How to stabilize highly active Cu^+ cations in a mixed-oxide catalyst

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Abstract

Mixed-metal oxides exhibit novel properties that are not present in their isolated constituent metal oxides and play a significant role in heterogeneous catalysis. In this study, a titanium-copper mixed-oxide (TiCuO_x) film has been synthesized on $\text{Cu}(111)$ and characterized by complementary experimental and theoretical methods. At sub-monolayer coverages of titanium, a Cu_2O -like phase coexists with TiCuO_x and TiO_x domains. When the mixed-oxide surface is exposed at elevated temperatures (600-650 K) to oxygen, the formation of a well-ordered TiCuO_x film occurs. Stepwise oxidation of TiCuO_x shows that the formation of the mixed-oxide is faster than that of pure Cu_2O . As the Ti coverage increases, Ti-rich islands (TiO_x) form. The adsorption of CO has been used to probe the exposed surface sites on the TiO_x - CuO_x system, indicating the existence of a new Cu^+ adsorption site that is not present on $\text{Cu}_2\text{O}/\text{Cu}(111)$. Adsorption of CO on Cu^+ sites of TiCuO_x is thermally more stable than on $\text{Cu}(111)$, $\text{Cu}_2\text{O}/\text{Cu}(111)$ or $\text{TiO}_2(110)$. The Cu^+ sites in TiCuO_x domains are stable under both reducing and oxidizing conditions whereas the Cu_2O domains present on sub-monolayer loads of Ti can be reduced or oxidized under mild conditions. The results presented here demonstrate novel properties of TiCuO_x films, which are not present on $\text{Cu}(111)$, $\text{Cu}_2\text{O}/\text{Cu}(111)$ or $\text{TiO}_2(110)$, and highlight the importance of the preparation and characterization of well-defined mixed-metal oxides in order to understand fundamental processes that could guide the design of new materials.

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1. Introduction

Mixed-metal oxides play a significant role in heterogeneous catalysis[1]. The combination of two or more metal oxides can lead to the synthesis of materials with novel structural and/or electronic properties that differ from their constituent metal oxide components, leading to better catalysts. Several factors can contribute to the novel properties of complex mixed-metal oxide systems, and systematic investigations aiming to the identification of fundamental chemical properties associated with such mixed-metal oxides is critical in order to design new catalysts, enhance the efficiency of existing systems, and unravel the catalytic reaction mechanisms over such active catalysts. Copper and titanium based materials are extensively used as catalysts. We have recently reported the preparation of a TiCuO_x mixed oxide catalyst, which stabilizes Cu^+ cations on the surface of the film and prevents the observed deactivation of Cu-based catalysts during the oxidation of CO at elevated temperatures [2, 3]. In order to clarify the properties of the combined titanium and copper mixed-oxides, we present in this study a detailed characterization of the synthesis of titanium-copper mixed-oxide (TiCuO_x) thin films. We compare the properties of the TiCuO_x film with Cu(111), $\text{Cu}_2\text{O}/\text{Cu}(111)$ and $\text{TiO}_2(110)$. CO is used as a probe molecule for spectroscopic studies. It is found that the top layer of the mixed-oxide film is composed of exclusively Cu^+ cations, and that strong adsorption of CO on these sites can play a significant role in catalytic reactions involving CO such as the water-gas shift reaction (WGSR)[4] and CO oxidation[2]. An increase in the stability of Cu^+ under oxidizing and reducing conditions is also important since copper-based catalysts are used under reducing environments in reactions such as the WGSR[5-7] and the hydrogenation of CO for the synthesis of methanol [8], as well as under oxidizing conditions in CO oxidation,[9-11] epoxidation of hydrocarbons [12-14] and partial oxidation of methanol to formaldehyde[15, 16].

