

**Interaction of Acid/Base Probe Molecules with Specific
Features on Well-Defined Metal Oxide Single-Crystal Surfaces**

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(ABSTRACT)

Acid/Base characterizations of metal oxide surfaces are often used to explain their catalytic behavior. 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 by the interactions between the probe molecules and the well-defined surface features. The adsorption of NH_3 at cation sites was used to characterize the Lewis acidity of SnO_2 (110) and Cu_2O (111) surfaces. The adsorption of CO_2 , a standard acidic probe molecule, was used to characterize the Lewis basicity of the oxygen anions on SnO_2 (110), Cu_2O (111), and Cr_2O_3 ($10\bar{1}2$) surfaces. BF_3 , while not a standard probe molecule, has been tested as a probe of the Lewis basicity of the oxygen anions on SnO_2 (110) and Cr_2O_3 ($10\bar{1}2$).

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). CO_2 is a poor probe of the Lewis basicity of oxygen anions on the metal oxide surfaces studied here. 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. 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 thermal desorption seems to provide a direct measure of the Lewis basicity of different surface oxygen species as long as they are thermally-stable in vacuum.

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