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Probing the Reactivity of ZnO and Au/ZnO Nanoparticles by Methanol Adsorption: A TPD and DRIFTS Study**

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The adsorption of methanol on pure ZnO and Au-decorated ZnO nanoparticles and its thermal decomposition monitored by temperature-programmed desorption (TPD) experiments and by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), both applied under continuous flow conditions in fixed bed reactors, is reported. Two distinguishable methoxy species are formed during methanol adsorption on ZnO differing in the C–O stretching bands. During the subsequent TPD experiments two different H₂ peaks are observed, indicating the conversion of methoxy into formate species. By applying different heating rates, activation energies of 109 kJ mol⁻¹ and 127 kJ mol⁻¹ for the selective oxidation of the two methoxy species are derived. Correspondingly, the methoxy decomposition results in two distinguishable formate species, which are identified by the asymmetric and symmetric OCO stretching bands on pure ZnO and Au/ZnO. Based on the decreased in-

tensities of the OH bands during methanol adsorption, which are specific for the various ZnO single crystal surfaces, on the different reactivities of these surfaces, and on the formate FTIR bands observed on ZnO single crystal surfaces, the two methoxy and the corresponding formate species are identified to be adsorbed on the exposed less reactive non-polar ZnO(10 $\bar{1}$ 0) surface and on the highly reactive polar ZnO(000 $\bar{1}$) surface. The simultaneous formation of H₂, CO, and CO₂ at about 550–600 K during the TPD experiments indicate the decomposition of adsorbed formate species. The CO/CO₂ ratio decreases with increasing Au loading, and a broad band due to electronic transitions from donor sites to the conduction band is observed in the DRIFT spectra for the Au-decorated ZnO nanoparticles. Thus, the presence of the Au nanoparticles results in an enhanced reducibility of ZnO facilitating the generation of oxygen vacancies.