Perspectives in Catalysis

Adsorbate (substrate)-induced restructuring of active transition metal sites of heterogeneous and enzyme catalysts

G.A. Somorjai and Y. Borodko

Department of Chemistry, University of California, and Materials Sciences Division of Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

Received 23 February 1999; accepted 25 March 1999

Adsorbate-induced restructuring of transition metal surfaces and those of transition metal clusters embedded in metalloproteins has been shown to be a dominant phenomenon by LEED surface crystallography and X-ray crystallography studies, respectively. The restructuring is thermodynamically driven and is more facile for low-coordination metal sites (surface defects, steps and kinks, and nanoclusters). Dynamic restructuring of catalytically active transition metal sites may occur on the time scale of catalytic turnover or faster. The structural flexibility of transition metal surfaces and clusters embedded in enzymes could provide for seamless evolutionary changes of catalytic chemistry from inorganic to more complex and selective bio-organic systems.

Keywords: catalyst restructuring, enzyme catalyst, heterogeneous and enzyme catalysts

Enzyme catalyst selectivity under mild conditions of reactions are a challenge for the heterogeneous catalytic community. The remarkable fact is that heterogeneous catalysts share a number of traits with one-substrate enzyme reactions. Among them the adsorbate-induced restructuring of active metal sites for both heterogeneous [1] and enzyme catalyst [2] systems is perhaps the most significant. A great body of data shows that conformational flexibility of heterogeneous catalytic and enzyme active sites are important ingredients of catalytic selectivity and activity.

The restructuring of transition metal crystal surfaces induced by the adsorption of atoms and molecules was determined by quantitative low-energy electron diffraction (LEED) surface crystallography studies [3]. One example, the surface structure of ethylene on the (111) crystal face of rhodium and platinum at 300 K, is shown in figure 1 (A) and (B) [4]. The development of Tensor LEED [5] provided the accuracy of measurements of changing bond distances and bond angles to show that metal atoms move to new equilibrium positions around the adsorption site in order to optimize the strength of the chemisorption bonds. Adsorbate-induced restructuring of transition metal surfaces has been determined by more than 100 LEED crystallography studies [6]. Scanning tunneling microscopy (STM) [7] and field ion microscopy (FIM) [8] investigations have shown massive restructuring of the metal crystal faces upon chemisorption, providing more qualitative but additional proof of this pervasive phenomenon that occurs rapidly at high adsorbate pressures.

Adsorbate-induced restructuring is thermodynamically driven to optimize the strength of the chemisorption bond. The exothermic heat of adsorption compensates for the relocation of metal atoms around the adsorption site that weakens metal–metal bonds, an endothermic process. For this reason, adsorbate-induced restructuring is more facile at low-coordination adsorption sites such as more open lower atomic density crystal faces (for example, the (110) vs. the (111) crystal face of rhodium [9]), at atomic steps and kinks at the surface, because there are fewer neighboring metal atoms that would relocate when adsorption occurs. Metal nanoclusters, which are the usual form of most transition metal catalysts, have more of their atoms at the surface and may have several configurations, all of them thermodynamically stable [10]. Adsorption of molecules of one type would cause restructuring one way, while a different adsorbate would stabilize another cluster structure.

Heterogeneous transition metal catalysis then occurs on metal surfaces that are restructured by the first monolayer of reactants that chemisorb under reaction conditions. The adsorbates that turn over to form the products may react on such a restructured surface that is stabilized by the stagnant, strongly bound adsorbate layer that forms first (for example, the hydrogenation of light olefins on Pt(111) [11–13]). Or the adsorbates that cause restructuring of the metal surface are the very species that turn over to desorb as product molecules (for example, CO oxidation on Pt(111) [14] or Pt(100) [15]). While adsorbate-induced restructuring of the transition metal surface is an essential step during heterogeneous metal catalysis, for the first case (light olefin hydrogenation), the turnover rate is not correlated with the rate of surface restructuring. Since metal surface restructuring occurs much faster than the catalytic turnover rate, the catalytic rate is “structure insensitive”. In the second case (CO oxidation), the rate of adsorbate-induced restructuring of the metal surface is equal to the catalytic turnover rate. In this circumstance, the catalytic reaction is “surface structure sensitive”.

