

CO oxidation on Pt(111): Deciphering the second mechanism using Slice Imaging

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Abstract

This study elucidates the underlying mechanism in the catalytic oxidation of CO on Pt(111), revealing a second reaction pathway that involves the reaction between weakly bound “physisorbed” CO molecules (CO_p) with adsorbed oxygen atoms. This reaction pathway is significant and dominates the oxidation process at high oxygen coverage and consequently under industrially relevant conditions. By implementing slice imaging to measure the kinetics we determine the rate constants for all reaction steps. The two reaction pathways have distinct CO_2 product velocity distributions which are identified in our experiment and allow for branching ratios to be extracted. The branching ratios are in perfect agreement with the rate constants reported we determine independently thus ensuring the self-consistency of our measurements. Our observations suggest a new mechanism for surface catalyzed exothermic reactions which in a way bridges the gap between the two generally accepted mechanisms, i.e., those of Langmuir-Hinshelwood and Eley-Rideal. Our results indicate that the formation of a *weakly bound physisorbed state* results in the adsorbed atom desorbing and colliding with the physisorbed atoms (*reverse Eley-Rideal*) that consequently releases most of the reaction exothermicity into the reaction products, in our case CO_2 translational and internal energy. The formation of these physisorbed states are favored by appropriate mass ratios such as a *relatively-heavy-gas* reactant collides with a *light-mass-adsorbed* molecule on a very *heavy surface* (*heavy-light-heavy*). As in gas phase reaction dynamics, this combination is very favorable for the formation of long lived complexes, our work presented here seems to indicate for the first time its relevance to surface catalyzed reactions.

