On the move

Heterogeneous catalysis: just as for enzymes, flexibility and mobility are emerging as key features of catalytically active metal surfaces.

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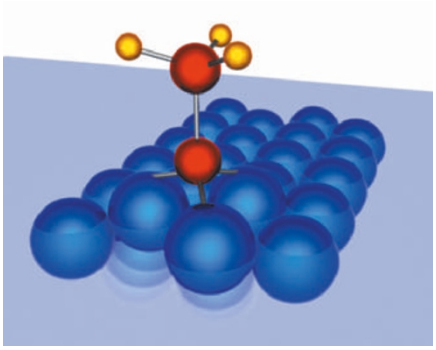
Catalysts have the remarkable property of facilitating a chemical reaction repeatedly without being consumed. In principle (if not in practice), a catalyst can function as long as reactants are available. Enzymes — which catalyse all aspects of cell metabolism — are the supreme masters of this art. We have used them from earliest times for leavening bread, curdling cheese and brewing beer.

In the twentieth century, a seemingly very different type of catalysis — heterogeneous catalysis, which uses small metal particles supported on solid surfaces — became the foundation for much of the chemical industry. It plays a central role in generating the feedstocks for making the synthetic materials that we use every day, from fuels to fertilizers. New experimental techniques have brought fresh insights into this form of catalysis, and it now seems that there are more similarities between enzymes and heterogeneous catalysts than initially meets the eye.

Heterogeneous catalysis usually involves the interaction between a reactant and the catalytic surface of small metal particles. This in turn activates chemical bonds within the reactant, resulting in their dissociation or rearrangement. For decades, studies of heterogeneous catalysts were largely empirical, involving little understanding at the molecular level. Theories of how they function emphasized the need for complementarity between reactant structure and the geometrical arrangement of atoms in the static catalyst surface. Now, more advanced methods of observation have allowed us to see these molecules during reactions in considerably more detail, and have revealed that this static view of catalysis is, in fact, wrong.

The advent of ultrahigh-vacuum surface science in the 1960s provided an entrée into the world of adsorbed molecules. However, it is only recently that modern techniques such as high-pressure scanning tunnelling microscopy have allowed experiments to be done under realistic (high pressure and temperature) conditions.

Exposure to reactants results in local restructuring of the catalytic surface. The formation of bonds between the metal atoms of the catalyst and the adsorbed molecules produces heat, providing energy to loosen the bonds between the metal atom and its neighbours. This allows it to move from its original position and thus strengthens the chemical bond between the adsorbed molecule and the metal. The fewer neighbours a surface metal atom has, and the stronger the bonding to the adsorbed molecules, the greater is the degree of restructuring that occurs. Also, it is not always the original reactant that bonds with the metal catalyst; it can be a derivative if the metal–adsorbate complex can form stronger bonds this way.



All change: formation of the catalytic intermediate ethylidyne causes catalyst surface restructuring.

The formation of strong chemical bonds at these active metal sites intuitively suggests that such sites will be blocked and prevented from participating in new reactions. But in fact the very same sites that are most active in bond activation are also catalytically the most active, and remain so. They can carry out bond activation repeatedly.

The reason for the continued catalytic activity is that it is not only the metal atoms that are on the move. Strongly adsorbed reactants on the metal surface are also mobile. In a model reaction (the hydrogenation of ethene to form ethane) used to understand the industrially important hydrogenation process, an important derivative species, ethylidyne, retains the ability to move over the surface despite being fairly strongly bound. The ethylidyne is not part of the catalytic process, but remodels active sites and then moves on, allowing ethene, which is adsorbed only weakly, to bind briefly and become rapidly hydrogenated. Impeding the mobility of ethylidyne slows the catalytic reaction. For example, if carbon monoxide is adsorbed on the catalyst surface, ordered, immobile surface structures containing both ethylidyne and carbon monoxide are formed which prevent mobility and block adsorption sites, 'poisoning' the catalytic reaction.

Thus, everything on the surface must move for catalysis to occur. The metal atoms move to restructure the surface as the ethylidyne forms; ethylidyne moves, thereby opening up active sites that allow new ethene molecules to adsorb weakly and hydrogenate rapidly. Without mobility there is no heterogeneous catalysis.

Flexibility in restructuring the sites where bond activation occurs is well known to those working on enzyme catalysts. Emil Fischer's static lock-and-key model for the interaction of an enzyme with its substrate was superseded by the induced-fit dynamic model of Daniel Koshland. In this model, chemisorption of the reacting molecule induces restructuring of the active enzyme, which results in structural and electronic alterations to both. Substrate binding and product release require the restructuring of both the active site and surrounding parts of the enzyme. Meanwhile, chemical-bond activation and catalytic turnover probably require both local restructuring and mobility of adsorbed species to and from the active sites.

The similarity in the behaviour of heterogeneous and enzyme catalysts at the molecular level could lead to the discovery of new selective catalysts if these two presently diverse fields were studied together. However, the natural habitat of enzymes is water at or near room temperature, whereas heterogeneous catalysts usually operate at high temperatures and in the presence of gaseous or liquid reactants at high pressures. Bridging the chasm between these diverse conditions and the vastly different chemical natures of the biological and industrial 'catalyst worlds' will be a real challenge. But if successful, such an approach could lead to new generations of selective catalysts that have both the high turnover, poison resistance and thermal stability of present-day heterogeneous systems and the selectivity for complex chemical rearrangements of enzymes. In short, it could help us to realize the goal of 'green chemistry' — producing desired product molecules while minimizing chemical waste. ■

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FURTHER READING

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