Coverage-Dependent Kinetics and Thermodynamics of Carbon Monoxide Adsorption on a Ternary Copper Catalyst Derived from Static Adsorption Microcalorimetry

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A reliable method for adsorption systems in equilibrium is established to derive coverage-dependent kinetics and thermodynamics from the volumetric data obtained during the static microcalorimetric measurement of heats of adsorption. The Wigner−Polanyi equation is applied to analyze the pressure change as a function of time during stepwise dosing of the adsorptive until thermodynamic adsorption−desorption equilibrium is established. For carbon monoxide adsorption on a hydrogen-reduced $Cu/ZnO/Al_2O_3$ catalyst, the adsorption rate constant (k_a) is found to be in the range from 10^{-6} to 10^{-4} Pa^{-1} s^{-1}, and the desorption rate constant (k_d) from 10^{-4} to 10^{-2} s^{-1}, both increasing with fractional coverage θ. The kinetically derived equilibrium constant $K(\theta)$ is in good agreement with $K(\theta)$ obtained from the adsorption isotherm. $RT \ln(Kp^0)$ and the differential heat of adsorption (q^{diff}) were found to decrease in parallel, reflecting a normal Temkin-type heterogeneity.