Catalysis and the Dance of the Seven Vales

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The ability of a catalyst to accelerate a chemical reaction is often ascribed to its ability to bind to and stabilize the transition state of a reaction more than it stabilizes the reactants or products. While this formulation is occasionally useful, it more often than not misses the point. In most cases, catalysts interact so profoundly with their substrates that the pathway that the catalyzed reaction follows and the transition states that the reaction traverses between its intermediates bear little or no resemblance to those displayed by the uncatalyzed reaction. Indeed, most catalytic reactions simply have no uncatalyzed counterpart with which to compare them. Like a talented dance partner, a catalyst can lead reactants to products in a way that was simply inconceivable in its absence.

A well-established example of the power of catalysis is the Suzuki reaction, in which a compound containing a carbon–boron bond and one containing a carbon–halogen bond are coupled through the action of a palladium catalyst to form a new carbon–carbon bond. Because of the selectivity of the reaction, its mild conditions, and the ready availability and stability of diverse aryl halides and arylboronates, the Suzuki reaction has been immensely useful for the production of biaryls in fine chemical synthesis (particularly in the pharmaceutical industry).[1] The importance of this and other metal-catalyzed carbon–carbon coupling reactions was recognized by the 2010 Nobel Prize in chemistry.

In many ways, the Suzuki reaction is an "easy" reaction to catalyze. An enormous number of palladium precatalysts have been found to catalyze this coupling reaction, often with very high turnover numbers. Metal-free Suzuki reactions have even been reported, though these reports have been questioned because of the ease with which adventitious traces of palladium catalyze the reaction.[2] In his Perspective in this issue,[3] Pérez-Lorenzo considers one class of catalysts, namely, palladium nanoparticles, and asks the most fundamental of questions in catalysis: homogeneous or heterogeneous? Because soluble discrete metal complexes can aggregate into metal nanoparticles under reducing conditions,[4] or to metal oxides under oxidizing conditions,[5] distinguishing between heterogeneous and homogeneous active catalysts is a longstanding problem in catalysis, and a number of tests for heterogeneity have been developed. As Pérez-Lorenzo describes, the Suzuki reaction has been reluctant to yield consistent answers to this question. Some nanoparticulate precatalysts give clear evidence of dissolving to atomic palladium as the active species; others, similar but not identical, give equally clear evidence that they are reacting as intact nanoparticles. Some of the ambiguity may arise because small Pd clusters may mimic aspects of both molecular and heterogeneous catalysts, but more likely, both surface Pd and molecular species are capable of catalyzing the reaction, and the balance between which species contribute the most to activity is a subtle one capable of being tipped one way or the other by small changes in reaction conditions. In all cases, however, regardless of the identity of the catalyst, there is little doubt about the general mechanism of coupling: oxidative addition of the aryl halide, transmetalation of the arylboronate, and finally reductive elimination of the biaryl. Many different dancers can apparently participate in the Suzuki coupling, but they all seem to execute the same series of steps.

The same cannot be said of the electroreduction of carbon dioxide to methane, discussed in the Perspective by Peterson and Norskov.[6] This is an evidently "hard" problem in catalysis, with known catalysts suffering from at best modest selectivities and activities and impractically high overpotentials. Peterson and Norskov map theoretically a progression of seven key bound intermediates in this eight-electron/eight-proton transformation. The depths of these seven valleys in the potential energy landscape vary systematically with the nature of the metal surface, but not all of the intermediates vary in the same way (in particular, carbon-bound and oxygen-bound intermediates show rather different trends in stability). This classic phenomenon of trade-offs in multistep catalytic reactions gives rise to a similarly classic "volcano" plot of activity, with copper at the apex both computationally and experimentally. This kind of analysis has proved very useful in interpolating to find locally optimal catalysts (e.g., by alloying).[7] However, for a catalyst so far from practicality, real advances will likely require more radical changes in mechanism. Several potentially interesting approaches, some homogeneous, some heterogeneous, and some hybrid, are suggested. Making progress in this reaction is no small matter. Reduction of carbon dioxide to a chemical fuel such as methane or methanol is one potential strategy to solve the key problem of transforming renewable but intermittent and spatially dispersed energy sources such as solar or wind power into concentrated and portable energy carriers. Finding good catalysts for CO_2 reduction could make an impact like that of the Suzuki catalysts in fine chemicals but in the much larger scale and more universally important chemical arena of energy use. Inventive new choreography for this reaction is thus urgently needed.

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