

Towards more general descriptors of reactivity in acid and oxidation catalysis by metal oxides

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The function of metal oxide surfaces as acid and redox catalysts is described here by combining kinetic and isotopic experiments, structural and surface characterization, and theoretical assessments of elementary steps and binding sites based on density functional theory (DFT). Such strategies exploit oxide clusters of known structure and diverse compositions and crystalline microporous materials that provide well-defined confining voids to develop rigorous descriptors of reactivity and selectivity. DFT-derived deprotonation energies (DPE) and the proton affinity of gaseous analogs of transition states combine to determine reactivity for a broad range of acid-catalyzed reactions. DPE values rigorously reflect the acid strength of oxides, but represent an incomplete descriptor of their catalytic reactivity, because interactions between organic moieties (e.g. intermediates, ion-pair transition states) and the solid acids depend on the ability of molecules and oxide surfaces to reorganize charge. This requires, in turn, that DPE values be separated into their covalent and ionic parts and that transition states for various reactions be classified in terms of their ability to recover a fraction of each DPE part upon formation of the relevant ion-pairs at transition states. Redox cycles that mediate oxidation reactions, with few exceptions, are limited by the rate of the elementary steps that reduce metal centers in oxides via C-H bond activations. These steps involve late transition states containing a nearly formed O-H bond, making H-addition energies (HAE) for metal oxides the relevant descriptor of reactivity, when properly averaged over all types of lattice oxygen atoms exposed. In acid and oxidation catalysis by oxides, these DFT-derived reactivity descriptors accurately describe measured rates and selectivities for diverse reactions. Such reciprocal benchmarking of theoretical methods and of mechanistic inferences from experiments requires the use of solids that preserve known structures during catalysis, as well as the interpretation of chemical reactivity data in terms of elementary steps and the normalization of rates by the number of active sites.

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