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Corlett Wood

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Contributing Papers
from

Benjamin Brady
Department of History
University of Virginia
Charlottesville, Virginia, USA

Billy O'Steen & Lane Perry
College of Education
University of Canterbury
Christchurch, New Zealand

John T. Yates, Jr.
Department of Chemistry
University of Virginia
Charlottesville, Virginia, USA

Pauline Oliveros
Department of Music
Rennselaer Polytechnic Institute & Mills College
Troy, NY, USA & Oakland, CA, USA

Jefferson Scholars Foundation
112 Clarke Court
P.O. Box 400891
Charlottesville, VA, 22904-4891

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"To see differently in this way for once, to want to see differently, is no small discipline"

The Search for the Active Site on Catalysts

John T. Yates, Jr.
Department of Chemistry
University of Virginia
Charlottesville, Virginia, USA

Abstract

Heterogeneous catalysis is a centrally-important component (about 20 %) of the GDP of the modern world. Catalysis at active surfaces gives us the only technology to make needed fuels, organic chemicals, and synthetic materials from petroleum and to produce pollution control in automotive exhaust systems. This article probes the development of our understanding at the atomic level of the active site for inducing chemistry at catalyst surfaces. The history covered extends from 1925 to the present, and includes past and recent work done at the University of Virginia.

Our lives are profoundly influenced by catalysts. These high tech materials speed up chemical reactions and provide substances which are highly desirable as intermediates for the manufacture of most synthetic organic materials such as plastics, paints and drugs. Additionally, liquid fuels from petroleum are refined using many types of catalysts. Everyone is familiar with the automotive catalyst used in all cars and light trucks in the US. These portable catalysts are at work removing toxic effluents from the exhaust, and have led, for example, to a 90% reduction in automotive pollution in the Los Angeles basin. Catalysts also play a major role in supplying artificial fertilizer to the world, being used to convert nitrogen in the atmosphere to ammonia and its salts. It has been estimated that the feeding of more than two billion persons is now possible due only to nitrogen-based artificial fertilizer, compared to the 19th and early 20th century and before, when animal wastes were the only source of fertilizer [1]. The contribution of catalysts to the gross domestic product of the US now exceeds 20% [2].

A key driving force in the development of catalysts is the understanding at the atomic level of how they work. Catalytic reactions generally occur in adsorbed layers of molecules held on surfaces in a layer only one-atom size in thickness. A catalytic chemical reaction occurs when a chemisorbed molecule (held on the catalyst surface by chemical bonding) breaks one of its chemical bonds. The catalyst works by bringing the molecular fragments from the bond-breaking events into reaction with other molecules or molecular fragments chemisorbed on the surface, producing new chemical bonds and thereby forming new molecules. A simple example shown in Figure 1 is the catalytic formation of water molecules by the breaking of H-H bonds and O-O bonds generating H_2O molecules. This is the catalytic combustion of hydrogen on a Pt catalyst.

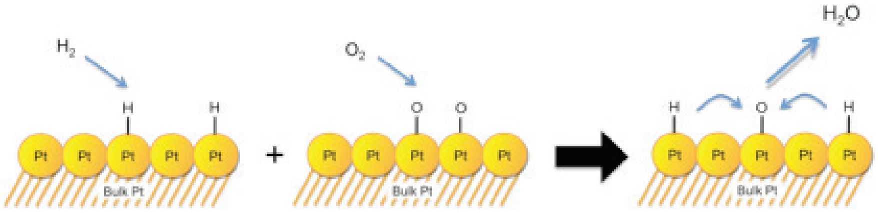

Figure 1: The successive chemical steps in the catalytic production of water from hydrogen and oxygen atoms on platinum atoms on a platinum catalyst. In the absence of the catalyst, the reaction will only take place at very high temperatures as an explosive event as for example in the destruction of the German dirigible, Hindenburg in 1937.

So how do catalysts work? This of course has to do with the particular catalytic reaction desired. But there are common chemical principles which must be present in a good catalyst. As one sees in Figure 1, a H_2 molecule approaches and chemically bonds to the Pt surface. The H-H chemical bond is broken and two Pt-H bonds are formed. Elsewhere the same thing is happening for O_2 molecules, forming Pt-O bonds. The Pt-H and Pt-O bonds must be strong enough so that these two bond dissociation processes will occur, but not so strong to prevent O-H bonds from forming and producing water molecules which leave the surface. It has been found that for water formation, Pt and the Pt- group metals are superior for the reaction. The superiority of Pt-group metals for many types of catalytic reactions has been demonstrated for over 100 years. Unfortunately, these metals are very rare and expensive. Therefore throughout the field of catalysis research substitute metals and alloys are constantly being sought for the Pt metals. One substitute is tungsten carbide, which is much less expensive than Pt [3].

