formate-mediated WGS reaction[8]. Small coverages of formate species has been detected by IR spectroscopy during the production of H_2 and CO_2 on highly active WGS catalysts[8]. The non-formation of methanol from the direct hydrogenation of formate, which in this case is suggested to play a spectator role, on copper catalysts was also reported recently[9, 10]. These experimental results combined with density functional theory (DFT) calculations showed a carboxyl species (HOCO) as a common intermediate for both methanol synthesis and reverse WGS. Our recent study identified carboxylate ($\text{CO}_2^{\delta-}$) as a stable surface species during the WGS reaction over inverse $\text{CeO}_x/\text{Cu}(111)$ and $\text{CeO}_x/\text{Au}(111)$ model catalyst systems[11]. Despite these studies, the role of formates in the WGS reaction and methanol synthesis is still not clear. Therefore, the characterization of formate species with respect to the thermal stability and reactivity (hydrogenation) on model systems is essential in order to understand its contribution to the WGS reaction and methanol synthesis.

More recently, we have established the importance of the unique morphology, electronic structure, and oxide nanoparticle-metal interface in the catalytic process by using inverse $\text{CeO}_x/\text{Cu}(111)$ model catalysts[11, 12]. This inverse catalyst consists of oxide nanoparticles supported on a metal substrate, and shows remarkable activity for the WGS and CO oxidation reactions,[12, 13] with rates of reaction much higher than either ceria films or $\text{Cu}(111)$. This effect has been associated with the presence of an oxide/metal interface. Therefore, in this study

we prepared and characterized formates on inverse $\text{CeO}_x\text{-Cu}_y\text{O/Cu(111)}$ model systems. Formic acid (HCOOH) deprotonates to produce formate on oxides, including CeO_2 [14, 15], as well as on Cu surfaces with and without pre-adsorbed O[16-38].

To understand the oxide/metal systems in detail, we first interrogate the metallic substrate. Even though the adsorption of HCOOH and the formation of formates on the (110)[17-30, 39] and (100)[31-38] surfaces of copper have been studied extensively, only a few studies have investigated these processes on the more energetically favored (111)[16, 40-43] surface mainly due to the decreased reactivity for the dissociation of HCOOH compared with the other two copper surfaces. However, it is well known that exposure of O/Cu(111) to HCOOH leads to formates due to the abstraction of the acidic H by chemisorbed O[40, 41]. These previous studies showed only the formation of bidentate formates with C_{2v} symmetry on Cu(111) with or without pre-adsorbed O[16, 40, 42]. Here we provide a detailed characterization of formates on different oxygen-covered Cu(111) systems and report the formation of formate with tilted geometry on $\text{Cu}_2\text{O/Cu(111)}$, which has not been observed on Cu(111).

The formation of formates on powder CeO_x , and $\text{CeO}_x\text{/CuO}$ catalysts, derived from methanol decomposition or during the WGS reaction, has been reported.[44-46] Exposure of $\text{CeO}_x\text{-Cu}_y\text{O/Cu(111)}$ to HCOOH leads to the formation of formates on both ceria and Cu sites. Formates on the surface can be bonded as bidentate (bonding through both O atoms) or monodentate (bonding through one O atom). Bidentate formates include a chelating bidentate where both O atoms are bonded to one surface atom and a bridging bidentate where two O are bonded to two surface atoms[47]. In this study, we identified the bonding configurations of formates on both ceria and Cu sites by infrared reflection absorption spectroscopy (IRRAS). Formates were further characterized with X-ray photoelectron spectroscopy (XPS). In addition, the reactivity of formates with respect to the hydrogenation was tested at elevated H_2 pressures up to ~200 Torr. The thermal decomposition of formates was also investigated by temperature programmed desorption (TPD).

2. Experimental Section

IRRAS experiments were performed in a combined ultra-high vacuum (UHV) surface analysis chamber and elevated-pressure reactor/IRRAS cell system[48]. The UHV system is equipped with Auger electron spectroscopy (AES), low energy electron diffraction (LEED), and TPD techniques. The elevated-pressure cell is coupled to a commercial Fourier transform infrared (FT-IR) spectrometer (Bruker, IFS 66v/S) for IRRAS experiments. The Cu(111) single crystal held tightly using a Ta loop embedded in a groove machined around the crystal edge. The Ta loop was attached directly to the manipulator feed-through which was used for both mechanical support and heating/cooling. The sample temperature was measured by a K-type thermocouple attached to the top edge of the crystal. The Cu(111) sample was cleaned by repeated cycles of Ar⁺ sputtering and annealing to 850 K. The CeO₂-Cu₂O/Cu(111) systems were prepared by vapor deposition of cerium metal in an O₂ atmosphere (1.0×10^{-7} Torr) at 550 K and subsequent oxidation for ~ 10 min. The reduced-ceria (CeO_{2-x})/Cu(111) systems were prepared by the reduction of the oxidized CeO₂-Cu₂O/Cu(111) system with CO at 700 K. These CeO_x-Cu_yO/Cu(111) systems have been well characterized previously by our group using scanning tunneling microscopy (STM)[12, 13, 49]. Formic acid was degassed by several freeze-pump-thaw cycles prior to exposure to the Cu(111) sample by backfilling the IRRAS cell via a precision leak valve. IRRA spectra were collected at 4 cm⁻¹ resolution using a grazing angle of approximately 85° to the surface normal. All of the IR spectra collected were referenced to a background spectrum acquired from the sample prior to its exposure to formic acid. The TPD experiments were performed using UTI 100 C mass spectrometer with 2 K/s linear heating rate.

XPS experiments were conducted at the National Synchrotron Light Source (NSLS) at beamline U12a. This beamline and its UHV end station have been described in detail previously[15]. Sample cleanliness and adsorbate characterization data were collected with synchrotron radiation. The C 1s and O 1s regions were excited at 405 and 615 eV, respectively with 0.3 eV resolution. The binding energies were calibrated relative to the Cu(111) Fermi energy.

3. Results and Discussion

3.1 HCOOH adsorption and reaction on Cu₂O/Cu(111) and O/Cu(111)

In order to obtain insights on the nature of formates formed on Cu sites without ceria, first we prepared and characterized formates on CuO_x systems. Figure 1 shows the IRRA spectra obtained after adsorbing multilayer HCOOH on Cu₂O/Cu(111) at 100 K and subsequent annealing to the specified temperatures. The Cu₂O/Cu(111) is prepared by exposing the Cu(111) surface to ~600 L of O₂ at 650 K[50]. HCOOH multilayers form on Cu₂O/Cu(111) at 100 K, as shown in the top spectrum in Figure 1a, and the peak assignments are given in Table 1. The HCOOH multilayer spectrum is mainly dominated by the C=O stretching $\nu(\text{C=O})$ at 1723 cm⁻¹. After annealing to 150 K, the multilayer desorbs and IR peaks were observed at 777, 1353, 1379, 1555, 1698 and 2923 cm⁻¹. The peaks at 1698, 1555 and 1379 cm⁻¹ can be assigned to the C=O stretching ($\nu(\text{C=O})$), asymmetric OCO stretching ($\nu_{\text{as}}(\text{OCO})$), and in-plane C-H bending ($\delta(\text{C-H})$) modes of HCOOH, respectively. The relatively weak peaks at 777, 1353, and 2923 cm⁻¹ can be attributed to a small amount of formate formed at 150 K. After annealing to 175 K, five peaks are observed at 777, 1364, 1679, 2853 and 2930 cm⁻¹. The peaks at 777, 1364, 2853 and 2930 cm⁻¹ can be assigned to bidentate formate (α -formate) as shown in Table 1 and as reported previously[20, 51]. The structure of the α -formate is shown in Figure 2a. The peak at 1679 cm⁻¹ is due to the C=O stretching mode of the remaining HCOOH co-adsorbed with formate on the surface at 175 K. The results shown in Figure 1a indicate the conversion of HCOOH adsorbed on Cu₂O/Cu(111) at 100 K to formate at 175 K.