2. Experimental and Theoretical Methods

Infrared reflection absorption spectroscopy (IRRAS) experiments were performed in a combined ultra-high vacuum (UHV) surface analysis chamber and ambient pressure (AP) reactor/IRRAS cell system[17]. The UHV system is equipped with Auger electron spectroscopy (AES), low energy electron diffraction (LEED), and temperature programmed desorption (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) sample was

cleaned with Ar^+ sputtering followed by annealing to 850 K for 15 minutes. The TiCuO_x systems were prepared by the deposition of Ti on $\text{Cu}_2\text{O}/\text{Cu}(111)$, which was obtained by exposing $\text{Cu}(111)$ to 600 L of O_2 at 650 K, at 300 or 650 K in $\sim 5.0 \times 10^{-7}$ Torr O_2 and subsequent oxidation under the same oxygen pressure at 600-650 K for ~ 10 min. The $\text{TiCuO}_x/\text{Cu}(111)$ sample was exposed to CO 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 CO adsorption.

Scanning tunneling microscopy (STM) experiments were carried out in an Omicron variable temperature STM system with a base pressure $< 1 \times 10^{-10}$ Torr. The substrate temperature of $\text{Cu}(111)$ was measured by a K-type thermocouple, which was installed on a linear motion feedthrough and pressed against the top of the sample surface. A resistive heater positioned at the back of the sample could increase the sample temperature up to 1000 K. Chemically etched W tips were used for imaging the surface.

Spin-polarized DFT calculations were performed using a plane-wave basis using the VASP code[18] and the PBE[19] functional. In order to treat the highly localized $3d$ orbitals of Ti and Cu ions, DFT+U[20] with $U_{\text{eff}} = 4.5$ eV for Ti ions and $U_{\text{eff}} = 5.2$ for Cu ions were applied. The reliability of these U_{eff} values was experimentally verified by the XPS/UPS spectra[21]. The interaction between the ionic core and the valence electrons was described by the projector augmented wave method,[22] and the valence electrons with a plane wave basis up to an energy cutoff was 400 eV. The Brillouin zone was sampled at the Γ -point. The convergence criteria for the electronic structure and the geometry were 10^{-4} eV and $0.01 \text{ eV/\AA}$ respectively. The Gaussian smearing method with a finite temperature width of 0.1 eV was used in order to improve convergence of states near the Fermi level. The same model used in our previous study to described $\text{TiCuO}_x/\text{Cu}(111)$ was implemented[2]. The bottom layer of the $\text{Cu}(111)$ was fixed during optimizations and the other atoms were allowed to fully relax.

3. Results and Discussion

3.1 Preparation of $\text{TiCuO}_x/\text{Cu}(111)$

Figure 1 shows STM images obtained during the synthesis of titanium-copper mixed-oxide (TiCuO_x) surfaces. Before the deposition of Ti, a $\text{Cu}(111)$ surface is oxidized to form a

Cu₂O film. Figure 1A shows the image of Cu₂O(111)/Cu(111), which was obtained by exposing Cu(111) to 600 L of O₂ at 650 K[23]. [ENREF 21](#) After the deposition of sub-monolayer doses of Ti on the Cu₂O/Cu(111) film under $\sim 5.0 \times 10^{-7}$ Torr of O₂ at 300 K, well-dispersed titanium clusters (TiO_x) are formed on the surface, and the underlying Cu₂O(111) film is partially reduced. The change in oxidation of the copper oxide film is evident in STM images as the disruption of the well-ordered Cu₂O rows from Figure 1A to the disordered structure underlying the bright TiO_x nanoparticles in Figure 1B. Oxidation of the TiO_x clusters in Figure 1B at elevated temperatures (600 K) in $\sim 5.0 \times 10^{-7}$ Torr of O₂ for ~ 10 min leads to the formation of a TiCuO_x film, with well-ordered terraces as shown by Figure 1C[2]. Figure 1C shows a high resolution STM image of the mixed oxide, which exists on the large terraces in Figure 1D. In addition to a well ordered TiCuO_x phase, titanium rich islands also form as shown by Figure 1D. As the Ti coverage is increased by further deposition, the density of titanium rich islands also increases.