The activity of catalysts depends upon the availability of active surface sites which are particularly capable of supporting catalytic reactions. On the surface of a catalyst, if one were to examine it with a microscope able to resolve individual atoms (as can now be done in the laboratory), one would see that a mixture of types of crystal sites is available. Some will be smooth atomic planes; some will be atomically rough regions of the surface. In 1925, in an amazingly prescient research paper [4], H.S. Taylor of Princeton University first envisioned the active catalytic site. He imagined that the surface of nickel catalyst particles (granules) consisted of Ni atoms which were multiply bound to other nickel atoms, as well as Ni atoms which were less-well bound. These poorly-bound Ni atoms were envisioned as active sites for catalysis and are sometimes referred to as Taylor sites. The idea behind this was simple: Taylor correctly reasoned that the ability of a Ni atom to break a chemical bond of a nearby molecule would increase if the Ni atom was less well coordinated to other Ni atoms. The provision of this model for the active catalytic site was based upon speculation alone, since our ability to directly observe such surface sites in the laboratory did not take place until the late 1970's with the advent of the scanning tunneling microscope and other types of high resolution electron microscopes. In addition, in 1925 and until about 1990, it was impossible for chemical theory to predict the catalytic activity of Taylor sites. The original figure from Taylor's paper is shown in Figure 2.

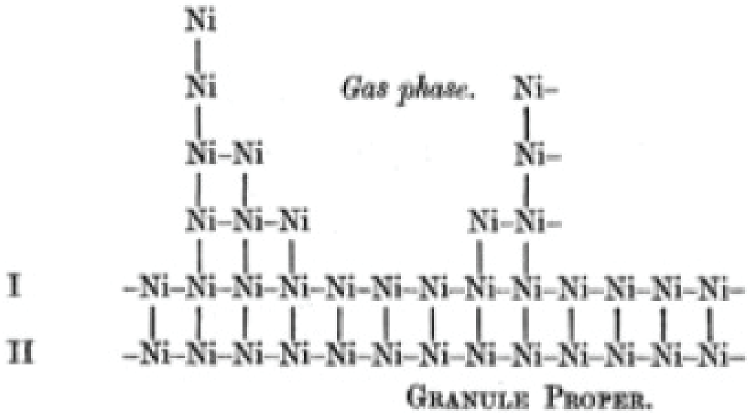
Ni
Ni
Gas phase.
Ni-
Ni-Ni
Ni-
Ni-Ni-Ni
Ni-Ni-
I
-Ni-Ni-Ni-Ni-Ni-Ni-Ni-Ni-Ni-Ni-Ni-Ni-Ni-
II
-Ni-Ni-Ni-Ni-Ni-Ni-Ni-Ni-Ni-Ni-Ni-Ni-Ni-
Granule Proper.

Figure 2: H.S. Taylors's model of the active site of a nickel catalyst[4]. The Ni atoms less well coordinated (or bound) to neighbor Ni atoms were postulated to be catalytically active compared to other Ni surface atoms.

Experiments of many types were used between 1925 and the present to elucidate the active site for catalytic bond breaking in simple molecules. One of these molecules, carbon monoxide, has been investigated by many to determine which type of active site most readily causes C-O bond breaking to make carbon and oxygen atoms on a catalytic surface. CO is an important molecule industrially, as it is used in many technologies as a source of carbon. For example, in South Africa, CO made from coal and steam is catalytically converted to hydrocarbon liquid fuels (artificial gasoline) using the world-famous Fischer-Tropsch catalytic process. This catalytic reaction has resulted in South-African independence from underground petroleum stocks. Figure 3 shows one experiment in which active sites were probed on a platinum-group metal, ruthenium (Ru). Ruthenium is a well-known Fischer-Tropsch catalyst. A single crystal of Ru was cut to expose periodic atomic steps separated by atomically smooth terraces. When a mixture of isotopically-labeled CO molecules is adsorbed and then desorbed by programmed heating, C-O bond breaking will result in isotopic mixing in the desorbing CO, where C-O bond breaking has occurred followed by C-O bond reformation. Above about 480 K, isotopic mixing takes place as CO molecules on the atomic steps sites desorb. On a crystal containing no atomic steps and on the smooth terrace sites, isotopic mixing does not occur as CO desorbs, proving that the Taylor sites, made specifically in the laboratory on the stepped crystal, are active for C-O bond breaking [5]. Other spectroscopic studies have shown that C-O bond vibrations are not observable on the atomic step sites when intact CO molecules have been dissociated by heating to 480 K [6].

