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The History of Catalysis. From the Beginning to Nobel Prizes

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ABSTRACT
Although the effects of catalysis are known from very ancient times, the understanding of the phenomena started only in the 18th century and in due course led to the awarding to two Nobel prizes at the beginning of the 20th century.

KEYWORDS: Catalysis, mechanism, platinum, platinum group metals, fermentation, sulfuric acid

Resumen (La historia de la catálisis. Desde sus principios hasta los premios Nobel)
Aun cuando los efectos de la catálisis son conocidos desde la antigüedad, la comprensión del fenómeno comenzó sólo en el siglo XVIII y con el tiempo culminó con la adjudicación de dos Premios Nobel en el siglo XX.

Introduction

Catalysis is a phenomenon known from very ancient times, although not so its theory or characteristics; nowadays it plays a fundamental role in the manufacture of the vast majority of chemicals used by our society. The term *catalysis*, proposed in 1835 by Jöns Jakob Berzelius (1779-1848), comes from the Greek words *kata* meaning down and *lyein* meaning loosen. Berzelius wrote that by the term catalysis he meant "the property of exerting on other bodies an action which is very different from chemical affinity. By means of this action, they produce decomposition in bodies, and form new compounds into the composition of which they do not enter" (Berzelius, 1835).

According to Kilani and Batis (Kilani, Batis and Chastrette, 2001), by the end of the 18th and the beginning of the 19th centuries the accumulation of experimental data relative to the modification of diverse chemical reactions by the presence of small amounts of foreign substances was enough to see the beginning of explanation of the phenomena in a frame outside the theory of chemical affinity. Nevertheless, for certain reactions like decomposition catalysis was due to the activity of solids previously heated and could be attributed to heat.

Here we trace the development of the concept and its explanation, from the dawn of its history until the first Nobel Prizes were awarded in 1909 and 1912 for significant contribution in the field. By the beginning of the 19th century the catalytic properties of many metals, notably platinum, had been noticed and extensively investigated, and a crude description of homogeneous catalysis using an unstable intermediate was suggested. By the 1830s the pieces of the puzzle were falling in place, the phenomenon was given its present name, and physical adsorption proposed as its possible mechanism.

Development

The art of producing alcohol from sugar by fermentation is known from the beginning of human history. The first known use of inorganic catalysts is from 1552 when Valerius Cordus (1514-1554) used sulfuric acid to catalyze the conversion of alcohol to ether (Cordus, 1575). In 1781 Antoine Augustin Parmentier (1737-1813) observed that potato starch mixed with distilled water and cream of tartar (potassium hydrogen tartrate), acquires a sweet taste after several months, which is more pronounced if acetic acid has been added (Parmentier, 1781). This reaction was more thoroughly studied by Johann Wolfgang Döbereiner (1780-1849) who found that starch dissolved in water is fermented into alcohol; he assumed that the starch was first converted into sugar (Döbereiner, 1816). He also discovered the catalytic action of manganese dioxide on the thermal decomposition of potassium chlorate, the basis for the preparation of oxygen (Kauffman, 1999).

In 1811 Sigismund Konstantin Kirchhoff (1764-1833) discovered that heating an aqueous solution of starch with mineral acids changed it into a gum, dextrin and raisin sugar, without the acids being modified by the reaction and without release of gas. Treating the resulting solution with alkali recovered all the acid employed (Kirchhoff, 1811).

In 1833 Anselme Payen (1795-1871) and Jean-François Persoz (1805-1868) (Payen and Persoz, 1833) found that the transformation of starch discovered by Kirchhoff was attributable to the action of a special substance, which they called

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diastase (amylase). Payen and Persoz found that the activity of diastase is eliminated by heating to 100°C. Payen established the theory of beer fabrication, discovered the process actually used for obtaining dextrin, determined its composition, and showed it to be an isomer of starch. In 1878 Willy Kühne (1837-1900) suggested the name *enzyme* for biological catalysts.

In the late eighteenth century Johann Rudolph Deiman (1743-1808), Adrien Paets von Trootswijk (1752-1837), Anthoni Lauwerenburg (1758-1820), Nicolas Bondt (1765-1796), and Pieter Nieuwland (1764-1794), reported that *gaz hydrogène carboné huileux* (ethylene) could be prepared by treating 25 parts of alcohol with 75 parts of concentrated sulfuric acid, without external heating, and also by passing alcohol or ether vapors through a glass tube containing silica or alumina, or simply through an empty tube of clay. This work may be considered the first systematic study of catalytic reactions by metals; it was mentioned in a report read by Antoine Francois de Fourcroy (1755-1809) on December 16, 1796 (Fourcroy, 1797ab). The report was considered so important that it was recommended be published in the *Journal des Savants Etrangers* (Passagez, 1935).

