

Rational Modification of Active Sites on Heterogeneous Catalysts

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The design of new catalysts requires an understanding of how atomic configuration, electronic structure and reaction environment influence activity and selectivity of a particular reaction. In this lecture, three examples of rationally modifying active sites will be discussed. In the first case, the function of catalytic sites associated with structurally-distinct Ti atoms in titania-silica mixed oxides depends strongly on composition and homogeneity of mixing. Specifically, Ti atoms in TiO₂ and Ti-rich mixed oxides are octahedrally-coordinated to oxygen, whereas Ti atoms in Si-rich mixed oxides are tetrahedrally-coordinated to oxygen. The appearance of acidity in titania-rich mixed oxides arises from the local charge imbalance associated with tetrahedrally-coordinated silica chemically mixing with the octahedral titania matrix. As the silica concentration in the mixed oxide increases, the Ti atoms shift to tetrahedral coordination and now function as sites for selective olefin epoxidation with hydroperoxide. In the second case, the activity of ruthenium nanoparticles for ammonia synthesis is substantially influenced by the presence of basic promoters. However, alkaline earth and lanthanide promoters are often found to be superior to alkali metal promoters, which is not consistent with the rank of promoter basicity. Results from a variety of spectroscopic tools combined with steady state and transient kinetic studies indicate that basic promoters on Ru lower the activation barrier for dinitrogen activation while simultaneously increasing the surface coverage of hydrogen atoms. Thus, optimal promotion of Ru is achieved by properly balancing these two effects. In the final example, the role of liquid water on oxidation catalysis by gold is explored. Gold catalysts that are inactive for CO oxidation in the gas phase become very active in liquid water, especially at high pH. Likewise, selective oxidation of glycerol over gold in the aqueous phase is influenced substantially by hydroxyl concentration. New paths for catalytic reactions involving hydroxyl groups on Au surfaces are enabled by operating in the aqueous phase. These examples demonstrate how modifying the local structure of a catalytic site, adding basic promoter compounds to metal surfaces and performing reactions in the condensed phase can be used to influence the observed rate and selectivity of solid catalysts.