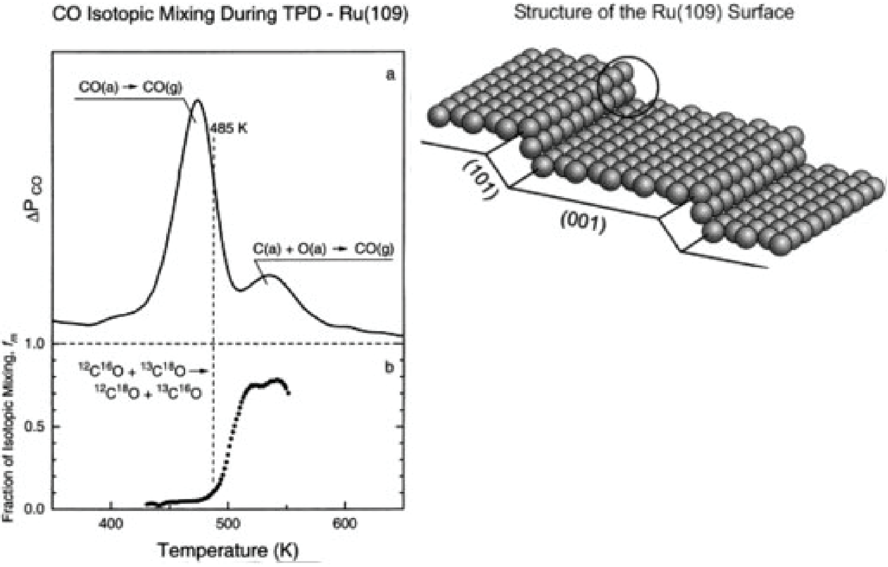

Figure 3: Thermal desorption of isotopically-mixed CO from Ru(109), a stepped single crystal exhibiting rows of active sites separated by atomically-smooth terraces. The fraction of isotopically-mixed CO molecules is strongly enhanced above about 480 K when CO molecules have dissociated and then recombined to desorb from the atomic steps [5].

Recently, a new type of active site has been discovered. Gold, normally not an active metal for catalytic reactions, has been found to exhibit high catalytic activity when it exists as nanometer-sized particles supported on a high area oxide surface [7]. By using modern spectroscopic and theoretical methods, Isabel Green working with Professor John T. Yates, Jr. in the University of Virginia Chemistry Department and Dr. Wenjie Tang, working with Professor Matt Neurock in the University of Virginia Chemical Engineering Department, have discovered the origin of the catalytic activity of the small Au particles. The active sites are located at the boundary between the gold particles and a titanium dioxide support, around the perimeter of the gold particles. As shown in Figure 4, a blue O_2 molecule is bound between a gold atom and a titanium ion at the gold-particle perimeter. This active site is called a dual catalytic site since two dissimilar atoms are involved, causing the O-O bond to weaken and to break. The O atoms produced react with neighbor CO molecules to produce CO_2 at very low temperatures [8]. A schematic diagram of the active catalyst is shown in Figure 4.

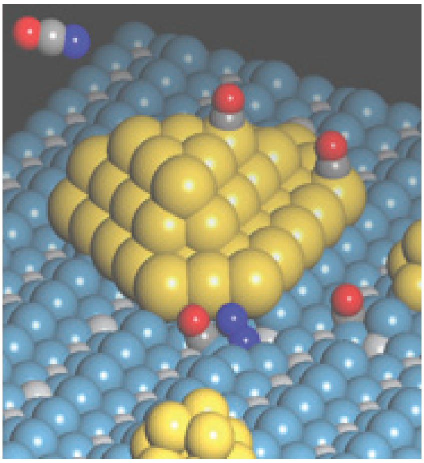

Figure 4: Active site for O_2 activation on a nanometer-gold/titanium dioxide composite catalyst showing a dual perimeter catalytic site dissociating an O_2 molecule (right-hand molecule-blue) and subsequently reacting with CO (left-hand molecule-red and brown) to make CO_2[8].

It is of interest to look back almost 60 years to research at the University of Virginia on the topic of the active catalytic site. At that time, Professor A.T. Gwathmey, an electrochemist, working before the advent of modern surface science, prepared highly polished single crystal spheres of copper and nickel. These spheres exposed atomically-rough vicinal crystal planes like that shown in Figure 3 and located on borders next to smooth crystal planes. On the spherical crystal, the vicinal planes are geometrically oriented to make a symmetrical pattern. Gwathmey found that both the carburization (from C-H bond dissociation of hydrocarbons) and the oxidation (from O-O bond dissociation of O_2) of these crystals lead to visually-beautiful and symmetrically arranged decorated layers of carbon or oxide thin films which were localized on the atomically-rough vicinal planes. Thus, working more than a quarter-century after H.S. Taylor, Gwathmey [9] first successfully observed the enhanced bond-breaking activity of atomically rough metal surfaces, confirming Taylor's postulate [4]. These and other studies set the ground for surface scientists' detailed experimental and theoretical study of active sites using impressive modern tools of surface chemistry and surface physics. The story of active catalytic sites is not over, since current opportunities using nanomaterials will lead to many new and useful catalysts containing active sites which may someday be designed on fundamental principles. The examples shown in this article are partly from the author's work, but many other examples of the probing of active catalytic site are present in the literature.

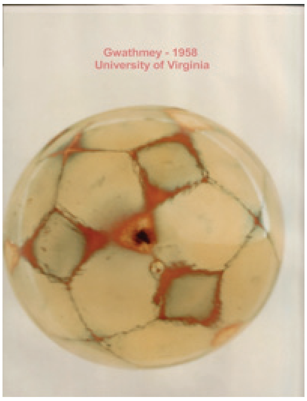

Figure 5 Decoration patterns for the oxidation of a spherical single crystal of copper where oxidation was enhanced at atomically rough sites symmetrically located on the surface [9].

Acknowledgements

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