Heterogeneous catalytic reactions are, in fact, divided into "structure-insensitive" and "structure-sensitive" classes [16,17]. Also, the unique catalytic activity at low-coordination defect sites that restructure most readily upon chemisorption is well demonstrated by catalytic reaction studies using single-crystal surfaces [18,19]. Thus, the dynamic restructuring of surfaces upon adsorption and during catalytic reactions is an omnipresent, dominant feature of chemisorption and catalytic reactions on transition metal surfaces.

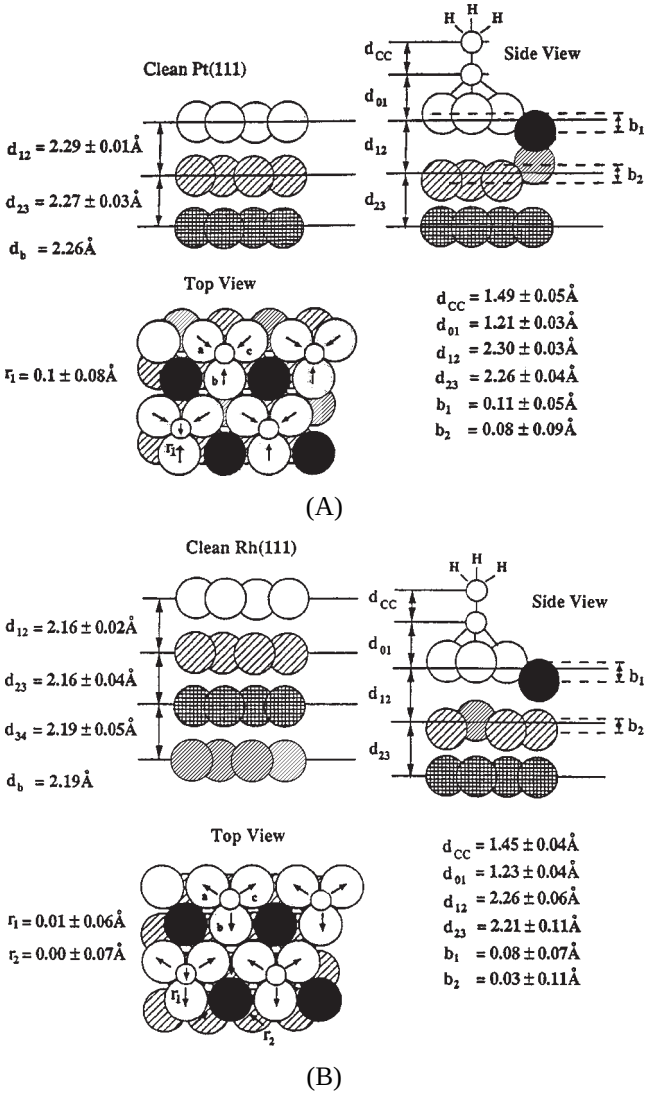

Figure 1. The 0.25 monolayer p(2 × 2) fcc-site ethylidyne–Pt(III) (A) and hcp-site ethylidyne–Rh(III) (B) structures.

Turning to bio-organic systems that contain transition metal clusters, metalloproteins, and metalloenzymes, recent structural studies reveal the restructuring of the metal sites upon adsorption of the substrate [20] (a common name for the adsorbate in this field of chemistry). The charge transfer that occurs upon adsorption certainly contributes to changes of bond length, bond angles, and confirmation around the metal adsorption sites [21].

Comparison of the X-ray structures of deoxyhemoglobin and oxyhemoglobin shows the restructuring of the metal-containing binding sites [22–24]. This was also found for hemocyanin, another oxygen carrier that contains a copper binuclear binding site (figure 2) [25].

It has also been suggested [26], based on available data, that enzymes utilize structural flexibility, induced by the adsorption of the substrate to maximize reaction rate and selectivity of enzyme-catalyzed reactions. Single-molecule enzyme dynamic studies of cholesterol oxidase detect slow fluctuation of protein conformation that influences the rate of the reaction [27]. In some enzymes, the active sites display more conformational flexibility than the enzyme molecule as a whole [28].