Figure 1b shows the IRRA spectra collected after annealing of the multilayer HCOOH to 175 K and higher temperatures. The top spectrum in Figure 1b and the bottom spectrum in Figure 1a are the same. After annealing to 200 K, two new features appear at 1626 and 1566 cm⁻¹. The peak at 1626 cm⁻¹ disappears upon annealing to 325 K whereas the intensity of the peak at 1566 cm⁻¹ increases with annealing temperature and the maximum intensity is

achieved after annealing to 350 K. The peak at 1626 cm^{-1} is most likely due to the C=O stretching, $\nu(\text{C=O})$, of monodentate formate (γ -formate)[20, 51] as shown in Figure 2c. After annealing to 350 K, the peak at 1364 cm^{-1} splits into two features at 1367 and 1355 cm^{-1} . The peak at 1367 cm^{-1} is associated with the peak at 1566 cm^{-1} as shown in the following section and they can be attributed to the tilted bidentate-formate (β -formate) as reported previously for the formates on Ag(111)[51]. The schematic of β -formate with short and long O-Cu bond distances is shown in Figure 2b. The peaks at 1367 and 1566 cm^{-1} are for $\nu_s(\text{OCO})$ and $\nu_{as}(\text{OCO})$ modes of β -formate, respectively. The in-plane C-H deformation $\delta(\text{C-H})$, which is expected around $\sim 1360\text{ cm}^{-1}$, is most likely masked by the $\nu_s(\text{OCO})$ absorption. According to the metal surface selection rule in the IRRAS, the $\nu_{as}(\text{OCO})$ modes of α -formate are not IR active and hence cannot be seen in the IR spectrum[52]. The spectra in Figure 1b show the formation of three types of formates, α , β and γ , following the adsorption of multilayer HCOOH on $\text{Cu}_2\text{O}/\text{Cu}(111)$ at 100 K and subsequent annealing.

Figure 3 shows the IRRA spectra obtained following the adsorption of submonolayer coverages of HCOOH on $\text{Cu}_2\text{O}/\text{Cu}(111)$ and $\text{O}/\text{Cu}(111)$ at 100 K and subsequent annealing to the specified temperatures. Chemisorbed O on Cu(111) ($\text{O}/\text{Cu}(111)$) was obtained by exposing Cu(111) to 100 L of O_2 at 300 K[53, 54]. At the lowest exposure (0.03 L) on $\text{Cu}_2\text{O}/\text{Cu}(111)$, bidentate formate is formed as shown by the peak at 1350 cm^{-1} in the top spectrum in Figure 3a. After increasing the HCOOH exposure to 0.25 L, two peaks appear at 1356 and 1673 cm^{-1} for bidentate formate and HCOOH, respectively. After annealing this HCOOH and bidentate formate layer to 200 K, a weak feature at 1572 cm^{-1} and a shoulder around 1366 cm^{-1} on the peak centered at 1356 cm^{-1} start to appear concomitantly. After annealing to 225 K, the peak centered at 1356 splits into two features at 1366 and 1354 cm^{-1} and the intensity of the peak at 1569 cm^{-1} increases. Upon annealing to 275 K, the peak at 1572 cm^{-1} slightly shifts to 1569 cm^{-1} . With further annealing to higher temperatures, the peaks at 1366 cm^{-1} and 1569 cm^{-1} grow

simultaneously. This data indicates that the peak at 1569 cm^{-1} is associated with the peak at 1366 cm^{-1} and they can be assigned to β -formate as described in the previous section. The maximum intensities of these two peaks are achieved after annealing to 300 K. Further annealing to 350 K, leads to the complete disappearance of the peaks for β -formate at 1366 and 1572 cm^{-1} whereas the peak for α -formate is still present at 1351 cm^{-1} , indicating the slightly higher thermal stability of α -formate than that of β -formate. Upon annealing to 400 K, α -formate decomposes completely. These results clearly show the formation of both α - and β -formate on $\text{Cu}_2\text{O}/\text{Cu}(111)$ after annealing the submonolayer HCOOH adsorbed at 100 K to higher sequential temperatures as indicated in Figure 3a. The results in Figure 3a also show that only α -formate forms initially and then β -formate starts to appear as the temperature increases. An increase in temperature leads to the dissociation of any remaining molecular HCOOH into formates, as well as to the rearrangement of the formates that already exists on the surface. Most likely, both processes contribute to the formation of β -formates. In order to compare the formation of formates on $\text{Cu}_2\text{O}/\text{Cu}(111)$ with that on chemisorbed O on $\text{Cu}(111)$ [$\text{O}/\text{Cu}(111)$], a similar experiment was performed with $\text{O}/\text{Cu}(111)$ as described in the following section.

Figure 3b shows the IRRA spectra obtained after the adsorption of submonolayer coverages of HCOOH on $\text{O}/\text{Cu}(111)$ at 100 K and subsequent annealing to the specified temperatures. Following the adsorption of HCOOH at 100 K, three main peaks are observed at 1363 (with a shoulder at 1344), 2846 , and 2927 cm^{-1} , which can be assigned to bidentate formate as shown in Table 1. The peak at 1363 cm^{-1} becomes sharper after annealing to 150 K. Upon annealing to 175 K, a new feature appears at 1344 cm^{-1} . Further annealing to higher temperatures leads to the gradual decrease of the intensity of the peak at 1363 cm^{-1} and to the increase of the intensity of the peak at 1344 cm^{-1} . After annealing to 225 K, the peak at 1363 cm^{-1} disappears completely and only the peak at 1344 cm^{-1} is present. The intensity of the peak at 1344 cm^{-1} , associated with isolated bidentate formate species [16, 55], decreases

gradually upon annealing to higher temperatures and disappears completely at 400 K due to the complete decomposition of the formate species. The peaks observed at 2846 and 2927 cm^{-1} after annealing to 150 K also shift to 2828 and 2916 cm^{-1} , respectively, upon annealing to higher temperatures. Although the two peaks at 2828 and 2916 cm^{-1} are seen for the α -formate, they are not clearly observed in the α - and β -formate mixed layer as shown in Figure 3a; instead only weak peaks appear in this region most likely due to the interaction between α - and β -formates. Absence of IR peaks in the range 1500-1600 cm^{-1} completely rules out the formation β -formate on the O/Cu(111) surface. The observation of the peak shifts upon annealing to higher temperatures can be attributed to the presence of interactions between the formates and remaining HCOOH on the surface as described in our previous study of formates on Cu(111)[16]. The spectra in Figure 3 shows that the β -formate forms only on the oxidized Cu(111) surface. This conclusion is further supported by the results observed on the system prepared by exposing the Cu(111) to 300 L O_2 at 300 K. Annealing the adsorbed multilayer of formic acid on this oxidized Cu(111) system to 275-300 K also showed a weak peak at 1561 cm^{-1} for β -formate in addition to the peak at 1364 cm^{-1} for α -formate (data not shown). The formation of a small amount of β -formate on this system is due to the presence of oxidized Cu as shown by the peak at 2101 cm^{-1} for adsorbed CO as shown previously[56]. α -formates on Cu(111) can also be obtained by exposing O/Cu(111) to HCOOH at 300 K as shown in the bottom spectrum in Figure 3b. The decomposition of α -formate occurs as dehydrogenation releasing CO_2 and H_2 as shown by TPD (data not shown).