In 1817 Humphry Davy (1778-1819) reported that he "was making experiments on the increase of the limits of the combustibility of gaseous mixtures of coal gas and air by increase of temperature…when I was accidentally led to the knowledge of the fact, and at the same time, to the discovery of a new and curious series of phenomena…that oxygen and coal gas in contact with the hot wire combined without flame, and yet produced enough heat to preserve the wire ignited, and to keep up their own combustion…A temperature much below ignition only was necessary for producing this curious phenomenon…The same circumstance occurred with certain inflammable vapors…ether, alcohol, oil of turpentine, and naphtha…I have tried…various metals; but succeeded only with platinum and palladium; with copper, silver, iron, gold, and zinc, the effect is not produced" (Davy, H., 1817). Davy suggested that his discovery could be used to build a non-explosive lamp to be employed in mining operations. Humphrey's Davy discovery may be considered the first clear evidence that a chemical reaction between two gaseous reactants can occur on a metal surface *without* the metal being chemically changed.

In 1820, Edmund Davy (1785-1851) reported that boiling a mixture of platinum sulfate with alcohol or ether precipitated a black substance in a finely divided state (Davy, E., 1820). Heating the powder produced a feeble explosion accompanied by a flash of red light and reduction of the platinum. Davy studied the properties of the powder and indicated "it is tasteless and does not affect litmus paper…It seems to undergo no change by exposure to the air for some time. When it is heated gently on a slip of platinum or paper, a hissing noise or a feeble explosion is produced and a flash of red light accompanies this effect and the platinum is reduced… When the powder is brought into contact with ammonia gas, a crackling noise is produced and becomes red and scintillates…Oxygen gas does not affect the powder at the common temperature of the air, but by a moderate heat there is a slight combustion, which seems to indicate the presence of a little inflammable substance…I have already employed it as an easy means of affording heat and light. To produce heat it is only necessary to moisten any porous substance, such as sponge, cork cotton, asbestos, sand, etc., with alcohol or whiskey, and to let a particle of the powder fall on the substance so moistened; it immediately becomes red hot, and remains so until the spirit is consumed…"

Louis-Jacques Thenard (1777-1857) did some research on the subject of alcoholic fermentation and concluded that all sugary juices, in the process of spontaneous fermentation, deposited a substance which resembled beer yeast and had the power of fermenting pure sugar. He believed that this yeast was *animal* in nature (Thenard, 1803), since it contained nitrogen and yielded ammonia on distillation (Thenard, P., 1950). Thenard asked himself: All of our knowledge about fermentation indicates that sugar matter changes into alcohol and carbon dioxide by means of an intermediate body. How does it operate on sugar? In spite of all his efforts, he was unable to provide a satisfactory answer.

In 1820, when Thenard was studying the effect of finely divided metal on hydrogen peroxide, he compared this phenomenon to the action of yeast in alcoholic fermentation (Thenard, P., 1950). Louis Pasteur (1822-1895) quoted Thenard's analysis of the fermentation process in his well-known memory about alcoholic fermentation (Pasteur, 1860).

Thenard's work on wine fermentation and the decomposition of hydrogen peroxide by metals and certain organic materials may be considered the origin of his interest in catalysis, although he did not know the meaning of the phenomena. Hearing about Döbereiner's results he was astounded to see that the same material that decomposed water peroxide by simple contact was able to induce the reaction between oxygen and hydrogen. Pierre-Louis Dulong (1785-1838) and Thenard verified and confirmed Döbereiner's results (Dulong and Thenard, 1823a). They found that a sponge of palladium was also able to ignite hydrogen; a sponge of iridium heated very strongly also realized this reaction producing water. Hydrogen and NO_2 or hydrogen and NO in the presence of platinum sponge at room temperature, reacted yielding water and ammonia (Dulong and Thenard, 1823ab). Dulong and Thenard also reported that the platinum sponge became incandescent when it was contacted by hydrogen intimately mixed with air. Platinum, reduced to a very fine powder, or as a wire or sheet, did not act even slowly, at room temperature. Although these results seemed to suggest that the porosity of the metal was an essential condition for the phenomenon to take place, it was easy to prove it wrong. Dulong and Thenard reduced the platinum to a very thin sheet and found that in this state the metal also acted at room temperature over a mixture of oxygen and hydrogen; the reaction became as the sheet was thinned, sheet, even with explosion.

