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Research Note

The influence of ZnO on the differential heat of adsorption of CO on Cu catalysts: a microcalorimetric study

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Abstract

The differential heat of adsorption of carbon monoxide on carefully reduced copper catalysts employed in methanol synthesis was measured by means of a Tian–Calvet calorimeter to probe the influence of ZnO. A ternary catalyst ($Cu/ZnO/Al_2O_3$) and two binary catalysts (Cu/ZnO and Cu/Al_2O_3) were prepared by coprecipitation and characterized by N_2 physisorption (BET surface area), temperature-programmed reduction (TPR), N_2O-reactive frontal chromatography (N_2O RFC), and methanol synthesis activity measurements. The shape of the adsorption isotherms, the initial heat of adsorption, and the coverage dependence of the heat of adsorption were found to be different for the catalysts with and without ZnO. The initial heat of adsorption turned out to be inversely correlated with the activity for methanol synthesis: $Cu/ZnO/Al_2O_3$ had the lowest initial heat of adsorption of 68 kJ mol^{-1} and was the most active catalyst for methanol synthesis. Cu/ZnO showed a somewhat higher heat of adsorption of 71 kJ mol^{-1} and a lower activity, and Cu/Al_2O_3 had the highest initial heat of adsorption of 81 kJ mol^{-1} and the lowest activity. The decrease in the heat of adsorption of CO induced by the presence of ZnO is rationalized by strong metal–support interactions (SMSI); i.e., ZnO_x species are assumed to cover the Cu metal surfaces presumably as Zn + O coadsorbate under reducing conditions.

Keywords: Microcalorimetry; Differential heat of adsorption; Carbon monoxide; Copper; Zinc oxide; Strong metal–support interactions (SMSI)