The formation of formates on O/Cu(111) and $\text{Cu}_2\text{O}/\text{Cu}(111)$ was further investigated by using synchrotron-based high resolution XPS (data not shown). Multilayers of HCOOH were condensed onto a O/Cu(111) surface at 90 K. The C 1s region shows one peak for HCOOH multilayers (90 K) at 290.0 eV. After annealing the sample to 175 K, the multilayer HCOOH

desorbed and a peak appeared at 288.0 eV, which can be assigned to the C of formates and remaining HCOOH on the surface. The C 1s peak shifts to 287.5 eV after annealing to 300 K, and can be assigned to formate species [16, 17]. All of the formates completely decompose upon annealing to 500 K. These results indicate that formic acid deprotonates to produce formate species on the surface at 175 K and after annealing to 300 K, all of the formic acid, has either desorbed or converted to formate, which is stable above 400 K. These results are comparable with IRRAS data.

The formation and stability of formates on Cu₂O/Cu(111) were also monitored using XPS (data not shown). Multilayers of HCOOH were condensed onto a Cu₂O/Cu(111) surface at 90 K. The C 1s region shows a broad peak centered at 288.5 eV due to the coadsorption of HCOOH and formate. IRRAS data also show the formation of formate at 100 K, as shown in Figure 3a. After annealing the sample to 175 K, a majority of the multilayer HCOOH desorbed and the peak observed at 287.5 eV can be assigned to the C of formates. Further annealing to higher temperature leads to either desorption of HCOOH or its conversion to formate, and by annealing to 400 K, the majority of the formates have decomposed. These results indicate that formic acid deprotonates to produce formate species on the surface by 175 K and after annealing to 300 K, formic acid has either desorbed or converted to formate which is stable above 400 K. These results are similar to the observed IRRAS data described in the previous section. The above IRRAS and XPS results clearly show that HCOOH deprotonates to form formates following its adsorption on O/Cu(111) and Cu₂O/Cu(111) at ~100 K and subsequent annealing to 300 K. The exposure of Cu₂O/Cu(111) systems to HCOOH at 300 K was also investigated and results are described in the following section.

3.2 Formates on Cu₂O/Cu(111) at 300 K

Figure 4a shows a series of IRRA spectra as a function of HCOOH exposure to the Cu₂O/Cu(111) at 300 K. At the lowest exposure (0.05 L), two peaks appear at 1354 and 1367 cm⁻¹ for $\nu_s(\text{OCO})$ stretching modes of α - and β -formates, respectively. After a 0.1 L exposure, a

peak for $\nu_{as}(\text{OCO})$ stretching of β -formate starts to appear at 1569 cm^{-1} . These three peaks at 1354 , 1367 and 1569 cm^{-1} grow with increasing exposures. At an exposure of 0.4 L , the intensities of the peaks at 1354 and 1367 cm^{-1} are identical but at a 1.3 L exposure the intensity of the peak at 1367 cm^{-1} is larger than that of the peak at 1354 cm^{-1} , indicating that more β -formate than α -formate forms with increased HCOOH exposures. The surface is saturated with formates at 3.7 L , where the $\nu_s(\text{OCO})$ peak of β -formate appears at 1367 cm^{-1} with a shoulder around 1354 cm^{-1} for α -formate. The spectrum obtained after the saturation also shows four peaks at 2849 , 2889 , 2927 and 2967 cm^{-1} for $\nu(\text{C-H})$ and combination bands, $\nu_{as}(\text{OCO}) + \delta(\text{C-H})$, respectively. The spectrum for formates adsorbed on $\text{Cu}_x\text{O}/\text{Cu}(111)$ is also displayed in Figure 4a (bottom spectrum) for comparison. This $\text{Cu}_x\text{O}/\text{Cu}(111)$ sample was prepared by exposing $\text{Cu}(111)$ to 10^6 L of O_2 at 300 K , prior to HCOOH exposure at 300 K . The IRRA spectra for formates prepared on $\text{Cu}_2\text{O}/\text{Cu}(111)$ and $\text{Cu}_x\text{O}/\text{Cu}(111)$ are similar as shown by the two bottom spectra in Figure 4a indicating the formation of α - and β -formates with similar composition regardless of the nature of the oxide layer.

Figure 4b shows a series of IRRA spectra obtained after annealing the saturated formate system (3.7 L HCOOH exposure), as shown by the top spectrum in Figure 4b, to the specified temperatures. Upon annealing to 325 K , no change in the IRRA spectrum is observed whereas annealing to 350 K leads to appearance of a peak at 1354 cm^{-1} , which was seen as a shoulder at lower temperatures, due to the beginning of the decomposition of β -formates. The TPD spectra obtained from the system with the saturation formate coverage, as shown by the top spectrum in Figure 4b, shows the decomposition of formates formed on $\text{Cu}_2\text{O}/\text{Cu}(111)$ as dehydrogenation releasing CO_2 and H_2 (data not shown).

We also investigated the reactivity of formates with respect to their hydrogenation. The formates on $\text{O}/\text{Cu}(111)$ or $\text{Cu}_2\text{O}/\text{Cu}(111)$ cannot be hydrogenated even at 200 Torr H_2 pressure

and 300 K, as shown by the top two spectra in Figure 5, due to the high stability of both α - and β -formates. These results indicate that α - and β -formates may not be an intermediate species in the methanol synthesis over Cu catalysts. This agrees with the results reported for the hydrogenation of formates on supported (Cu/SiO₂) and unsupported Cu catalysts where formates were not hydrogenated even at a H₂ partial pressure of 6 bar[9, 10].

3.3 Formates on ceria films

In order to obtain insights on the nature of formates adsorbed solely on the CeO_x sites, first we performed experiments with a ceria film where ~90 % of the Cu(111) surface is covered by CeO_x. An uncovered fraction of the Cu surface exists as Cu₂O due to the oxidation during the sample preparation. Figure 6 shows the IRRA spectra obtained following the exposure of oxidized-ceria (CeO₂/Cu(111)) film to HCOOH at 300 K and subsequent annealing to the specified temperatures. At 300 K, formic acid dissociatively adsorbs onto the surface to form formates, hence no features appear for molecularly adsorbed HCOOH. At the saturation exposure, three main features appear at 1377, 1362, and 1253 cm⁻¹, as seen in the top spectrum in Figure 6. The features at 1377 and 1362 cm⁻¹ can be assigned to the symmetric O-C-O stretches, $\nu_s(\text{OCO})$, of formates as reported previously for bidentate formates on CeO₂(111)/Ru(0001)[14] and as shown in Table 1. The presence of two symmetric O-C-O stretches in the IR spectrum at 1377 and 1362 cm⁻¹ indicate the formation of two different types of bidentate formates species on the CeO₂/Cu(111) system. The peak at 1253 cm⁻¹ can be assigned to symmetric O-C-O stretches $\nu_s(\text{OCO})$ of monodentate formate as reported previously[54]. In addition, weak features are observed at 2932, 2842, 1610 and 1570 cm⁻¹. The weak peak at 1610 cm⁻¹ can be attributed to either the asymmetric O-C-O stretches, $\nu_{as}(\text{OCO})$, of bidentate formates on reduced ceria (CeO_{2-x}) or the asymmetric O-C-O stretches $\nu_{as}(\text{OCO})$ of monodentate formates. Since this peak disappears simultaneously with the peak for monodentate formate at 1253 cm⁻¹ upon annealing to