Figure 2 shows the XP spectra of TiO_x-CuO_x/Cu(111) in the Ti 2p, and Cu 2p regions as a function of Ti coverage. These TiO_x-CuO_x/Cu(111) films were prepared by the deposition of Ti on Cu₂O/Cu(111) at 650 K in $\sim 5.0 \times 10^{-7}$ Torr of O₂ and subsequent oxidation under the same oxygen pressure at 650 K for ~ 10 min. The Ti 2p spectra show that Ti is fully oxidized as Ti⁴⁺ under the preparation conditions applied. The corresponding Cu L₃VV Auger spectra in Figure 2C show the presence of Cu⁺ in the TiO_x-CuO_x/Cu(111) systems. Unlike CeO_x/Cu(111),[11] the presence of TiO_x does not induce any further oxidation of the Cu₂O surface under the applied oxidation conditions (5.0×10^{-7} Torr of O₂ pressure and 650 K temperature), based on the total amount of observed oxygen by XPS.

3.2 Adsorption of CO on TiCuO_x/Cu(111)

The adsorption of CO was used to probe the exposed surface sites on the TiO_x-CuO_x/Cu(111) films. IRRAS data from the adsorption of CO on a surface where Ti was deposited at 300 K on the Cu₂O film is shown in Figure 3, and presents two features at 2085 and 2117 cm⁻¹. After the oxidation of this system at 300 K, only one peak appears at 2117 cm⁻¹ for the adsorbed CO on oxidized Cu sites of a disordered Cu₂O film[24, 25]. Oxidation of this system at 650 K with 5.0×10^{-7} Torr of O₂ for ~ 10 min leads to the formation of a TiCuO_x film as shown in Figure 1. The IRRAS data of adsorbed CO on this oxygen-annealed system also gives

two peaks, which are shifted to 2098 and 2128 cm^{-1} . The peak at 2098 cm^{-1} can be assigned to CO adsorbed on Cu^+ of well-ordered $\text{Cu}_2\text{O}(111)$ domains by comparison with the spectrum for the adsorbed CO on $\text{Cu}_2\text{O}/\text{Cu}(111)$ as shown by the top spectrum in Figure 3[26]. The peak at 2128 cm^{-1} is attributed to CO adsorbed on Cu^+ sites on well-ordered TiCuO_x terraces[2] The bottom spectrum in Figure 3 is similar to the spectra obtained from systems prepared by the deposition of Ti on $\text{Cu}_2\text{O}/\text{Cu}(111)$ at 650 K in $\sim 5.0 \times 10^{-7}$ Torr of O_2 and subsequent oxidation under the same oxygen pressure at 650 K for ~ 10 min as shown below in Figures 5 and 7. The results in Figure 3 show that high temperature (600-650 K) oxidation is necessary for the formation of TiCuO_x with sub-monolayer coverages of titanium.

As the coverage of Ti is increased in the synthesis of TiCuO_x films, the intensity of the IRRAS peak of adsorbed CO at 2129 cm^{-1} also increases, as shown in Figure 4, confirming the assignment made above this peak to CO adsorbed on Cu^+ sites from TiCuO_x . At Ti coverages above 75%, a small peak of CO adsorption at higher frequencies is observed, which is related to the formation of TiO_x reach islands as observed by STM. When the surface is fully covered by TiO_x , the weak interaction of CO with this phase prevents its adsorption at temperatures above 90 K.

3.3 Adsorption and thermal desorption of CO on $\text{TiCuO}_x/\text{Cu}(111)$

In order to investigate the thermal stability of CO adsorbed on the $\text{TiCuO}_x/\text{Cu}(111)$ mixed-oxide film, a series of IR spectra were collected as a function of temperature as shown in Figure 5. The IRRA spectrum obtained for the saturated CO adsorption on $\text{Cu}_2\text{O}/\text{Cu}(111)$ is also displayed for comparison as shown by the top spectrum in Figure 5. Following the saturation adsorption of CO on $\text{TiCuO}_x/\text{Cu}(111)$ at 90 K, two peaks appear at 2098 and 2129 cm^{-1} , which can be assigned to CO adsorbed on Cu^+ of $\text{Cu}_2\text{O}(111)$ and TiCuO_x domains respectively, as described in the previous section[2, 26]. The observation of two IRRA peaks at 2098 and 2129 cm^{-1} indicates the presence of TiCuO_x and pure Cu_2O -like phases. The reduced intensity of the peak at 2098 cm^{-1} for the $\text{TiCuO}_x/\text{Cu}(111)$ system with respect to the intensity for pure $\text{Cu}_2\text{O}(111)/\text{Cu}(111)$ is due to the conversion of a fraction of Cu_2O to TiCuO_x . As the temperature is increased, the intensity of the peak at 2098 cm^{-1} for CO adsorbed on Cu^+ sites of pure Cu_2O gradually decreases and the peak completely disappears by 180 K. Similar results were observed for the adsorbed CO on $\text{Cu}_2\text{O}/\text{Cu}(111)$, [26] further confirming the presence of a pure Cu_2O -like

