

Modeling of CO + NO Reaction on Rh: Density Functional Theory and Microkinetic Modeling Studies

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Concern over the concentration of NO_x in the atmosphere has motivated efforts to explore approaches to reduce its level of emission from automobile and industrial gas discharge. One potential solution involves the reduction of NO by reducing agents such as CO promoted by transition metal catalysts. Rhodium, in particular, has been proven to be one of the effective catalysts for the conversion of NO. Several mechanistic details remain fairly unresolved despite significant studies. For instance, the specific pathways for NO to N₂ conversion which is a critical step in the pollution-control process are not completely understood. Experimental studies on Rh(111) surface exposed to NO + CO beam indicate that the recombination of surface nitrogen atoms - a step usually assumed to be the one responsible for N₂ production – does not occur readily under typical reaction conditions. On the other hand, an alternative branch starting with the formation of an intermediate species N₂O followed by its decomposition to gaseous N₂ and adsorbed O was suggested. However, various TPD experiments ruled out this alternative route in view of the absence of N₂O in the TPD spectra. We have examined the inclusion of N₂ formation pathways both via atomic recombination of N atoms and via the N₂O species in the realistic description of NO + CO reaction on Rh(111). Our density functional theory (DFT) calculations indicate that the latter branch is not the main reaction route. Microkinetic modeling analyses also reveal the rate limiting step in the reaction network and establish that the surface N recombination route is the dominant pathway for N₂ formation on this surface.