375 K, the peak at 1610 cm^{-1} can be assigned tentatively to asymmetric O-C-O stretches $\nu_{\text{as}}(\text{OCO})$ of monodentate formates. The observed frequency separation between asymmetric and symmetric O-C-O stretches ($1610-1253\text{ cm}^{-1} = 366\text{ cm}^{-1}$) agrees with previous studies where it has been reported that the frequency separation should be larger than 250 cm^{-1} for monodentate species[57, 58]. In addition, Li et al. have assigned peaks at 1599 and 1248 cm^{-1} to monodentate formates on bulk ceria[57]. This evidence further supports the assignment of the peaks at 1253 and 1610 cm^{-1} to monodentate formates, which are only observed on the ceria film. Since the Cu(111) surface is not completely covered with CeO_2 , formates can form on Cu_2O sites and the weak peak at 1570 cm^{-1} is due to such formates. The peaks at 2932 and 2842 can be assigned to the combination band ($\nu_{\text{as}}(\text{OCO}) + \delta(\text{C-H})$) and C-H stretches $\nu(\text{CH})$ of formates, respectively. Upon annealing the formate layer to 375 K, the IR features at 1253 , 1570 and 1610 cm^{-1} completely disappear and the two resolved features at 1377 and 1362 cm^{-1} become a single peak at 1377 cm^{-1} with lower intensity. The disappearance of the peak at 1253 and 1610 cm^{-1} upon annealing to 375 K indicates the lower thermal stability of monodentate formates, compared with the bidentate species. This is in agreement with previous studies showing that monodentate formate on bulk CeO_2 is thermally less stable than bidentate formate[57]. All of the peaks completely disappear after annealing to 475 K due to the complete decomposition of formates. Formates have also been stabilized on powder CeO_x/CuO samples and characterized using infrared spectroscopy[44]. Observed peaks for $\nu(\text{C-H})$ and combination bands, $\nu_{\text{as}}(\text{OCO}) + \delta(\text{C-H})$, of formates formed during WGS reaction on ceria sites of powder CeO_x/CuO are similar to those observed on $\text{CeO}_x\text{-Cu}_y\text{O}/\text{Cu}(111)$ in this study[44, 59]. However, the peaks in the range $1300-1600\text{ cm}^{-1}$ for formates on powder CeO_x/CuO systems are overlapped with carbonate features on powder systems; hence a clear peak assignment for formates in the range $1300-1600\text{ cm}^{-1}$ cannot be made on powder systems. The IR peaks observed for formates derived from decomposition of methanol on pure ceria nano-crystals are also similar to the features for formates on ceria sites of $\text{CeO}_x\text{-Cu}_y\text{O}/\text{Cu}(111)$ [43].

Figure 6 also shows the IRRA spectra obtained after exposing HCOOH to a reduced-ceria ($\text{CeO}_{2-x}/\text{Cu}(111)$) film at 300 K and subsequently annealing to the specified temperatures. In the $\text{CeO}_{2-x}/\text{Cu}(111)$ system, approximately 90% of the Cu(111) surface is covered by CeO_{2-x} , and was prepared by reducing the oxidized $\text{CeO}_2/\text{Cu}(111)$ with CO at 700 K. Three peaks at 1610, 1377, and 1297 cm^{-1} are observed following HCOOH exposure to $\text{CeO}_{2-x}/\text{Cu}(111)$ at 300 K. Only very weak features are observed in the C-H stretch region, 2800-3000 cm^{-1} . The peak at 1610 cm^{-1} can be assigned to asymmetric O-C-O stretches whereas the peaks at 1377 and 1297 cm^{-1} are due to symmetric O-C-O stretches of formates. Note that the C-H bending mode, $\delta(\text{C-H})$, may also contribute to the peak at 1377 cm^{-1} . The presence of two symmetric O-C-O stretches in the IR spectrum at 1377 and 1297 cm^{-1} indicates the formation of two different types of bidentate formates species on the $\text{CeO}_{2-x}/\text{Cu}(111)$ system. After increasing the annealing temperatures, the intensities of IR peaks gradually decrease and all the peaks disappear by 525 K due to the complete decomposition of formates.

3.4 Formates on inverse nano- $\text{CeO}_x/\text{Cu}(111)$

Figure 7a shows the IRRA spectra obtained following the exposure of $\text{CeO}_2\text{-Cu}_2\text{O}/\text{Cu}(111)$ to HCOOH at 300 K and subsequent annealing to the specified temperatures. In this nano- CeO_2 system, approximately 15% of the Cu(111) surface is covered by CeO_2 . During the preparation of CeO_2 nanoparticles on Cu(111), the Cu(111) surface is also oxidized to form a Cu_2O -like layer as reported previously[12, 13]. The IRRA spectrum obtained following the formation of formates from HCOOH on $\text{Cu}_2\text{O}/\text{Cu}(111)$ without CeO_2 is also displayed (top spectrum) for comparison. The formates on $\text{Cu}_2\text{O}/\text{Cu}(111)$ show main peaks at 1569 cm^{-1} and 1366 with a shoulder at ~ 1350 . In addition, four weak features are observed in the 2800-3000 cm^{-1} region. The peak at 1569 cm^{-1} can be assigned to tilted bidentate formates (β) whereas the two unresolved features centered at 1366 cm^{-1} are due to both β and α (bidentate formate with C_{2v} symmetry) as described in sections 3.1 and 3.2, and as shown in Figure 2a and 2b. At the lowest

HCOOH exposure (0.2 L) on nano-CeO₂-Cu₂O/Cu(111), two peaks appear at 1372 and 1354 cm⁻¹. As the HCOOH exposure is increased to 0.4 L, an IR peak starts to appear at 1569 cm⁻¹ and it gradually grows with increasing HCOOH exposures. With larger HCOOH exposures, the two features at 1372 and 1354 cm⁻¹ become a single peak at 1364 cm⁻¹ with a shoulder around 1372 cm⁻¹. The peaks at 1372 and 1354 cm⁻¹ can be assigned to the symmetric O-C-O stretches, $\nu_s(\text{OCO})$, of formates. The peak at 1569 cm⁻¹ is assigned to the asymmetric O-C-O stretches, $\nu_{as}(\text{OCO})$, of β formates on Cu sites as described in sections 3.1 and 3.2. The symmetric O-C-O stretches, $\nu_s(\text{OCO})$, of the formates on Cu sites are in the 1343-1367 cm⁻¹ range and overlap with those associated with formates on CeO₂. The structure of the formates on CeO₂ (α_c) is derived from the observed IRRAS spectrum combined with the surface selection rules as described later and is shown in Figure 2d. The C-H stretch region, 2800-3000 cm⁻¹ is complex due to the interactions between different types of formates (α , β and α_c) and has peaks at 2927, 2888 and 2845 cm⁻¹. After annealing the formate layer to 360 K, the peak at 1569 cm⁻¹ completely disappears whereas the peak at 1364 cm⁻¹ splits into two less intense peaks at 1376 and 1350 cm⁻¹. This observation indicates that formates on Cu-related sites are thermally less stable than on CeO₂ sites, and this is further confirmed by the TPD data shown in Figure 7b. After annealing to 400 K, all of the IR features completely disappear due to the complete decomposition of formates in contrast to the formates on CeO₂ films, which are stable to above 450 K, as shown in Figure 6.

