IRRAS and DFT Investigations of Ultrathin ZnO Films Formed on Ag(111)

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Reactivity at metal-oxide interfaces is of fundamental importance in heterogeneous catalysis. Herein, we report a thorough surface-science study on the growth and chemical activity of ultrathin ZnO films on Ag(111) by grazing-emission X-ray photoelectron spectroscopy and temperature-dependent infrared reflection–absorption spectroscopy using CO as a probe molecule. The chemical activity of the formed ZnO films is probed by measuring the stretch frequency and binding energy of adsorbed CO. [1] Our results provide solid evidence for the formation of closed ultrathin ZnO films which are characterized by a single, sharp CO band at 2146 cm^{-1} for isolated CO molecules with a binding energy of 0.24 eV, indicating a rather weak interaction between CO and ZnO thin layers. The wurtzite-type ZnO islands are formed for thickness above 2 ML on Ag(111), the corresponding frequency at 2183 cm^{-1} and binding energy of 0.30 eV are consistent with those reported for CO adsorption on ZnO single-crystal surfaces. [1] Interestingly, these results are in contrast to the observation of a significantly enhanced interaction of CO with ultrathin ZnO films on Cu(111) showing a substantial red-shift of the CO vibrational frequency with respect to the gas phase value. [2] In order to interpret these differences of ZnO thin layer supported on these two coinage metals, we carried out a theoretical analysis using density functional theory calculations. We show that bilayer ZnO forms a flat graphitic-like structure on Ag compared to the previously reported strongly corrugated ZnO film formed on Cu. Our results thus illustrate the variety of ZnO phases that can be formed and the pronounced influence of the metal substrate for ultrathin ZnO films.

References:

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