Activation of Carbon Dioxide on ZnO Nanoparticles Studied by Vibrational Spectroscopy†

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The activation of CO_2 on clean and hydroxylated ZnO nanoparticles has been studied by ultrahigh vacuum FTIR spectroscopy (UHV-FTIRS). Exposing the clean ZnO powder samples to CO_2 at 300 K leads to the formation of a number of carbonate-related bands. A detailed assignment of these bands was carried out using isotope-substitution experiments with $C^{18}O_2$. On the basis of vibrational and thermal stability data for ZnO single crystal surfaces, a consistent description of the interaction of CO_2 with ZnO powder particles can be provided: (1) on the mixed-terminated ZnO($10\bar{1}0$) facets, a tridentate carbonate is formed; (2) on the polar, O-terminated ($000\bar{1}$) facets, a bidentate carbonate species is formed via CO_2 activation at oxygen vacancy sites; and (3) additional monodentate or polydentate carbonate species are formed at defect sites such as steps, edges, kinks, and vacancies. The formation of carbonate-related vibrational bands is observed at an exposure temperature as low as 100 K, thus demonstrating the high activity of ZnO nanoparticles with regard to CO_2 activation.