The TPD spectra obtained from a system with a saturation coverage of formate species (Figure 7a, 2.0 L HCOOH exposure) on nano-CeO₂-Cu₂O/Cu(111) are displayed in Figure 7b. H₂, H₂O, CO, and CO₂ desorption were monitored in the TPD experiment. In the thermal decomposition of formate, CO₂ desorbs giving a peak at 372 K with a shoulder around 382 K. The low temperature CO₂ desorption feature is associated with the decomposition of formates on Cu sites whereas the high temperature shoulder at ~382 K is due to the decomposition of formates on CeO₂. These observations correlate with the IRRAS data obtained during stepwise

annealing of the formate system to 400 K as shown in Figure 7a. The absence of H₂O and the simultaneous desorption of CO₂ with H₂ indicate the decomposition of formates as dehydrogenation instead of dehydration.

Figure 8 shows the comparison of IRRA spectra for formates formed on nano-CeO₂-Cu₂O/Cu(111), CeO₂/Cu(111) (without Cu₂O), and nano-CeO_{2-x}/Cu(111) systems. The top IRRA spectrum was obtained following the exposure of nano-CeO₂-Cu₂O/Cu(111) to HCOOH at 300 K. The Cu₂O in the nano-CeO₂-Cu₂O/Cu(111) system can be selectively reduced by CO to obtain nano-CeO₂/Cu(111) without Cu₂O as determined by CO adsorption at 120 K. The nano-CeO₂/Cu(111) system without Cu₂O was prepared by the reduction of nano-CeO₂-Cu₂O/Cu(111) with CO ($\sim 2.0 \times 10^{-7}$ Torr for 1 hr. at 700 K). The IRRA spectrum for formates formed on nano-CeO₂/Cu(111) without Cu₂O shows peaks at 1357, 2840 and 2928 cm⁻¹ as shown by the middle spectrum in Figure 8. The peak centered at 1357 cm⁻¹ is due to the formates on CeO₂ and Cu sites whereas the peaks 2840 and 2928 cm⁻¹ are for the formates on metallic Cu sites[16]. This data indicates that formates form on both ceria and metallic Cu sites following the exposure of nano-CeO₂/Cu(111) (without Cu₂O) to HCOOH at 300 K. This data shows that Cu₂O in nano-CeO₂-Cu₂O/Cu(111) is reduced selectively before reducing CeO₂. Further reduction of nano-CeO₂/Cu(111) with CO leads to the formation of nano-CeO_{2-x}/Cu(111). Exposure of the further reduced nano-CeO_{2-x}/Cu(111) system to HCOOH at 300 K leads to the bottom spectrum in Figure 8. Figure 9a shows the IRRA spectra obtained following the exposure of nano-CeO_{2-x}/Cu(111) to HCOOH at 300 K and after annealing the HCOOH-exposed sample to the specified temperatures. In this nano-CeO_{2-x}/Cu(111) system, approximately 15% of the Cu(111) surface is covered by CeO_{2-x}. The IRRA spectrum for the formates on Cu(111) prepared by exposing O/Cu(111) (chemisorbed O on Cu(111) without CeO_x) to HCOOH is also displayed in Figure 9a (top spectrum) for comparison. The formates that formed following the exposure of O/Cu(111) to HCOOH at 300 K show IR peaks at 1343, 2829, and 2917 cm⁻¹, which can be assigned to $\nu_s(\text{OCO})$, $\nu(\text{CH})$ and ($\nu_{as}(\text{OCO}) + \delta(\text{C-H})$) of bidentate (α) formate as described previously in section 3.1 and shown in Table 1. After the

saturation of nano-CeO_{2-x}/Cu(111) with formates, IR peaks appear at 2917, 2829, 1609, 1376, 1343, and 1297 cm⁻¹ as shown by the second spectrum from the top in Figure 9a. The peaks at 1609, 1376, and 1297 cm⁻¹ can be attributed to formates on CeO_{2-x} as described in the previous section. The structure of formates formed on CeO_{2-x} (β_c) is shown in Figure 2e. The peaks at 2917, 2829, and 1343 cm⁻¹ can be assigned to formates on Cu sites by comparison with the spectrum for formates on Cu(111) shown by the top spectrum. Similar peaks were also observed previously for formates formed on Cu(111)[16]. This data indicates that formates are present on both ceria and Cu sites following the exposure of nano-CeO_{2-x}/Cu(111) to HCOOH. After annealing the formate system to 375 K, the IRRA peaks for formates on Cu sites completely disappear whereas almost all of the formates associated with CeO_{2-x} remain on the surface. This observation clearly shows that formates on Cu sites are thermally less stable than that on CeO_{2-x} sites. The formates on CeO_{2-x} completely decompose after annealing to 475 K as shown by the bottom spectrum in Figure 9a. This data also indicates that formates on nano-CeO_{2-x}/Cu(111) are more stable than on nano-CeO₂-Cu₂O/Cu(111) where formates dissociate completely by 400 K (as shown in Figure 7a).

TPD spectra obtained from a system with saturation coverage of formate species are shown in Figure 9b, where H₂, H₂O, CO, and CO₂ desorption were monitored. In the thermal decomposition of formate, CO₂ desorbs showing two peaks at 390 and 430 K. The main desorption species of formates on nano-CeO_{2-x}/Cu(111) is CO₂ in contrast to the decomposition species from formates on ceria film, where dominant species is CO[15, 60]. The TPD data from the formates on ceria films described in section 3.3 also shows CO as a dominant desorption species (data not shown). These results indicate the different mechanism for the decomposition of formates on ceria film and CeO_{2-x} clusters on Cu(111). In Figure 9b, the low temperature CO₂ desorption peak at 390 K is associated with the decomposition of formates on Cu sites whereas the high temperature feature at 430 K is due to the decomposition of formates on CeO_{2-x}. These observations correlate with the IRRA spectra obtained during the stepwise annealing of the formate covered surface from 300 to 475 K as shown in Figure 9a. The absence of H₂O and the

simultaneous desorption of CO_2 with H_2 indicates the decomposition of formates as dehydrogenation instead of dehydration where H_2O and CO desorb together. Similarly to the case of formates on the various Cu surfaces, the formates on ceria cannot be hydrogenated either even at 200 Torr H_2 pressure and 300-350 K, as shown by the bottom two spectra in Figure 5, due to the high stability.

