Chapter 8
Summary, Overall Conclusions and Recommendations For Future Work

8.1 Summary

Acid/Base characterizations of metal oxide surfaces have been used often to explain the catalytic behavior of oxide materials. However, the vast majority of these studies have been performed on powders or supported oxides, and there is very little information available in the literature on the interaction of acid/base probe molecules with well-defined oxide surfaces of known coordination geometry and oxidation state. The well-defined, single crystal surfaces of Cu_2O (111), SnO_2 (110) and Cr_2O_3 $(10\bar{1}2)$ were investigated for their acid/base properties in ultra-high vacuum.

NH_3 was used as a probe of the Lewis acidity of cation sites on SnO_2 (110) and Cu_2O (111) surfaces. NH_3 appears to be a good probe of Sn cations on SnO_2 (110) surfaces. Based on NH_3 heats of adsorption, four-coordinate Sn^{2+} cations at bridging oxygen vacancies on the “reduced” surface appear to be more acidic than five-coordinate Sn^{4+} cations. The stronger interactions with Sn^{2+} cations are attributed to a predominant covalent contribution to the NH_3-Sn bond. The Lewis acidity of the Sn cations based on NH_3 heats of adsorption goes through a maximum with the formation of a "reduced" surface, and a similar trend is seen in the extent of dissociation of methanol. Four-coordinate Sn^{2+} cations form stronger covalent bonds with NH_3 and methanol, most likely due to a greater molecular overlap between the empty 5sp states and the lone pairs available on NH_3 and methanol. The introduction of in-plane oxygen vacancies on the

"highly-defective" surface reduces the heats of adsorption of the associated cations possibly due to a higher electronic charge density around the cations associated with in-plane oxygen vacancies.

The Lewis acidity of Cu_2O (111) has also been investigated using NH_3 as a probe molecule. NH_3 undergoes reversible molecular adsorption on Cu_2O (111) surfaces with no dissociation observed, and bonds to the surface Cu^+ cations at low coverage via the nitrogen lone pair of the molecules, accompanied by a transfer of electrons to the surface Cu^+ cations. Unlike the case of NH_3 adsorption on SnO_2 (110) surfaces where different cation sites can be distinguished in TDS, no differences are observed in TDS for NH_3 adsorption on the nearly-stoichiometric and $(\sqrt{3}\times\sqrt{3})R30^o$ Cu_2O (111) surfaces. The lack of variation seen while using NH_3 as a probe of acidity of Cu^+ cations suggests the sites around the oxygen vacancies on the $(\sqrt{3}\times\sqrt{3})R30^o$ surface are of either equal or less acidity than the Cu^+ sites on the nearly-stoichiometric surface.

CO_2 was used as a probe of Lewis basicity (oxygen anions) on Cr_2O_3 $(10\bar{1}2)$, SnO_2 (110), and Cu_2O (111) surfaces. On Cr_2O_3 $(10\bar{1}2)$, CO_2 interacts primarily with cation/anion site pairs to form bidentate carbonates that are stable at room temperature. These sites are associated with five-coordinate Cr^{3+} cations and three-coordinate O^{2-} anions on the stoichiometric, non-polar $(10\bar{1}2)$ surface. Terminating the surface cations with chromyl oxygen (Cr=O) via dissociative O_2 chemisorption prevents this interaction and gives rise to a weakly-bound CO_2 moiety, tentatively identified as a monodentate carbonate. Differences in coordination of these carbonate species make the heats of adsorption a poor measure of the basicity of surface oxide ions. Terminating the surface cations with chlorine adatoms completely blocks the interaction between CO_2 and the

surface. On SnO_2 (110) and Cu_2O (111) surfaces, no evidence of any vacuum-stable carbonate species was seen in TDS or XPS. Hence, CO_2.adsorption provides no insight into the nature of these surfaces under our experimental conditions

BF_3, while not a standard probe molecule, has been tested as a probe of the surface basicity of oxygen anions on Cr_2O_3 $(10\bar{1}2)$ and SnO_2 (110) surfaces. BF_3 clearly probes differences in three-coordinate O^{2-} anions and terminal chromyl oxygen (Cr=O) on Cr_2O_3 $(10\bar{1}2)$. Heats of adsorption of BF_3 show that terminal chromyl oxide anions are stronger Lewis bases than three-coordinate O^{2-} anions. BF_3 interacts directly with surface oxygen making it a direct probe of oxygen "base" sites on Cr_2O_3. The use of BF_3 as a probe molecule is complicated by some dissociation and the slow build-up of surface boron and fluoride during consecutive thermal desorption runs. Heats of adsorption of BF_3 show an opposite trend for characterizing the apparent basicity of Cr_2O_3 surfaces than the heats of adsorption of CO_2.

The Lewis basicity of SnO_2 (110) has also been investigated using BF_3 as a probe molecule. BF_3 interacts directly with surface oxygen making it a direct probe of oxygen "base" sites on SnO_2 (110), and provides a reasonable probe for the basicity of thermally-stable 3-coordinate O^{2-} anions. However, BF_3 reacts with the more labile bridging oxygen, and no distinctive feature is observed using TDS which can be used as a measure of the basicity of bridging oxygen anions on SnO_2 (110). These results indicate a limitation in the usefulness of BF_3 for probing surface oxygen species that are not thermally stable in vacuum. As on Cr_2O_3 $(10\bar{1}2)$, the use of BF_3 as a probe molecule is complicated by some dissociation and the slow build-up of surface boron and fluoride during consecutive thermal desorption runs.

