

New Catalysts, Catalytic Structures, and Reactions

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Recently advances in synthesis methodology and characterization techniques have propelled catalysis research into a new era when it becomes possible to custom-design catalysts with specific active sites and environments. This is particularly evident in examples where synthetic routes developed for macromolecules and nanostructures, and bio-inspired chemical interactions are employed for catalyst synthesis. The consequence is the potential to develop new catalysts for new catalytic reactions. In this presentation, examples from the literature and from our laboratory are described and discussed to explore this new frontier, and to examine the promises and present limitations of the new methods, with the hope to stimulate new ideas and new approaches.

One class of new catalysts is the bifunctional acid-base catalysts. The cooperative effect of acid and base sites in promoting catalytic chemical transformation is common in enzymes. New catalysts have been prepared where basic sites are anchored adjacent to acid sites, and one-step Michael's addition is achieved. Since there are many choices of solids of various acid strengths, it is possible to vary the acid-base pair, thereby manipulating the activity and selectivity for such reactions. Acid-base pairs can also be introduced using templating technique.

Another class of catalysts consists of functional groups positioned in nanostructures. An example is a functional core trapped in a porous nanocage, which could also possess functional groups. Two methods to synthesize porous nanocage have been explored in our laboratory. One method uses self-assembled micelles as structure-directing agent, and the second method uses dendritic structures. The dendritic method is more tedious, but offers much enhanced flexibility in the size of the nanocage, the nature of the entrapped core, and the variety of functional groups. These nanocages also provide the possibility of molecular size selection for the reactant and/or product.

Asymmetric macromolecules also have the ability to carry different types of catalytic functional groups at specific positions. An example provided by nature is a protein molecule. However, synthesis of asymmetric macromolecules is difficult. An exception is polypeptide which can be synthesized by the well-established solid-state method. An extension of this method has now been developed for macromolecules containing Si-O backbones, and various functional groups can be appended at specific positions along the backbone. This opens the possibility of designing complex catalytic structures.

Nano-metallic particles of specific shapes can now be prepared. Likewise, nano-size oxide particles have been prepared that can be used as catalyst or catalyst support. In the latter case, the high density of surface defects in small particles affects the properties of the

supported metal. Finally, there are various methods to prepare isolated oxometal clusters. These isolated clusters demonstrate different redox properties than large clusters, and consequently different catalytic oxidation behavior.

These examples and others illustrate the rapid advances achieved in recent years in catalyst synthesis. Now, we can exercise much better control of catalyst properties through synthesis than ever before. Thus, the time is ripe to explore new catalytic reactions that have not been possible before, and we will speculate on some of the possibilities.