3.5 Reverse spillover of formates from CeO_{2-x} to Cu(111)

In the nano- $\text{CeO}_{2-x}/\text{Cu}(111)$ system formates are formed on both Cu and CeO_x sites as described in the previous section. The formates on Cu sites are most likely located at the proximity of the boundary of CeO_{2-x} nanoparticles due to the following reasons. During the reduction of nano- $\text{CeO}_2\text{-Cu}_2\text{O}/\text{Cu}(111)$ with CO to obtain nano- $\text{CeO}_{2-x}/\text{Cu}(111)$, first Cu_2O reduces to Cu and then CeO_2 reduces to form CeO_{2-x} . Therefore, this nano- $\text{CeO}_{2-x}/\text{Cu}(111)$ system has CeO_{2-x} nanoparticles and exposed metallic Cu areas without any chemisorbed O. On metallic Cu(111) sites, HCOOH cannot be deprotonated to form formates at 300 K as shown previously[16]. Oxygen must be present on the surface to form formate from HCOOH on Cu(111) at 300 K. Even though formates cannot be formed following the exposure of clean Cu(111) to HCOOH at 300 K, the exposure of this nano- $\text{CeO}_{2-x}/\text{Cu}(111)$ to HCOOH leads to the formation of formates on metallic Cu(111) sites, in addition to CeO_{2-x} sites. There are two ways to obtain formates on Cu(111), either O must be available on Cu(111) or the formates formed on CeO_{2-x} (or at the interface) could spill over to Cu(111). Since there is no O on Cu(111) after the CO reduction, as tested by adsorption of CO as a probe molecule, we propose that the O in the CeO_{2-x} nanoparticles or at the interface of $\text{CeO}_{2-x}\text{-Cu}$ abstracts the acidic H from HCOOH to form formates, which then spillover to Cu(111) sites. Therefore, these formates should be located at the proximity of the boundary of CeO_{2-x} nanoparticles. This conclusion is further supported indirectly by the spectra shown in Figure 10, which displays IRRA spectra of formates formed on three different nano- $\text{CeO}_{2-x}/\text{Cu}(111)$ systems with variable degrees of reduction. Two nano- $\text{CeO}_{2-x}/\text{Cu}(111)$ systems were obtained by reducing nano- $\text{CeO}_2\text{-Cu}_2\text{O}/\text{Cu}(111)$ with two different

CO exposures ($\sim 5.0 \times 10^{-6}$ and $\sim 1.0 \times 10^{-6}$ Torr for 1 hour at 700 K, top two spectra). The third system was prepared by exposing the nano-CeO_{2-x}/Cu(111) (after reducing the nano-CeO₂-Cu₂O/Cu(111) with $\sim 1.0 \times 10^{-6}$ Torr of CO for 1 hour at 700 K) to 100 L of O₂ at 300 K to obtain chemisorbed O or O at the interface (bottom spectrum). In these three nano-CeO_{2-x}/Cu(111) systems, formates are present on both copper and ceria sites. The formates on copper sites show IR peaks at ~ 2917 , ~ 2827 and ~ 1342 cm⁻¹ as described in the previous section. As the degree of reduction of nano-CeO_{2-x}/Cu(111) is decreased, the intensities of the IR peaks for formates on Cu sites increase. The relative intensity of the peak at 1342 cm⁻¹, which is attributed to formates on Cu sites, is lower than that of the peak for formates on CeO_{2-x} at 1295 cm⁻¹ on the heavily reduced nano-CeO_{2-x}/Cu(111) system (top spectrum) whereas the relative intensity of the peak at 1342 cm⁻¹ is higher than that of the peak for formates on CeO_{2-x} at 1295 cm⁻¹ on the nano-CeO_{2-x}/Cu(111) system (middle spectrum). In addition, the amount of formates on Cu sites can be increased by adding chemisorbed O (while maintaining the reduced state of ceria) as shown in the bottom spectrum in Figure 10. The data in Figure 10 shows that formates adsorbed on Cu(111) can be obtained from HCOOH at 300 K with the assistance of the O associated with CeO_{2-x} nanoparticles, most likely at the interface.

3.6 XPS Results - formates on nano-CeO_x/Cu(111)

The formation of formate and its stability on nano-CeO₂-Cu₂O/Cu(111) and nano-CeO_{2-x}/Cu(111) was monitored using XPS, and the C 1s spectra are shown in Figures 11a and 11b, respectively. Multilayers of HCOOH were condensed onto a nano-CeO₂-Cu₂O/Cu(111) surface at 90 K. After annealing the HCOOH-exposed nano-CeO₂-Cu₂O/Cu(111) system to 300 K, two peaks were observed at 287.5 and 289.3 eV as shown in Figure 11a, which can be assigned to formates on Cu and ceria sites respectively[11, 16, 60]. At 400 K, a large fraction of formates on Cu sites has decomposed. Upon annealing to 450 K, formates on Cu sites completely decompose, but formates on the ceria sites remain on the surface, indicating the higher thermal stability of formates on ceria sites compared to Cu sites. Similar thermal stability

results were observed for the nano-CeO_{2-x}/Cu(111) system as shown in Figure 11b. Multilayers of HCOOH were condensed onto a nano-CeO_{2-x}/Cu(111) surface at 90 K. After annealing of HCOOH-exposed nano-CeO_{2-x}/Cu(111) system to 300 K, two peaks were observed at 287.5 and 289.3 eV as shown in Figure 11b, which can be assigned to formates on Cu and ceria sites respectively[11, 16, 61]. At 400 K, a large fraction of formates on Cu sites has decomposed. Upon annealing to 500 K, formates on Cu sites completely decompose, but a small amount of formates on ceria sites remain on the surface, indicating the higher thermal stability of formates on ceria sites compared with Cu sites. These results are in agreement to the IRRA data as shown in Figures 7a and 9a and TPD data in Figures 7b and 9b.

3.7 Structures of formates on CeO_x-Cu_yO/Cu(111)

IRRAS has the ability to identify the orientation of formates on the surface through the frequencies and surface selection rules[62]. Sexton has described the four possible point groups for a bidentate copper-formate surface complex and the surface selection rules to identify formate surface species from vibrational spectroscopy[36]. The free formate ion has C_{2v} symmetry that can be reduced upon bonding to a solid surface. The retention of both mirror planes preserves the C_{2v} symmetry and this indicates that the C-H bond must be perpendicular to the surface. Tilting of the C_{2v} axis away from the surface normal in either directions leads to the C_s symmetries (tilting about the molecular plane - $C_s(1)$, tilting along the molecular plane- $C_s(2)$). The symmetry of the adsorbed formate is further lowered to C_1 by tilting the C_{2v} axis randomly in both directions. Table 2 shows the symmetry species of the fundamental internal vibrational modes of formate derived from the various irreducible representations under the possible symmetry groups. According to the metal-surface selection rule, only totally symmetric vibrations (A , A_1 , A'), which have a dynamic dipole moment normal to the surface are infrared active.

Figure 3b shows peaks at 1344, 2828, and 2916 cm^{-1} assigned to $\nu_s(\text{OCO})$, $\nu(\text{CH})$ and $\nu_{as}(\text{OCO})+\delta(\text{C-H})$, respectively for the α -formate (Figure 2a). According to the metal surface selection rule in the IRRAS, the $\nu_{as}(\text{OCO})$ modes of α -formate (Figure 2a) with C_{2v} symmetry are not IR active and hence cannot be seen in the IR spectrum[52]. The observation of the $\nu_{as}(\text{OCO})$ modes at 1569 cm^{-1} (Figure 4) for β -formate indicates the reduction of symmetry to either $C_s(2)$ or C_1 as shown in Figure 2b and as reported previously for the formates on Ag(111).[51] The exact symmetry of β -formate ($C_s(2)$ vs. C_1) cannot be identified only from the observed IRRAS peaks since the failure to observe $\pi(\text{CH})$ may be due to its small dynamic dipole moment ($C(1)$ symmetry) or symmetry restriction ($C_s(2)$ symmetry).