An example of a remarkable facility for restructuring in both the free and protein-bound conditions is the iron–sulfur cluster widely utilized in biological systems [29]. When the inactive protein-bound cluster $[Fe_3S_4]^+$ in aconitase was exposed to urea, its cuboidal structure became linear [30]. Recent advances in X-ray crystallographic and spectroscopic studies of nitrogenase show that MoFe cofactor ($MoFe_7S_5$), which contains the binding site for dinitrogen, is extremely flexible [31–33]. Unlike high-temperature heterogeneous reduction reactions that use relatively weak reductants, like H_2 in ammonia synthesis ($N_2 + 3H_2 \rightarrow 2NH_3$), the biological nitrogen fixation needs a more powerful reducing agent [34,35]. To protect the reduced active sites in aerobic atmosphere and protic media, the enzyme utilizes high flexibility of metal active sites and a protein matrix to shield the reduced metal centers or to open them for approach of substrate and departure of product.

Thus, just as in the case of transition metal surfaces, the adsorption-induced restructuring of transition-metal-containing clusters in metalloproteins and enzymes appears to be a pervasive and dominant phenomenon. Its time scale,

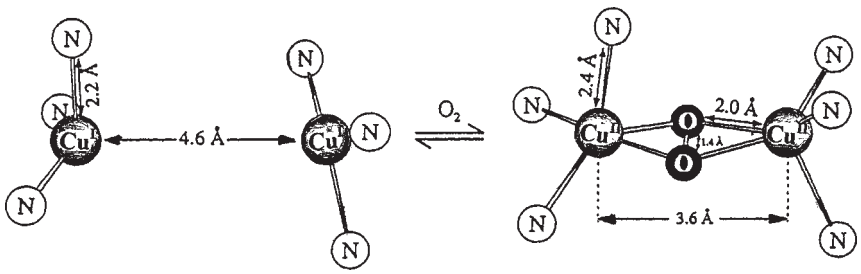

Figure 2. Initial and substrate-bound structures of hemocyanin adsorption site.

however, whether it occurs faster or on the time of catalytic turnover, has not been well researched as yet for a wide variety of systems to arrive at any firm assessment.

Equipped with solid evidence of adsorption-induced structural change around the active site both at transition metal surfaces that are active heterogeneous catalysts and for metalloproteins and enzymes, we propose that (1) there is strong similarity on the molecular level of structural changes that occur at the active sites during catalytic turnover of the two types of catalytic systems (heterogeneous and enzyme); and (2) dynamic restructuring of active sites (flexibility) upon adsorption of the reactants (substrates) is a key feature of catalytic turnover.

The similarity of atomic scale restructuring of transition metal surfaces and transition metal clusters that are embedded in bio-organic systems would permit seamless evolutionary changes of surface and catalytic chemistry from inorganic to the more complex organic systems. As the planet cooled, high turnover surface catalytic processes that may have involved nitrogen, carbon dioxide, carbon monoxide, and water conversion through ammonia synthesis, steam, and CO_2 reforming to produce hydrogen, methane, and higher molecular weight hydrocarbons less likely to occur as many of the elementary reactions are endothermic. Using light as an external energy source instead of heat, slower but more selective catalytic systems developed for nitrogen fixation, hydrocarbon conversion and oxygen production using the same or similar transition metal clusters to carry out the chemical processes that ultimately started to build the bio-organic complexity we live with today.

Acknowledgement

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the US Department of Energy under Contract No. DE-AC03-76SF00098.

