

The competitive pathways in the CO oxidation catalyzed by small transition metal clusters: The Eley-Rideal and Langmuir-Hinshelwood mechanisms

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The CO oxidation removes this pollutant from the exhaust pipes of vehicles using Pd, Pt or Rh as catalysts. We performed a quantum chemistry study on the CO + O₂ reaction catalyzed by small transition metal TM (TM =Pd, AuAg, AuNi) clusters using the PBE/TZ2P/ZORA method. The limiting step of this reaction at low temperature and coverage is the O₂ dissociation. TM clusters catalyze the breaking of the O=O bond, reducing the energy barrier from 119 kcal/mol without catalyst to ~35 kcal/mol. The charge transfer from TM to the O_{2,ad} antibonding orbital weakens, and finally breaks the O—O bond. The CO oxidation, catalyzed by small TM clusters, occurs either the Eley-Rideal (ER) mechanism or the Langmuir-Hinshelwood (LH) mechanism. The ER mechanism is activated with an energy barrier of 4.10 - 7.05 kcal/mol; whereas in the LH mechanism, the barrier energies to produce CO₂ are 7 - 15 kcal/mol. Additionally, the CO₂ formed is adsorbed, and about 7 - 25 kcal/mol are necessary to release the metal site.