The CeO_2 film shows dominant peaks for formates at 1377, 1362, 1253 cm^{-1} as shown in Figure 6. In addition, weak features are observed at 1610, 1570, 2842 and 2932 cm^{-1} . The peaks at 1377 and 1362 cm^{-1} are assigned to the symmetric O-C-O stretches, $\nu_s(\text{OCO})$, of bidentate formates on CeO_2 related sites. The absence of generally strongly absorbing asymmetric O-C-O stretches, $\nu_{as}(\text{OCO})$, indicates that it and $\delta(\text{CH})$, since they both share the same symmetry under all point groups, are dipole-forbidden in C_{2v} and $Cs(1)$. Therefore, formates on the ceria film must possess C_{2v} or $Cs(1)$ symmetry. The absence of $\pi(\text{CH})$ may be due to either symmetry restrictions (C_{2v} symmetry) or its small dynamic dipole moment ($Cs(1)$ symmetry). Therefore, the absence of $\pi(\text{CH})$ does not indicate that symmetry of formate is C_{2v} . The observation of the weak peak at 2842 cm^{-1} for $\nu(\text{CH})$ indicates the C-H bond must be at least nearly parallel to the surface normal. If formate has a $Cs(1)$ symmetry, most likely the $\nu(\text{CH})$ mode would not be able to be observed in the IR spectrum. Therefore, based on the observed IRRAS data and surface selection rules formates on the ceria film must possess slightly deviated C_{2v} symmetry. This assignment is further supported by the previous results[14] where the Ce-Ce distance in CeO_2

and O-O distance of formate radicals have been used to determine the symmetry of the formates. The nearest neighbor Ce-Ce distance ($3.93 \text{ \AA}$) of $\text{CeO}_2(111)$ is longer than the O-O distance in the formate radical ($2.36 \text{ \AA}$)[14] which causes deviation from C_{2v} symmetry towards $C_s(1)$ symmetry. However, this deviation is not large enough to make the asymmetric O-C-O stretches, $\nu_{\text{as}}(\text{OCO})$, IR active. Based on the above reasons and the previous studies [14, 51] the formates on CeO_2 nanoparticles possess approximately C_{2v} symmetry as depicted in Figure 2d (α_c). The presence of two peaks at 1377 and 1362 cm^{-1} for symmetric O-C-O stretches, $\nu_s(\text{OCO})$, indicates the existence of two different bidentate formate structures on CeO_2 related sites with approximately C_{2v} symmetry. The peaks at 1253 and 1610 cm^{-1} are for monodentate formates (γ_c -formate) on CeO_2 as reported previously[57] and as shown in Figure 2f.

The formates on CeO_{2-x} films show peaks at 1297 , 1377 and 1610 cm^{-1} as shown in Figure 6. The peaks at 1297 and 1377 cm^{-1} are assigned for symmetric O-C-O stretches, $\nu_s(\text{OCO})$, whereas the peak at 1610 cm^{-1} is for asymmetric O-C-O stretches, $\nu_{\text{as}}(\text{OCO})$, of formates on CeO_{2-x} sites. The presence of asymmetric O-C-O stretches, $\nu_{\text{as}}(\text{OCO})$, indicates the reduction of symmetry to either $C_s(2)$ or C_1 . The exact symmetry of formates ($C_s(2)$ vs. C_1) cannot be identified only from the observed IRRAS peaks since the failure to observe $\pi(\text{CH})$ may be due to its small dynamic dipole moment ($C(1)$ symmetry) or symmetry restriction ($C_s(2)$ symmetry). The very weak feature for $\nu(\text{CH})$ indicates that the C-H bond aligns more parallel to the surface. The C-H deformation, $\delta(\text{CH})$, expected at $\sim 1370 \text{ cm}^{-1}$, is probably masked by the $\nu_s(\text{OCO})$ peak at $\sim 1377 \text{ cm}^{-1}$. Based on the above analysis and the previously calculated structure on CeO_{2-x} film on $\text{Ru}(0001)$ [14], the bonding configuration of formates on CeO_{2-x} clusters can be derived as depicted in Figure 2e (β_c -formate). The presence of two peaks at 1377 and 1297 cm^{-1} for symmetric O-C-O stretches $\nu_s(\text{OCO})$ indicates the existence of two different bidentate formate structures on CeO_{2-x} sites.

The IRRA spectrum for formates on the nano-CeO₂ (CeO₂-Cu₂O/Cu(111)) system shows dominant peaks at 1364 and 1569 cm⁻¹ (see Figure 7a). The peak at 1364 cm⁻¹ consists of at least three unresolved features. In addition, weak peaks are also observed in the range 2840-2950 cm⁻¹. The comparison of the spectrum obtained from Cu₂O/Cu(111) indicates that nano-CeO₂-Cu₂O/Cu(111) system has formates on Cu₂O sites in addition to CeO₂ sites. Two types of formates, α and β , formed on Cu₂O/Cu(111), as described in section 3.1 and as shown in Figures 2a and 2b. α -formate with C_{2v} symmetry shows three infrared-active fundamental bands, $\nu(\text{CH})$, $\nu_s(\text{OCO})$, and $\delta(\text{OCO})$ at ~ 2850 , ~ 1350 , ~ 727 cm⁻¹ whereas β formate has two dominant peaks at ~ 1366 , and ~ 1570 cm⁻¹ as reported previously. The weak peaks observed in the range 2840-2950 cm⁻¹ are due to the $\nu(\text{CH})$ and the combination bands. The formates on CeO₂ relates sites on nano-CeO₂-Cu₂O/Cu(111) shows peaks at ~ 1360 and ~ 1375 due to the $\nu_s(\text{OCO})$ stretches of formates, similar to the ceria films. Therefore, formates on CeO₂ in both films and nano particles possess slightly deviated C_{2v} symmetry as depicted in Figure 2d (α_c - formate). The IRRA spectrum for formates on the nano-CeO_{2-x}/Cu(111) system has peaks at 1297, 1343, 1376, 1609, 2829, and 2917 cm⁻¹ as shown in Figure 9a. The comparison of the spectrum for formates on Cu(111) indicates that the nano-CeO_{2-x}/Cu(111) system has formates on Cu(111) sites in addition to that on CeO_{2-x}. The α formates with C_{2v} symmetry formed on Cu(111) following the exposure of O/Cu(111) to HCOOH at 300 K as described in section 3.1 and as shown in Figures 2a. α -formates showed peaks at 1343, 2829 and 2917 cm⁻¹ as shown in Figure 9a. The IR peaks for $\nu_s(\text{OCO})$ stretches of formates on CeO_{2-x} are at 1297, 1376 cm⁻¹ whereas $\nu_{as}(\text{OCO})$ stretches is at 1609 cm⁻¹, similar to the films. Therefore, formates on CeO_{2-x} in both films and nano particles possess similar symmetry as shown in Figure 2e (β_c -formate).

Conclusions

Three types of formates, namely, bidentate with C_{2V} symmetry (α), tilted bidentate (β), and monodentate (γ) are observed on oxidized Cu(111) systems. Only α -formate forms on Cu(111) following the exposure of O/Cu(111) to HCOOH at 300 K whereas both α - and β -formates form on $\text{Cu}_x\text{O}/\text{Cu}(111)$ and $\text{Cu}_2\text{O}/\text{Cu}(111)$. The stabilization of only β -formate on the oxidized Cu systems is attributed to the structural changes of the surface during the oxide formation and the presence of oxide on the surface. Exposure of nano- $\text{CeO}_2\text{-Cu}_2\text{O}/\text{Cu}(111)$ systems to HCOOH at 300 K leads to the formation of formates on both ceria and copper sites. The nano- $\text{CeO}_2\text{-Cu}_2\text{O}/\text{Cu}(111)$ system can be reduced by CO at 700 K to obtain nano- $\text{CeO}_{2-x}/\text{Cu}(111)$. In this process, Cu_2O is preferentially reduced before CeO_2 . Exposure of nano- $\text{CeO}_{2-x}/\text{Cu}(111)$ to HCOOH at 300 K leads to the observation of formates not only on ceria sites but also on Cu sites due to the reverse spillover of formates from CeO_{2-x} to Cu. By varying the reduction conditions the amount of O in the nano- $\text{CeO}_{2-x}\text{-Cu}_y\text{O}/\text{Cu}(111)$ can be altered, and hence the relative amounts of formate species on Cu and ceria sites can be controlled. The bonding configurations of these formates were derived from the results of IRRAS combined with surface selection rules. Formates with slightly deviated C_{2V} symmetry are observed on CeO_2 , whereas on CeO_{2-x} , the symmetry is reduced to $C_s(2)$ or C_1 . The thermal stability of these formates follows the order: formates on Cu sites < CeO_2 < CeO_{2-x} . None of these formates can be hydrogenated even at 200 Torr of H_2 pressure at 300-350 K indicating that formates with adsorption configurations observed here may not be intermediate species in the methanol synthesis over Cu/ceria-based catalysts. The thermal decomposition of all formates occurs as dehydrogenation by releasing CO_2 and H_2 , which indicates that the formate pathway may not be the most efficient, based on theoretical results, but it can contribute to the production of CO_2 and H_2 in the WGS reaction.

