Chapter 4

CO_2 Adsorption on SnO_2 (110) and Cu_2O (111) Surfaces

4.1 Introduction

CO_2 is one of the most common probe molecules used to study surface basicity [1-6]. CO_2 is often viewed as a weak Lewis acid, which probes basic sites due to its electropositive carbon atom [7]. CO_2 can form a variety of surface species on different metal oxides [8]. CO_2 has been shown to form carbonates and physisorbed species on CaO (100) [9], MgO (100) [10,11], TiO_2 (110) [12,13], and ZnO $(000\bar{1})$ surfaces [14]. CO_2 has also been shown to form carboxylates and physisorbed species on Cr_2O_3 (0001) [15] and ZnO (0001) surfaces [14,16-18]. Only physisorbed CO_2 was shown for MnO (100) [8] and NiO (100) surfaces [19]. Little is known about the surface properties of metal oxides that lead to basicity. Surface base sites on metal oxides are typically considered to be electron rich surface oxygen anions, which can donate electronic charge or bind acidic protons to form surface hydroxyl groups [20].

CO_2 adsorption on the well-defined surfaces of SnO_2 (110) and Cu_2O (111) was examined in an attempt to understand the details of the interaction of CO_2 at specific, well-defined sites on an oxide surface. Well-defined SnO_2 (110) and Cu_2O (111) surfaces were used in this study to investigate directly the effects of local site configuration and anion coordination number on CO_2 adsorption and its relationship to basicity.

4.2 Experimental

XPS experiments were run at a pass energy of 200 eV for the C 1s region. Using Ag $3d_{5/2}$ for calibration, a FWHM of 2.1 eV is resolved for a pass energy of 200 eV. A pass energy of 200 eV was used to achieve better signal-to-noise for the carbon 1s feature since carbon 1s has a small x-ray absorption cross section [21].

4.3 Results and Discussion

4.3.1 SnO_2 (110)

Thermal desorption spectroscopy (TDS) was used to study the adsorption of CO_2 on SnO_2 (110) surfaces. On the nearly-stoichiometric and "highly-defective" SnO_2 (110) surfaces, no CO_2 desorption features were detected that could not be attributed to the sample support hardware after CO_2 exposures at 190 K under UHV conditions. On the "reduced" and "less-defective" SnO_2 (110) surfaces, one small desorption feature is observed at 205 K with the exposure of 0.18 L CO_2 at 190 K in UHV. Due to similar CO_2 desorption behavior, the TDS spectrum shown in Figure 4.1 is typical of both these surfaces. For the low temperature (205 K) TDS feature, CO_2 desorption is seen immediately upon heating the surface. The observation suggests that an adsorption temperature of 190 K is not low enough to accommodate a fully-populated low temperature adsorption state. Hence, it is expected that a higher CO_2 coverage could be obtained with a lower adsorption temperature.

X-ray photoelectron spectroscopy (XPS) was used as a check for CO_2 uptake and carbonate formation following CO_2 adsorption on SnO_2 (110) surfaces. Surface carbonates and molecularly adsorbed CO_2 are distinguished in XPS by higher binding