References

[1] G.A. Somorjai, Catal. Lett. 12 (1992) 17; Ann. Rev. Phys. Chem. 45 (1994) 721.
[2] D.E. Koshland, Jr., J. Cell. Comp. Physiol. 54 (1959) 245; Adv. Enzymol. 22 (1960) 1.
[3] A.M. Wander, M.A. Van Hove and G.A. Somorjai, Phys. Rev. Lett. 67 (1991) 626.
[4] P.J. Rous, M.A. Van Hove and G.A. Somorjai, Surf. Sci. 226 (1990) 15.
[5] P.R. Watson, M.A. Van Hove and K. Herman, *Atlas of Surface Structures*, Vols. 1 A and B, J. Phys. Chem. Ref. Data, Monograph No. 5 (Am. Chem. Soc., New York, 1994).
[6] B.J. McIntyre, M. Salmeron and G.A. Somorjai, J. Vac. Sci. Tech. A 11 (1993) 1964.
[7] N. Krause and A. Gaussmann, Surf. Sci. 266 (1992) 51.
[8] J.D. Batteas, A. Barbieri, E.K. Starkey, M.A. Van Hove and G.A. Somorjai, Surf. Sci. 313 (1994) 341.
[9] M. Gierer, A. Barbieri, M.A. Van Hove and G.A. Somorjai, Appl. Surf. Sci. 391 (1997) 176.
[10] M. Simonetta, Nouv. J. Chim. 10 (1986) 533.
[11] P.S. Cremer, X. Su, Y.R. Shen and G.A. Somorjai, J. Am. Chem. Soc. 118 (1996) 2942.
[12] P.S. Cremer, X. Su, Y.R. Shen and G.A. Somorjai, J. Phys. Chem. 100 (1996) 16302.
[13] P.S. Cremer, X. Su, Y.R. Shen and G.A. Somorjai, J. Chem. Soc. Faraday Trans. 92 (1996) 4717.
[14] X. Su, P.S. Cremer, Y.R. Shen and G.A. Somorjai, J. Am. Chem. Soc. 119 (1997) 3994.
[15] R. Imbihl and G. Ertl, Chem. Rev. 95 (1995) 697.
[16] M. Boudart, Adv. Catal. 20 (1969) 153.
[17] M. Salmeron, R.J. Gale and G.A. Somorjai, J. Chem. Phys. 70 (1979) 2807.
[18] D.R. Strongin, S.R. Bare and G.A. Somorjai, J. Catal. 103 (1987) 289.
[19] S.M. Davis, F. Zaera and G.A. Somorjai, J. Am. Chem. Soc. 104 (1982) 7453.
[20] C.D. Garner, J. Chem. Soc. Dalton Trans. (1997) 3903.
[21] E.I. Steifel, J. Chem. Soc. Dalton Trans. (1997) 3915.
[22] M.F. Perutz and G. Fermi, *Haemoglobin and Myoglobin: Atlas of Molecular Structure in Biology*, Vol. 2 (Oxford University Press, New York, 1981).
[23] E. Antoin and M. Brunori, *Hemoglobin and Myoglobin in Their Reactions with Liquids* (North-Holland, Amsterdam, 1971).
[24] R.E. Dickerson and I. Geis, *Hemoglobin Structure, Function, Evolution, and Pathology* (Benjamin/Cummings, Menlo Park, CA, 1983).
[25] K.A. Magnus, B. Hayes, H. Ton-That, C. Bonaventura, J. Bonaventura and W.G. Hal, Proteins: Struct. Funct. Genet. 19 (1994) 302.
[26] W.P. Jencks, Ann. Rev. Biochem. 66 (1997) 1.
[27] H.P. Lu, L.Y. Xun and X.S. Xie, Science 282 (1998) 1877.
[28] C.L. Tsou, Science 262 (1993) 380.
[29] H. Beinert, R.H. Holm and E. Munck, Science 277 (1997) 653.
[30] M.C. Kennedy, T.A. Kent, M. Emptage, H. Merklet, H. Beinert and E. Münck, J. Biol. Chem. 259 (1984) 14463.
[31] J.B. Howard and D.C. Rees, Chem. Rev. 96 (1996) 2965.
[32] J. Kim and D.C. Rees, Nature 360 (1992) 553.
[33] J.T. Bolin, A.E. Ronco, T.V. Morgan, L.E. Martenson and N.H. Xuong, Proc. Natl. Acad. Sci. 98 (1993) 1078.
[34] P.E.M. Siegbahn, J. Westerberg, M. Svensson and R.H. Crabtree, J. Phys. Chem. 102 (1998) 1615.
[35] T.A. Bazhenova and A.E. Shilov, Coord. Chem. Rev. 144 (1995) 69.