phase in this $\text{TiO}_x\text{-CuO}_x/\text{Cu}(111)$ system. Even though the peak at 2098 cm^{-1} disappears completely at 180 K, the intensity of the peak at 2129 cm^{-1} only decreases slightly indicating a stronger adsorption of CO on Cu^+ sites of TiCuO_x than on Cu_2O . Since the intensity of the peak at 2129 cm^{-1} doesn't change in the temperature range of 180 to 200 K, the slight decrease in intensity observed at 180 K is probably not due to thermal desorption. Most likely, the desorption of the CO molecules associated with the peak at 2098 cm^{-1} leads to the intensity decrease of the peak at 2129 cm^{-1} due to some vibrational coupling between the two species, which results in a moderate intensity transfer from the low frequency to high frequency species[27]. The peak for CO adsorbed on Cu^+ of TiCuO_x disappears completely by 260 K. CO desorbs completely from rutile $\text{TiO}_2(110)$, $\text{Cu}_2\text{O}/\text{Cu}(111)$ and $\text{Cu}(111)$ at $\sim 150\text{ K}$, $\sim 180\text{ K}$ and $\sim 160\text{ K}$, respectively[26, 28]. Therefore, the results in Figure 5 clearly show that CO adsorbs more strongly on TiCuO_x than on either rutile $\text{TiO}_2(110)$ or $\text{Cu}_2\text{O}/\text{Cu}(111)$.

3.4 Adsorption of CO on $\text{TiCuO}_x/\text{Cu}(111)$ – DFT Calculations

On the basis of our previous study,[2] we constructed two different models to describe $\text{TiCuO}_x/\text{Cu}(111)$. The Cu^+ ions in the TiCuO_x film either uniformly locate on the surface layer (Model I, Figure 6a) or partially sink down to the subsurface layer (Model II, Figure 6b). Both surface structures have been observed experimentally for $\text{TiCuO}_x/\text{Cu}(111)$ using STM[2].

For CO adsorption on $\text{TiCuO}_x/\text{Cu}(111)$, three different sites of Cu^+ ions were considered: surface Cu^+ ions using Model I (Figure 6c), subsurface Cu^+ ions using Model II (Figure 6d), and surface Cu^+ ions using Model II (Figure 6e). The variation in the DFT calculated binding energy of CO, is obtained from $E_{\text{bind}} = E(\text{CO}/\text{surf}) - E(\text{surf}) - E(\text{CO})$, with the locations of CO and Cu^+ ion. The strongest binding site for CO is surface Cu^+ ions comprising a hexagonal Cu-motif with the central subsurface Cu^+ ion ($E_{\text{bind}} = -1.37\text{ eV}[\text{PBE} + \text{U}]$, Figure 6e). In comparison, the other two adsorption sites are less stable with E_{bind} of -0.85 eV (Figure 6c) and -1.05 eV (Figure 6d), respectively. In addition, the calculations with and without U_{eff} also influence the results. E_{bind} is lowered by 0.2 to 0.5 eV when going from PBE+U to PBE calculations depending on the structural motif; yet the trend in E_{bind} from one system to the next remains the same. Overall, our DFT calculations show that $\text{TiCuO}_x/\text{Cu}(111)$ is able to provide a lower E_{bind} to CO than $\text{Cu}_2\text{O}(111)$ with E_{bind} of -1.24 eV (PBE+U) according to the previous study[29]. That is, the formation of TiCuO_x film on $\text{Cu}(111)$ produces a new surface Cu^+ species, being able to bind

CO more strongly than that on Cu₂O(111). Our DFT results agree well with the observed experimental data discussed in the previous section.