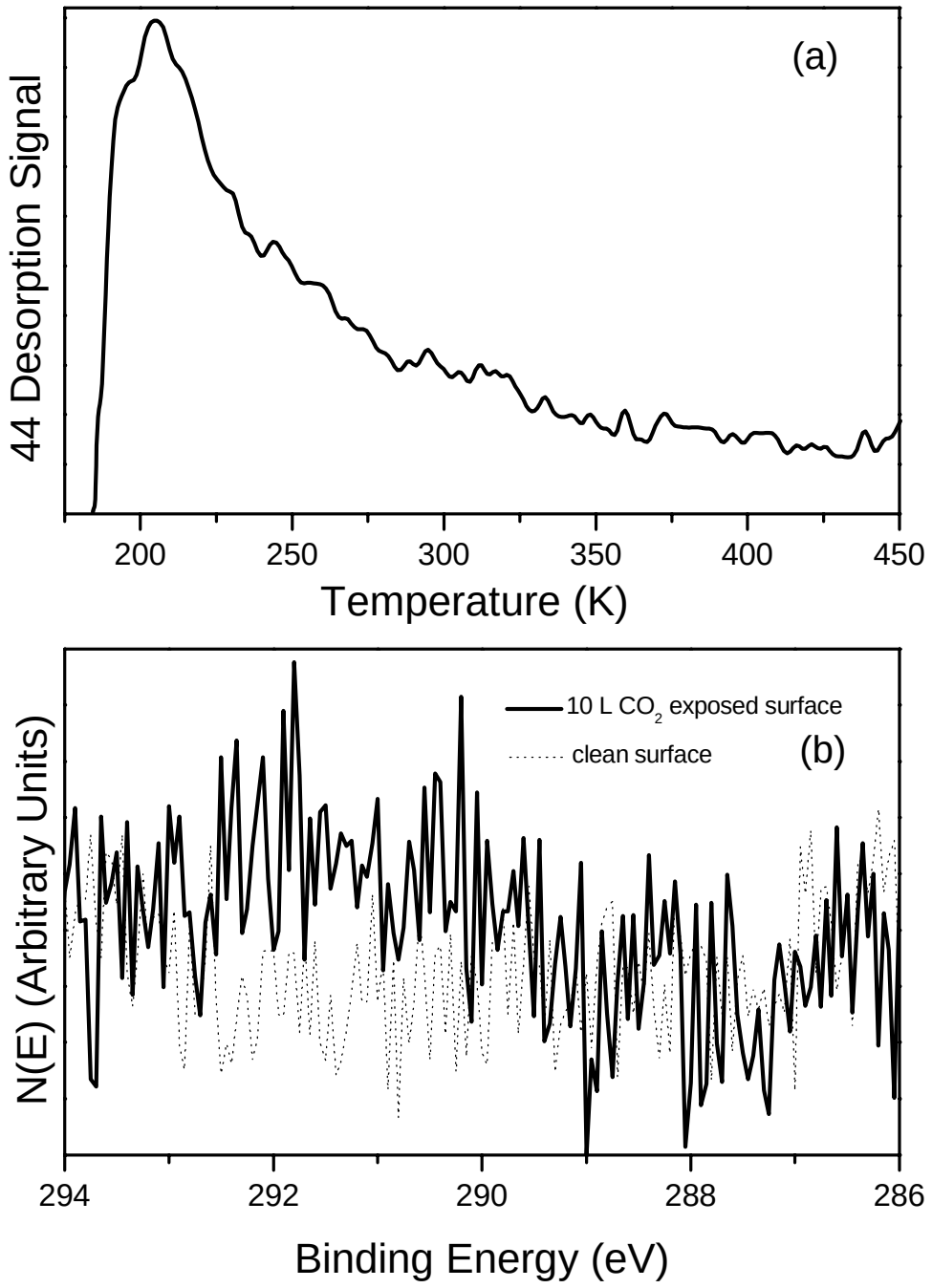

Figure 4.1 (a) Carbon dioxide TDS trace following adsorption for an exposure of 0.18 L CO_2 at 190 K in UHV on a "reduced" SnO_2 (110) surface, and (b) XPS spectra of the C 1s region of the clean "reduced" SnO_2 (110) surface (dotted spectrum) and the "reduced" SnO_2 (110) surface following a 10 L CO_2 exposure at 130 K in UHV (solid spectrum).

energies (289-292 eV) than other forms of surface carbon species reported on other surfaces [22,23]. Carbonates have been reported for Cu (110)-O and ZnO ($10\bar{1}0$) in the range of 289-290.4 eV [24,25]. Physisorbed CO_2 has been reported for Cu (110)-O and ZnO ($10\bar{1}0$) in the range of 291.8-292 eV [24,25]. No apparent C 1s XPS signal is detected following a 10 L CO_2 exposure at 125 K for the "highly-defective" surface and a 10 L CO_2 exposure at 150 K for the nearly-stoichiometric surface. Hence, no indication of CO_2 uptake on these surfaces is seen in XPS in agreement with the TDS results. XPS following a 10 L CO_2 exposure at 130 K for the "reduced" surface and a 10 L CO_2 exposure at 115 K for the "less-defective" surface reveals a small C 1s feature with a binding energy centered around 291.5 eV for each surface. The XPS spectra shown in Figure 4.1 are representative of the results obtained from both the “reduced” and “less-defective” surfaces. The 291.5 eV feature in XPS falls closest to the range of reported binding energies of physisorbed CO_2. Hence, the CO_2 that is associated with the 205 K desorption feature on the "reduced" and "less-defective" surfaces is likely representative of physisorbed CO_2. (Note: The adsorption temperatures of the XPS experiments are lower than those used for the TDS experiments.)

The SnO_2 sample was also exposed to CO_2 in a high-pressure cell at 1 atm total CO_2 pressure. Exposures of 7.6×10^8 to 1.5×10^9 L at 300 K and 370 K were examined in the high-pressure cell. The high temperature and high pressure conditions were used in an attempt to scale any activation barrier that might exist in the formation of a surface carbonate species. After the CO_2 exposures in the high-pressure cell, the sample was moved back to the preparation chamber for TDS runs using the mass spectrometer after the chamber pressure decreased to 1×10^{-9} Torr. On all the different modifications of the

SnO_2 (110) surface, no CO_2 desorption features are detected that could not be attributed to the sample support hardware.