8.2 Overall Conclusions

By studying probe molecules on well-defined metal oxide surfaces with known coordination geometry and oxidation state, an overall evaluation of NH_3, CO_2, and BF_3 as probe molecules can be made using the surfaces studied. NH_3 probed differences in Lewis acidity of Sn cations on SnO_2 (110), which had differences in coordination environments and oxidation states. But, NH_3 adsorption failed to provide any direct information on differences in Lewis acidity of Cu^+ cations in different local coordination geometries on Cu_2O (111). NH_3 adsorption on Cr_2O_3 (not reported in this dissertation) shows very little uptake in TDS experiments and gives no information on the acidity of Cr^{3+} sites on Cr_2O_3. On SnO_2 (110) and Cu_2O (111) surfaces, NH_3 directly interacts with metal sites through the nitrogen lone pair and transfers electrons to the metal sites. One limitation for NH_3 as an acid site probe is the repulsive interactions between NH_3 molecules in the adlayer limiting the surface coverage and possibly its ability to probe weaker acid sites if stronger acid sites are available.

CO_2, although a widely used probe of Lewis basicity in catalysis, has not been used on many low surface area, well-defined surfaces. On the metal oxide surfaces studied here, CO_2 is a poor probe of the Lewis basicity of oxygen anions. CO_2 does not strongly adsorb to either SnO_2 (110) or Cu_2O (111). On Cr_2O_3 $(10\bar{1}2)$, CO_2 does interact with oxygen sites but in two different coordinations, which vary with surface condition, making a comparison of basicity difficult. The results from well-defined Cr_2O_3 surfaces suggest that one should not consider CO_2 to be a simple acidic probe molecule for characterizing the basicity of oxide surfaces without first considering the resulting adsorbate conformation and the nature of the interrogated surface site. In the cases

studied here, CO_2 either does not adsorb, or it does not provide a clear set of results that can be related simply to Lewis basicity.

BF_3 seems to be a much better probe of the Lewis basicity than CO_2 for the well-defined metal oxide surfaces studied here. On SnO_2 (110) and Cr_2O_3 $(10\bar{1}2)$, the boron atom of BF_3 directly interacts with oxygen sites by accepting their electrons. BF_3 interacts similarly with three-coordinate O^{2-} anions on both SnO_2 (110) and Cr_2O_3 $(10\bar{1}2)$ surfaces. BF_3 thermal desorption seems to provide a simple and direct measure of the Lewis basicity of different surface oxygen species as long as they are thermally-stable in vacuum. One limitation of using BF_3 as a probe molecule on these surfaces is the dissociation of BF_3 and the subsequent build up of boron and fluorine on the surface.

8.3 Recommendations for Future Work

The greatest obstacle encountered during this work was the inability to study surface adsorbates using reflection adsorption infrared spectroscopy (RAIRS). The main problem in getting useful IR data was the limitations in the UHV system not allowing variable angles (near the Brewster angle) for a given metal oxide material. Vibrational data could be used to strengthen the identification of the bidentate or monodentate species for CO_2 adsorption on Cr_2O_3 $(10\bar{1}2)$ surfaces.

A small amount of dissociation of BF_3 is seen on both Cr_2O_3 $(10\bar{1}2)$ and SnO_2 (110) surfaces. The dissociation of BF_3 is possibly due to the effects of low-energy electrons that are present with ion gauges, mass spectrometers, X-ray photoelectron spectroscopy, etc. in UHV. A check for the vulnerability of BF_3 to dissociative electron attachment is needed. BF_3 can be exposed to the surface with all equipment turned off,

minimizing the production of low-energy electrons in the vacuum chamber. After the BF_3 exposure, a quick AES spectrum could be performed to see if any boron was left on the surface.

BF_3 as a probe of Lewis basicity could be used on Cu_2O (111) to see if BF_3 directly interacts with the oxygen anions on Cu_2O. No differences would be expected for the oxygen anions on the nearly-stoichiometric Cu_2O (111) surface and the $(\sqrt{3}\times\sqrt{3})R30^o$ Cu_2O (111) surface. It might be possible to quantify the number of oxygen vacancies created on the $(\sqrt{3}\times\sqrt{3})R30^o$ Cu_2O (111) surface using the uptake of BF_3 adsorption.

No differences were detected in TDS with NH_3 adsorption on Cu_2O (111) surfaces. The TDS spectra were run at low temperatures resulting in the formation of a bilayer of NH_3 on the surface. TDS spectra after exposing NH_3 above the bilayer temperatures on Cu_2O might make it easier to notice differences in desorption behavior or coverage between the nearly-stoichiometric and $(\sqrt{3}\times\sqrt{3})R30^o$ surfaces.

In this study, only NH_3 was studied as a Lewis acid probe of specific features on well-defined metal oxide surfaces. Many other probe molecules for Lewis acidity of different acid strengths and different steric consequences could be studied. NH_3 (studied here) along with methylamine (CH_3NH_2) and dimethylamine (CH_3NHCH_3) adsorption could be used to study how changes in the basicity of the probe molecule and the size of the probe molecule affect the probing of the Lewis acid sites on well-defined metal oxide surfaces. These probe molecules increase in basicity with increasing size [1].

Acid/Base characterizations could be done on Cu_2O (100) surfaces where oxygen-terminated and Cu-terminated surfaces can be obtained. NH_3 adsorption would be expected on the Cu-terminated surface and not on the oxygen-terminated surface, and

vice versa for BF_3 adsorption. Acid/Base characterizations of other single crystals like molybdenum carbide surfaces could also be investigated using NH_3 and BF_3 adsorption. The molybdenum would be expected to be the acid sites for NH_3 adsorption, and the carbon would be expected to be the base sites for BF_3 adsorption. The use of Mo_2C single crystals would allow one to investigate the basicity of atomic sites other than oxygen anions.

8.4 References

[1] R.J. Fessenden and J.S.Fessenden, Organic Chemistry (Brooks/Cole Publishing Co., Pacific Grove, CA 1990).