3.5 Stepwise oxidation of TiO_x/Cu₂O/Cu(111) to form TiCuO_x/Cu(111)

To further investigate the formation of TiCuO_x/Cu(111), we performed experiments by stepwise oxidation of a system prepared by the deposition of a higher load of Ti on Cu₂O/Cu(111) followed by CO adsorption at 120 K as a molecular probe. Figure 7 shows the IRRA spectra collected for the adsorbed CO at 120 K after the oxidation with the indicated O₂ exposures at 650 K. The as-prepared sample shows a peak at 2072 cm⁻¹ for the adsorbed CO on Cu(111)[25, 26, 30] with a weak feature at 2129 cm⁻¹ for the CO adsorbed on Cu⁺ of TiCuO_x indicating the absence of pure Cu₂O-like sites and the presence of only a small coverage of TiCuO_x. These results also show that Ti reduces the Cu₂O layer forming metallic copper by abstracting O from Cu₂O to form TiO_x, consistent with the reduction of the Cu₂O(111) film observed by STM and described above. After oxidation with ~ 15 L of O₂ at 650 K, the intensity of the peak at 2129 cm⁻¹ for CO adsorbed on Cu⁺ of TiCuO_x increases indicating the formation of TiCuO_x domains. As the degree of oxidation is increased further, the intensity of the peak at 2129 cm⁻¹ increases whereas the intensity of the peak at 2072 cm⁻¹ decreases simultaneously. After oxidation with ~ 150 L of O₂ at 650 K, the peak at 2072 cm⁻¹ almost completely disappears. The decrease of the intensity of the peak at 2072 cm⁻¹ is due to the chemisorption of O, which blocks the sites for CO adsorption, and the subsequent formation of the partially reduced Cu₂O “5-7” phase, which correlates with a weak peak at 2038 cm⁻¹ as observed in the inset of Figure 7[26]. In addition to these peaks, a weak feature also appears at ~ 2165 cm⁻¹ as shown in the inset. The peak at ~2165 cm⁻¹ is most likely associated with the formation of titanium rich islands shown in Figure 1, since its frequency is closer to the features for CO on defects of TiO₂(110) and the intensity of this feature grows at higher Ti coverage, but disappears when the surface is completely covered with TiO_x as shown in Figure 4. These results suggest that the peak at ~ 2165 cm⁻¹ is most likely due to the adsorbed CO at the interface between Ti rich islands and the modified Cu-oxides. The system obtained following the oxidation with ~ 300 L of O₂ shows peaks at 2097 and 2129 cm⁻¹ for the CO adsorbed on Cu⁺ sites of Cu₂O and TiCuO_x respectively, as shown by the bottom spectrum in Figure 7. In the stepwise oxidation process, first TiCuO_x forms then further oxidation increases TiCuO_x coverage while forming

Cu₂O as shown by the peak at 2097 cm⁻¹. These results show that the formation of TiCuO_x is faster than that of Cu₂O.

3.6 Stability of TiCuO_x/Cu(111) under reducing and oxidizing conditions

In order to characterize the stability of TiCuO_x films, the reduction of TiO_x-CuO_x/Cu(111) under elevated pressures of CO at 300 K was investigated and the in situ AP-IRRAS results are presented in Figure 8. At 1.0 mTorr of CO pressure, an intense peak appears at 2129 cm⁻¹ for adsorbed CO on Cu⁺ sites of TiCuO_x. As the pressure was increased to 50.0 mTorr, two new features appear at 2094 and 2106 cm⁻¹ due to CO adsorption on Cu⁺ sites of Cu₂O and metallic Cu sites with very low coordination number, respectively, [10] in addition to the gas phase features as reported previously[23]. At a pressure of 100 mTorr, a new peak appears at 2070 cm⁻¹, related to the adsorption of CO on metallic Cu sites with high coordination number on Cu(111) terraces, while the peak at 2094 cm⁻¹ related to Cu₂O domains disappear as the surface is reduced under the CO environment. However, the peak at 2129 cm⁻¹ stays without changing its intensity. At 1.0 Torr of CO pressure, two main peaks at 2129 and 2070 cm⁻¹ are present indicating that the TiCuO_x phase is stable whereas Cu₂O is reduced completely under 1.0 Torr of CO pressure at 300 K. The results in Figure 8 clearly show that Cu₂O in the TiO_x-CuO_x/Cu(111) system can be reduced selectively.