CO_2 physisorbs on the "reduced" and "less-defective" SnO_2 surfaces, but none is seen on the nearly-stoichiometric and "highly-defective" SnO_2 surfaces. One possibility for the difference in behavior is that the lone pair on the Sn^{2+} cations available on the "reduced" and "less-defective" surfaces donates electrons to the carbon atom of the CO_2 molecule. The electron donation is probably small but enough to stabilize a weakly-adsorbed CO_2 species on these surfaces.

4.3.2 Cu_2O (111)

Thermal desorption spectroscopy (TDS) was also used to study the adsorption of CO_2 on Cu_2O (111) surfaces. On the nearly-stoichiometric Cu_2O (111) surface, one small CO_2 desorption feature was detected near 175 K following an exposure of 0.18 L CO_2 at 120 K in UHV (shown in Figure 4.2). TDS runs on the oxygen-deficient $(\sqrt{3}\times\sqrt{3})R30^{\circ}$ surface yields similar results. The TDS spectrum shown in Figure 4.2 is typical for both surface preparations.

X-ray photoelectron spectroscopy (XPS) was used as a check for CO_2 uptake and carbonate formation following CO_2 adsorption on Cu_2O (111) surfaces. No apparent C 1s signal is detected in XPS for a 10 L CO_2 exposure on the nearly-stoichiometric or oxygen-deficient Cu_2O surface at 120 K in UHV (shown in Figure 4.2), suggesting the desorption feature seen in TDS is from a very small coverage.

The Cu_2O sample was also exposed to CO_2 at 1 atm in the high-pressure cell. CO_2 exposures in the range of 7.6×10^{8} to 1.8×10^{11} L were examined at 300 K, 370 K,

