

Probing the Surface Heterogeneity of Polycrystalline Zinc Oxide by Static Adsorption Microcalorimetry. 1. The Influence of the Thermal Pretreatment on the Adsorption of Carbon Dioxide

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The adsorption of carbon dioxide on differently pretreated polycrystalline ZnO was studied by thermodynamic and kinetic methods. The uptake of CO₂ observed in a static Tian–Calvet microcalorimeter reached saturation at about 5 μmol/m², corresponding to about half of the exposed Zn²⁺ sites after a thorough thermal pretreatment at 450 °C for 4 h. The saturation uptake was found to be correlated inversely with the amount of residual hydroxyl groups on the ZnO surfaces. At room temperature, the adsorption of CO₂ was found to occur in two steps. Initially, the adsorption was nonactivated, and the exposed surfaces were saturated at a very low equilibrium pressure ($p \ll 1$ Pa) with an initial differential heat of adsorption (q^{diff}) of 100–120 kJ/mol, a standard entropy of $-190 \text{ J mol}^{-1} \text{ K}^{-1}$, and an adsorption rate constant of $10^{-5} \text{ Pa}^{-1} \text{ s}^{-1}$. During the second stage, an inhibiting effect was observed; the equilibrium coverage increased slowly with increasing pressure, q^{diff} decreased rapidly with increasing coverage, and the rate of adsorption was low. Temperature-programmed desorption measurements indicated the formation of strongly adsorbed polydentate carbonates at higher temperatures with an adsorption energy between 120 and 160 kJ/mol.