In order to investigate the stability of TiCuO_x under oxidizing conditions, experiments were carried out by exposing the mixed-oxide film to CO + O₂ (1:10) at 300 K. In this experiment CO is also used as a probe molecule. Figure 9 shows the IRRA spectra collected under CO + O₂ (1:10) at 300 K. At 1.0 mTorr of CO pressure, the IRRA spectrum shows a peak at 2128 cm⁻¹ for the adsorbed CO on Cu⁺ of TiCuO_x. After the addition of 10.2 mTorr of O₂, a new feature starts to appear at 2148 cm⁻¹, related to adsorption of CO on Cu²⁺ of CuO[10] and the intensity of this peak gradually increases with time. After 65 min under CO + O₂, the peak at 2148 cm⁻¹ saturates and the peak at 2128 cm⁻¹ stays the same before and after the addition of O₂, indicating that Cu₂O is oxidized to CuO but Cu⁺ of TiCuO_x is stable under the oxidizing conditions applied in this experiment.

4. Conclusions

TiCuO_x thin films can be prepared by depositing Ti on Cu₂O/Cu(111) in 5.0x10⁻⁷ Torr of O₂ at either 300 K or 650 K, followed by oxidation of the mixed-oxide at 600-650 K under the same oxygen pressure for ~ 10 min. TiO_x-CuO_x/Cu(111) systems with sub-monolayer coverages of Ti contain three phases: Cu₂O, TiCuO_x, and TiO_x islands. Formation of the TiCuO_x phase is faster than that of pure Cu₂O phase during the stepwise oxidation of the Ti-deposited Cu₂O/Cu(111) system. CO adsorbs more strongly on TiCuO_x than on rutile TiO₂(110), Cu₂O or Cu(111). Pure Cu₂O can be easily reduced or oxidized under mild conditions, while domains of TiCuO_x are very stable under both the same reducing and oxidizing conditions. These results show the novel properties of titanium-copper mixed-oxides, TiCuO_x, leading to the formation and stabilization of Cu⁺ surface sites, which is the optimal oxidation state of Cu for various oxidation reactions.

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Figure Captions

Figure 1. STM images obtained during the preparation of $\text{TiO}_x\text{-CuO}_x$ by the deposition of Ti on $\text{Cu}_2\text{O/Cu(111)}$ at 300 K and subsequent oxidation at 600 K. (A) $\text{Cu}_2\text{O/Cu(111)}$ before deposition of Ti. (B) After deposition of Ti on $\text{Cu}_2\text{O/Cu(111)}$ at 300 K. (C)-(D) After oxidation at 600 K with $\sim 5.0 \times 10^{-7}$ Torr of O_2 for ~ 10 min.

Figure 2. XP spectra of $\text{TiO}_x\text{-CuO}_x\text{/Cu(111)}$ in the (A) Ti 2p, and (B) Cu 2p regions as a function of Ti coverage. (C) The Cu $\text{L}_{3\text{VV}}$ Auger spectra. The $\text{TiO}_x\text{-CuO}_x\text{/Cu(111)}$ systems were prepared by the deposition of Ti on Cu_2O , which was obtained by exposing Cu(111) to 600 L of O_2 at 650 K in $\sim 5.0 \times 10^{-7}$ Torr of O_2 , at 650 K in $\sim 5.0 \times 10^{-7}$ Torr of O_2 and subsequent oxidation under the same oxygen pressure at 650 K for ~ 10 min.

