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Fundamental Characterization of Metal Surfaces at Relevant Conditions for Catalysis
Caracterización fundamental de superficies metálicas a condiciones relevantes para la catálisis

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Heterogeneous catalysis involves chemisorption, reactions of chemisorbed species, and desorption of the products formed. The enthalpies and entropies for these elementary steps and their transition states provide the thermodynamic context that allows rigorous interpretations of the rates and selectivities of chemical reactions mediated by surfaces. The measurement of rates and/or thermodynamic properties at conditions relevant for catalysts and in the absence of mass and heat transport limitations are required for the proper reactor and catalyst design. Different challenging examples are provided, in which chemical rates and/or thermodynamic properties are measured under rigorous kinetic or thermodynamic conditions, giving information regarding the nature of the active metal surfaces and their role at reaction conditions. Among the cases to be presented are the alkane oxidation reactions on noble metals, Pd-PdO phase transition and its consequences for catalysis, and the surface characterization of metals by H_2 chemisorption at elevated temperatures.

Alkane-O_2 (CH_4 and C_2H_6) reactions are highly exothermic and tend to occur within the length scale of conductive or convective heat and mass transfer, which lead to severe gradients within undiluted catalyst pellets and reactors. Extensive dilution within the pellets and reactor has been used to get kinetic and isotopic data for Alkane-O_2 reactions on supported Pt, Rh and Pd. These data have shown that CO and H_2 do not form via direct alkane partial oxidation but instead via sequential combustion-reforming pathways. Alkane-O_2 reactants form CO_2 and H_2O on Pt in three kinetic regimes (KR), each with distinct rate equations, kinetically-relevant steps, most abundant surface intermediates (MASI), and cluster size effects. Transitions among these regimes are determined by the prevalent steady-state coverages of chemisorbed oxygen (O*), which are given by O_2 pressure when O_2 dissociation is equilibrated and by O_2 to Alkane ratios when it is irreversible. Mechanistic interpretations remain valid for other metals such as Pd, and the difference in reactivity among metals is correlated to O* binding strengths when O* is involved in the kinetically-relevant steps. On Pd and Rh, however, the clusters undergo phase transition to PdO and RhO_2, leading to an additional kinetic regime characterized by an abrupt increase in reactivity caused by the transition from metal to oxide. Ex-situ O_2 uptake measurements, at equilibrium, were performed to correlate the oxygen content during the phase transition with the measured rates at reaction conditions.

Another example is given by the use of dissociative H_2 chemisorption methods at conditions relevant for catalysis as a thermodynamic probe instead of mere site counting technique, in which differential enthalpies and entropies of adsorption are obtain to probe the non-uniformity of cluster surfaces. H-atoms formed via H_2 dissociation are attractive titrants because of the reversible nature of the adsorption processes and the well-defined adsorption stoichiometry, but also because of the ubiquitous involvement of H-atoms in hydrogenation-dehydrogenation catalysis.