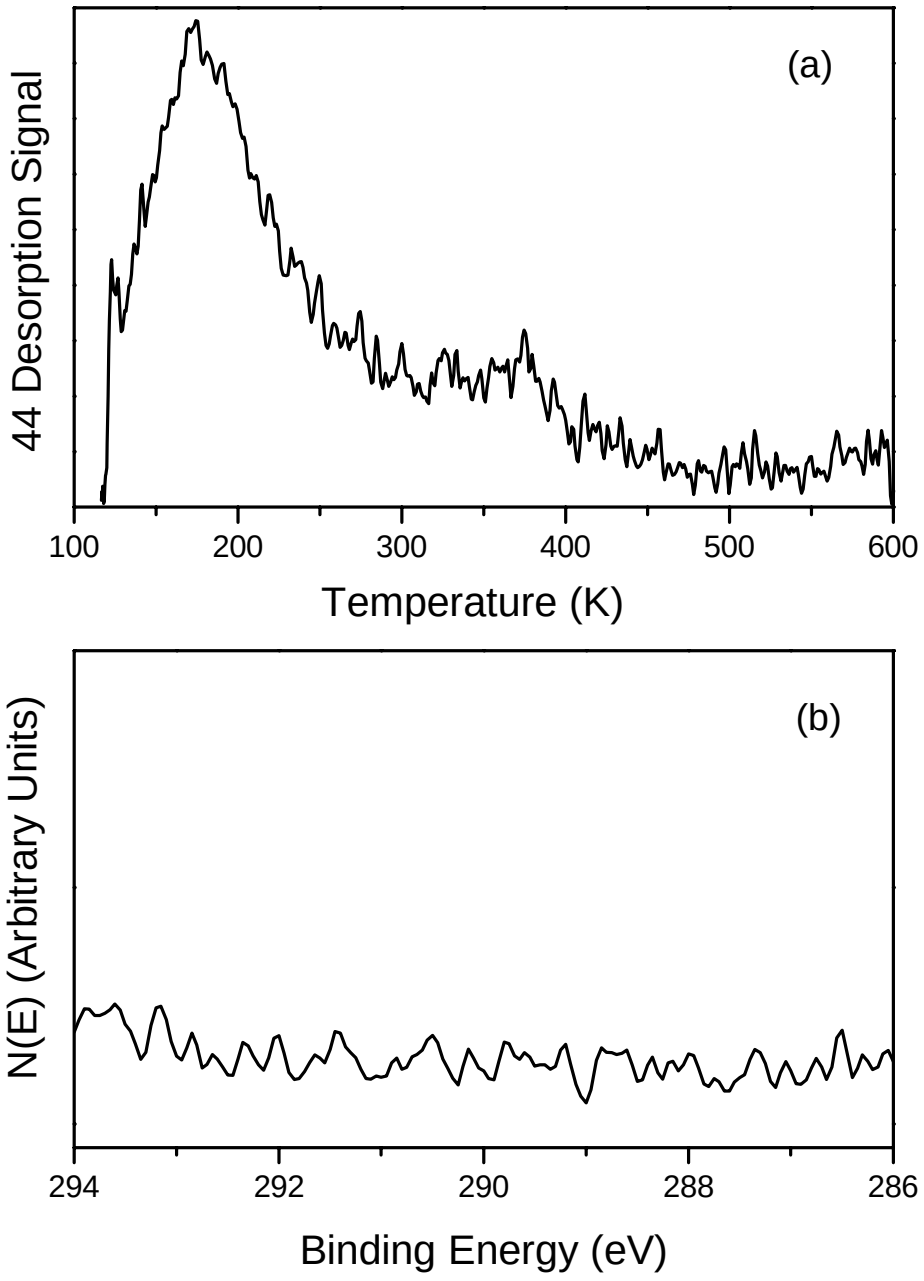

Figure 4.2 (a) Carbon dioxide TDS traces following adsorption for exposures of 0.18 L to 1.43 L at 120 K in UHV on a nearly-stoichiometric Cu_2O (111) surface, and (b) a XPS spectrum of the C 1s region following a 10 L CO_2 exposure at 120 K in UHV on a nearly-stoichiometric Cu_2O (111) surface

420 K, and 470 K in the high-pressure cell. The high temperature and high pressure conditions were used in an attempt to scale any activation barrier that might exist in the formation of a surface carbonate species. After the CO_2 exposures in the high-pressure cell, the sample was moved back to the preparation chamber for TDS runs using the mass spectrometer after the pressure pumped down to 1×10^{-9} Torr. All the observed CO_2 desorption features could be attributed to the sample support hardware.

4.3.3 Implications

The CO_2 uptake is small on SnO_2 (110) and Cu_2O (111) surfaces over a wide range of adsorption temperatures and pressures. No vacuum-stable carbonates are observed on either material. The low temperature CO_2 features seen in TDS can be attributed to very small coverages of physisorbed CO_2 or CO_2 adsorbed at defect sites on SnO_2 (110) and Cu_2O (111) surfaces. Like the metal oxide surfaces MnO (100) [8] and NiO (100) [19], no stable CO_2 species was formed on SnO_2 (110) or Cu_2O (111) surfaces. In previous studies involving polar ZnO (0001) surfaces, the lack of reactivity on the O-terminated polar surface was attributed to the absence of accessible cation/anion pairs [26]. Cu_2O and SnO_2 surfaces have cation/anion pairs that are always available; hence the lack of a stable carbonate species cannot be related to the site pair accessibility. Given the lack of formation of a stable carbonate species and the small uptake of physisorbed CO_2 on SnO_2 (110) and Cu_2O (111), it is clear that CO_2 is a poor probe molecule for characterizing the properties of these surfaces.

The lack of a stable CO_2 species present on SnO_2 (110) and Cu_2O (111) surfaces is somewhat surprising. CO_2 adsorption on SnO_2 powders at room temperature has been

studied using infra-red spectroscopy (IR), and the spectra indicate that CO_2 forms a stable unidentate surface carbonate on SnO_2 powders [27]. Cluster and periodic ab intio calculations on the adsorption of CO_2 on the nearly-stoichiometric SnO_2 (110) surface predict that CO_2 is chemisorbed on the bridging oxygens in a metastable state in the limit of zero coverage [28]. As the CO_2 coverage increases, the calculations predict the formation of chemisorbed CO_2 on the nearly-stoichiometric surface becomes unfavorable due to adsorbate-adsorbate repulsions [28]. In IR studies of CO_2 on CuO powders, CO_2 was found to only weakly adsorb on CuO supported by SiO_2 [29]. In another IR study of CO_2 on CuO powders, the formation of a carbonate complex is speculated with the possibility of defects in the oxide lattice causing individual lines to appear in the IR spectrum [30].

These single crystal surfaces are not as complex as true powder or supported catalysts, but the availability of defects (like oxygen vacancies) might have been expected to give a significant reactivity with CO_2. While these results are surprising, they are similar to other studies of CO_2 adsorption on other single crystal oxide surfaces such as ZnO (0001), ZnO $(000\bar{1})$, CeO_2 (111), MgO (100), TiO_2 (110), YSZ (100) (YSZ = yttria-stabilized zirconia), and YSZ (110) [31]. It appears that a significant interaction of CO_2 with well-defined oxide surfaces like Cr_2O_3 $(10\bar{1}2)$ is the exception rather than the rule.

4.4 Conclusions

On SnO_2 (110) and Cu_2O (111) surfaces, no evidence of any vacuum-stable carbonate species was seen in TDS or XPS. CO_2 is a poor probe molecule for examining these surfaces.

4.5 References

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