

Tuning into Better Catalysts

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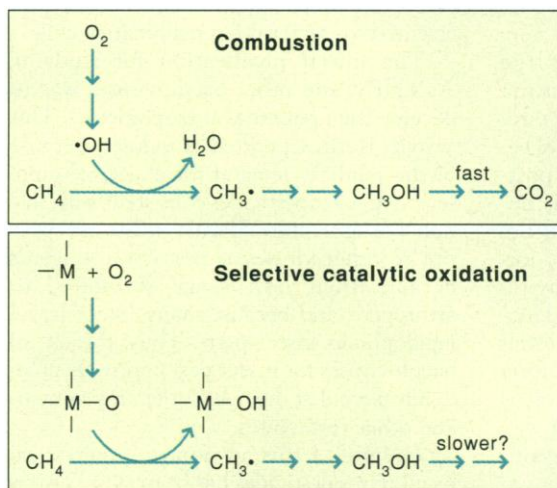
Composer and teacher Arnold Schönberg was reportedly fond of setting a problem in counterpoint before a class; after the students had reported their (often very) different solutions, Schönberg would pose the key question: What is the basic principle behind all the solutions? The same question often arises in science, and it seems to apply particularly to the field of catalysis. How are we to progress from the Edisonian approach of trial-and-error that has characterized most of the history of catalyst development to a more rational basis for design? At a minimum, we need to understand, at the most fundamental level attainable, why a particular approach succeeds. On page 1849 of this issue, Gardner and Mayer suggest an approach to gaining some of this understanding for the important problem of C–H bond oxidation (1).

The selective oxidation of C–H bonds in hydrocarbons is one of the outstanding challenges in catalysis. Attractive targets include the direct oxidation of methane to methanol or of higher alkanes to terminal alcohols, commercially important transformations that are currently achieved by less-efficient indirect routes. However, because of the low chemical reactivity of the C–H bonds that must be broken to get these reactions started, simple reaction with oxygen occurs only at high temperature; that is, in combustion. Under such conditions we are dealing with extremely reactive, nonselective radicals such as OH, and the relative reactivity of different C–H bonds is determined almost exclusively by bond strength. But the C–H bonds of alcohols are considerably weaker than those of alkanes, so there is a strong predilection for complete oxidation to carbon dioxide and water; it is exceedingly difficult to achieve significant yields of the desired products (see figure).

The role of a catalyst in oxidation is to interact with oxygen to generate a species that is still sufficiently reactive to break the C–H bond but is much more selective and works under much milder conditions. We know this is possible, because there are biological catalysts that do it very successfully. A class of heme iron enzymes, known collectively as cytochromes P-450, effects a wide variety of selective alkane hydroxylations; another class, the methane monooxygenases (non-heme iron and cop-

per enzymes), efficiently convert methane to methanol (2). There have also been some (modest) successes with synthetic catalysts, including both soluble species (many of them designed to mimic the biological catalysts to some degree) that operate at ambient temperature and heterogeneous catalysts that function at high temperatures (but below those of combustion) (3).

Now how do we exploit what we know of these successful solutions to design still better ones? A good first step would be to identify the key characteristics of the active site that are responsible for success, but this



Mechanistic interpretation of the challenge inherent in selectively oxidizing methane to methanol.

has not proven an easy task. For example, the process known as oxidative coupling of methane, where methane reacts with oxygen over a metal oxide catalyst to give higher hydrocarbons (ethane, ethylene, and so forth) rather than combusting to carbon dioxide, has been the most actively studied problem in heterogeneous catalytic oxidation during the past decade (4). A large number of widely varying catalysts show at least moderate activity and selectivity for this process. What do they have in common? Proposals have included global properties—such as basicity, ionic mobility, and electronic conductivity—and specific active site structures. Many of the latter have focused on the idea that because radicals such as OH readily cleave C–H bonds, the active form of oxygen on the catalyst must also have unpaired electron density, perhaps as O^- , O_2^- , or F-center defects, although non-paramagnetic species such as O^{2-} and O_2^{2-} have also been put forth. Similarly, it has

been suggested that the active iron-oxo center in cytochrome P-450 and model compounds has significant unpaired electron density at oxygen, which is responsible for its reactivity (5).

Given the vast differences between the detailed structure of the active sites in the various catalysts, is it too farfetched that a relatively simple principle might govern reactivity at the most fundamental level of the initial C–H bond cleavage for most or all of them? None of the above proposals appears to do the job. Gardner and Mayer now offer us a different way to approach the problem (1): look not at the starting structure of the active site, but at the energetics of the abstraction of hydrogen by that site. Using the oxidation of toluene by a permanganate ion as a model, they compare the reactivity for hydrogen atom abstraction to that by radicals such as OH and show that the reactivity correlates nicely with the energy of the O–H bond formed even though permanganate is not a radical.

This finding suggests that the details of the ground state are not that important—as long as the new O–H bond formed is sufficiently strong, the reaction will proceed. This approach also has the potential advantage of leading directly to quantitative, rather than merely qualitative, interpretations of relative reactivity. Of course, this is but a small first step toward the ultimate goal of rational catalyst design. For one thing, high activity for C–H bond cleavage is only one of the requirements for a selective oxidation catalyst, and it is not at all clear how to extend such bond energy-reactivity correlation studies from a model system to the “real” world, especially for heterogeneous catalysts, where the species whose energies must be known are not well-defined. Nonetheless, the implications for better mechanistic understanding of a wide variety of important oxidation catalysts (which may be more closely related than their variety would at first suggest) appear well worth pursuing.

References

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