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TABLE 1: Vibrational Frequencies (cm⁻¹) and Mode Assignments for HCOOH and HCOO⁻ ^a

Assignments	Formic Acid	Formates (from this work)					
		Cu sites			CeO _x sites		
		α (Cu ⁰)	β (Cu ⁺)	γ (Cu ⁺)	α_c (Ce ⁴⁺)	β_c (Ce ³⁺)	γ_c (Ce ⁴⁺)
$\delta(\text{OCO})$	724	764	~776	obscured			
$\pi(\text{OH})$	971						
$\pi(\text{CH})$	1079						
$\nu(\text{C-O})$	1241						
$\nu_s(\text{OCO})$		1341-1356	1360-1366		1354-1377	~1297	1253
$\delta(\text{C-H})$	1388		obscured			~1377	
$\nu_{as}(\text{OCO})$	1550-1555		1566-1571			~1610	1610
$\nu(\text{C=O})$	1723,1698			1626			
$\nu(\text{OH}) + \nu_{\text{comb}}$	2578, 2742						
$\nu(\text{CH})$	2932	2828-2829	~2889	obscured	2828-2851		
$\nu_{as}(\text{OCO}) + \delta(\text{C-H})$		2917	~2967	obscured	2932-2939		

^aReferences [14, 20, 41, 51, 52, 53, 55]

TABLE 2. Symmetry Species of the Fundamental Internal Modes of Formates

Modes	Symmetry			
	C_{2v}	$C_s(1)$	$C_s(2)$	C_1
$\nu(\text{CH})$	A ₁	A'	A'	A
$\nu_a(\text{OCO})$	B ₁	A''	A'	A
$\nu_s(\text{OCO})$	A ₁	A'	A'	A
$\delta(\text{CH})$	B ₁	A''	A'	A
$\pi(\text{CH})$	B ₂	A'	A''	A
$\delta(\text{OCO})$	A ₁	A'	A'	A

Figure Captions

Figure 1. IRRA spectra obtained after adsorbing HCOOH multilayers on Cu₂O/Cu(111) at 100 K and subsequent annealing to the specified temperatures.

Figure 2. Bonding configurations of formates on CeO_x-Cu_yO/Cu(111) systems. The structure of formates on Cu sites: (a) bidentate (α) with C_{2v} symmetry, (b) tilted formates (β) and (c) monodentate (γ). Formates formed on ceria sites: (d) bidentate (α_c), (b) tilted-bidentate (β_c) and monodentate (γ_c).

Figure 3. A series of IRRA spectra obtained following the adsorption of submonolayer coverage of HCOOH on (a) Cu₂O/Cu(111) and (b) O/Cu(111) at 100 K and subsequent annealing to the specified temperatures. The IRRA spectrum obtained following exposing O/Cu(111) to HCOOH at 300 K (bottom spectrum in b) is also shown.

Figure 4. A series of IRRA spectra obtained (a) following HCOOH exposure to Cu₂O/Cu(111) at 300 K and (b) subsequent annealing to the specified temperatures. The spectrum for the formate prepared by exposing Cu_xO/Cu(111) to HCOOH at 300 K is also displayed in Figure 4a for comparison. The Cu_xO/Cu(111) sample was prepared by exposing Cu(111) to 10⁶ L of O₂ at 300 K

Figure 5. IRRA spectra of formates on Cu₂O/Cu(111) and nano-CeO₂/Cu₂O/Cu(111) obtained before and after exposure to 200 Torr H₂ at 300-350 K.

Figure 6. IRRA spectra obtained following HCOOH exposure to ceria films at 300 K and subsequent annealing to the specified temperatures. The oxidized and reduced ceria films are

shown as $\text{CeO}_2/\text{Cu}(111)$ and $\text{CeO}_{2-x}/\text{Cu}(111)$, respectively. $\sim 90\%$ of the Cu surface is covered with ceria.

Figure 7. (a) IRRA spectra obtained following the exposure of nano- $\text{CeO}_2\text{-Cu}_2\text{O}/\text{Cu}(111)$ to HCOOH at 300 K and subsequent annealing to the specified temperatures. The IRRA spectrum for formates on $\text{Cu}_2\text{O}/\text{Cu}(111)$ (without CeO_2) is also displayed (top spectrum) for comparison. (b) TPD spectra of H_2 , H_2O , CO and CO_2 after exposing nano- $\text{CeO}_2\text{-Cu}_2\text{O}/\text{Cu}(111)$ to 2.0 L HCOOH (saturation coverage of formate species) at 300 K. The corresponding IRRA spectrum is shown in Figure 6a.

Figure 8. Comparison of IRRA spectra of formates formed on nano- $\text{CeO}_2\text{-Cu}_2\text{O}/\text{Cu}(111)$, $\text{CeO}_2/\text{Cu}(111)$, and nano- $\text{CeO}_{2-x}/\text{Cu}(111)$.

Figure 9. (a) IRRA spectra obtained following the exposure of nano- $\text{CeO}_{2-x}/\text{Cu}(111)$ to HCOOH at 300 K and subsequent annealing to the specified temperatures. The IRRA spectrum for formates on $\text{Cu}(111)$ is also displayed (top spectrum) for comparison. (b) TPD spectra of H_2 , H_2O , CO and CO_2 obtained after exposing nano- $\text{CeO}_{2-x}/\text{Cu}(111)$ to 2.0 L HCOOH (saturation coverage of formate species) at 300 K. The corresponding IR spectrum is shown in Figure 8a.

Figure 10. Comparison of IRRA spectra of formates formed following the exposure of nano- $\text{CeO}_{2-x}/\text{Cu}(111)$ systems with different degrees of reduction to HCOOH at 300 K. These reduced-ceria systems were prepared by reducing nano- $\text{CeO}_2\text{-Cu}_2\text{O}/\text{Cu}(111)$ (a) with CO ($\sim 5.0 \times 10^{-6}$ Torr for 1 hour at 700 K) (b) with CO ($\sim 1.0 \times 10^{-6}$ Torr for 1 hour at 700 K) (c) exposing the reduced-ceria system in (b) to 100 L of O_2 at 300 K.

Figure 11. Soft X-ray photoelectron spectra (sXPS) of the C 1s region after annealing the HCOOH-exposed sample, (a) nano-CeO₂-Cu₂O/Cu(111) and (b) nano-CeO_{2-x}/Cu(111) at 90 K, to the specified temperatures.

Figures

Figure 1.

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