Figure 3. IRRA spectra obtained following the adsorption of CO after the deposition of Ti on Cu_2O at 300K and the oxidation at 300 and 650 K. The IRRA spectrum obtained from the saturated CO adsorption on $\text{Cu}_2\text{O/Cu(111)}$ is also displayed for comparison as shown by the top spectrum.

Figure 4. IRRA spectra of CO adsorption at 90 K on TiCuO_x thin films as a function of Ti coverage. The IRRA spectrum obtained from the saturated CO adsorption on $\text{Cu}_2\text{O/Cu(111)}$ is also displayed for comparison as shown by the top spectrum. The $\text{TiO}_x\text{-CuO}_x\text{/Cu(111)}$ was prepared by the deposition of Ti on Cu_2O , which was obtained by exposing Cu(111) to 600 L of O_2 at 650 K, at 650 K in $\sim 5.0 \times 10^{-7}$ Torr of O_2 and subsequent oxidation under the same oxygen pressure at 650 K for ~ 10 min.

Figure 5. IRRA spectra obtained following the adsorption of CO on $\text{TiO}_x\text{-CuO}_x\text{/Cu(111)}$ at 90 K and subsequent annealing to the specified temperatures. The IRRA spectrum obtained from the saturated CO adsorption on $\text{Cu}_2\text{O/Cu(111)}$ is also displayed for comparison as shown by the top spectrum. The $\text{TiO}_x\text{-CuO}_x\text{/Cu(111)}$ was prepared by the deposition of Ti on Cu_2O , which was

obtained by exposing Cu(111) to 600 L of O₂ at 650 K, at 650 K in $\sim 5.0 \times 10^{-7}$ Torr of O₂ and subsequent oxidation under the same oxygen pressure at 650 K for ~ 10 min.

Figure 6. DFT calculations of CO adsorption on TiCuO_x/Cu(111). (a), (b): Model surfaces with different Cu⁺ locations. (c)~(e): Location and E_{bind} of CO on each model. The reference E_{bind} for the adsorption of CO on Cu₂O (111) is -1.24 eV[29]. Black hexagonal frame on (a) and (b) represents the surface motif of Cu network.

Figure 7. IRRA spectra obtained following the adsorption of CO at 120 K on as prepared TiO_x-CuO_x/Cu(111) and subsequent stepwise oxidation with the specified O₂ exposures at 650 K. The IRRA spectrum obtained from the saturated CO adsorption on Cu₂O/Cu(111) is also displayed for comparison as shown by the top spectrum. The TiO_x-CuO_x/Cu(111) was prepared by the deposition of Ti on Cu₂O, which was obtained by exposing Cu(111) to 600 L of O₂ at 650 K, at 650 K in $\sim 5.0 \times 10^{-7}$ Torr O₂. Stepwise oxidation was carried out at the specified O₂ exposures at 650 K. The inset in Figure 6 is the expanded view around 2129 cm⁻¹ of the spectrum associated with the system obtained after the oxidation with ~ 150 L of O₂ (second spectrum from the bottom).

Figure 8. IRRA spectra obtained during the reduction of TiO_x-CuO_x/Cu(111) under the specified CO pressures at 300 K. The TiO_x-CuO_x/Cu(111) was prepared by the deposition of Ti on Cu₂O, which was obtained by exposing Cu(111) to 600 L of O₂ at 650 K, at 650 K in $\sim 5.0 \times 10^{-7}$ Torr of O₂ and subsequent oxidation under the same oxygen pressure at 650 K for ~ 10 min.

Figure 9. IRRA spectra collected under CO + O₂ (1:10.2 mTorr) as a function of time at 300 K. All the spectra were collected under the specified pressures. The TiO_x-CuO_x/Cu(111) was prepared by the deposition of Ti on Cu₂O, which was obtained by exposing Cu(111) to 600 L of O₂ at 650 K, at 650 K in $\sim 5.0 \times 10^{-7}$ Torr of O₂ and subsequent oxidation under the same oxygen pressure at 650 K for ~ 10 min.

Figures

Figure 1.

Figure 2.

Figure 3.

Figure 4

Figure 5.

Figure 6

Figure 7.

Figure 8.

Figure 9.