A very thin platinum sheet rolled up over a glass cylinder or suspended freely in an explosive mixture did not produce any sensible effect, even after several days, but the same sheet crumpled and burred, detonated the mixture instantly (Dulong and Thenard, 1823a).

Davy had considered the phenomenon to be an exclusive result of the mutual action between the fluids, without consideration of the nature of the vessels that contained them. According to Dulong and Thenard, the contrary was true; the combination took place at a different temperature for each solid substance that came into contact with the combustible substance. All these observations revealed a kind of action that could not be explained by any known theory. Dulong and Thenard tried to discover if electricity played a role in these phenomena and concluded that so far, and by default, they could only explain most of the observed effects by assuming a pure electrical origin, but without understanding how (Dulong and Thenard, 1823b).

As told by Prandtl (Prandtl, 1950), Johann Wolfgang Döbereiner's (1780-1849) work on heterogeneous catalysis was an initial outgrowth of his interest in platinum, which he needed for manufacturing chemically resistant laboratory vessels. In order to obtain a supply of this metal for the manufacture of laboratory vessels and also to recover the accompanying metals, Döbereiner began to work up two pounds of American platinum ore in 1812. In 1821 Döbereiner repeated the experiments of Humphry and Edmund Davy and found that platinum black, which he name *platinschwarz*, caused alcohol to combine, at room temperature, with the oxygen of the atmosphere to form a product that he called *oxygen ether*, and also acetic acid. A most significant fact was that platinum not only oxidized alcohol to acetic acid completely but also remained unchanged by the reaction, a finding that suggested its possible use for the direct production of vinegar from alcohol (Döbereiner, 1823ab, 1828).

As stated by Kaufmann (Kaufman, 1999) Döbereiner correctly regarded this important discovery as due to the activity of the platinum rather than to the action of the ethanol on platinum, as the Davys had mistakenly assumed. In the beginning he thought that platinum was a sub-oxide: "The platinum sub-oxide, moreover, does not undergo any change during this transformation of the alcohol and can be immediately used again to acidify fresh, perhaps limitless, quantities of alcohol…a circumstance that permits its use for the large-scale preparation of acetic acid (Döbereiner, 1823b).

In 1823 Döbereiner prepared platinum sponge by igniting ammonium hexachloroplatinate (V) and made a remarkable observation. On directing on the sponge a jet of hydrogen issuing from a gasometer through a capillary held at a distance of 4 cm, so that it was admixed with air, the metal became red or white hot almost immediately and the hydrogen caught fire. The action took place at room temperature or even at –10°C (Prandtl, 1950). In Döbereiner's words: "There now followed in a few moments that strange reaction; the volume of the gases diminished and after ten minutes all the admitted air had condensed with the hydrogen to form water" (Döbereiner, 1828, 1836; Kauffman, 1999).

This discovery, producing fire without flint and tinder, created a real sensation and was immediately tested and confirmed by numerous chemists and physicists. Berzelius, in his *Jahres-Bericht* (Berzelius, 1823-1825), wrote: "From any point of view the most important and, if I may use the expression, the most brilliant discovery of last year is, without doubt, that fine platinum powder has the ability to unit oxygen and hydrogen even at low temperatures…made by Döbereiner" (Kauffman, 1999).

In those days, when there was no simple way to produce fire, Döbereiner's discovery led immediately to its application, the hydroplatinic lamp, also called *briquet à hydrogène* (hydrogen lighter) or *Döbereiner Feuerzeug* (Döbereiner lamp). The *Döbereiner Feuerzeug* was used for lighting purposes for about 100 years until replaced by the phosphorus match.

In 1832 Döbereiner discovered that sulfur dioxide can be oxidized to sulfur trioxide by air in the presence of platinum, but in the industrial application of this discovery he was anticipated by Peregrine Phillips, a Bristol vinegar merchant, who in 1831 had already obtained an English patent for the manufacture of sulfuric acid (Phillips, 1831; McDonald, 1960, 1965; Robertson, 1975; Wisniak, 2005).

In 1838 Kuhlmann patented a process for the manufacture of sulfuric acid by the oxidation of sulfur over finely divided platinum supported on glass or other acid-resistant material (Kuhlmann, 1838ab; Gay-Lussac, Thenard and Pelouze, 1839; Kauffman, 1999).

William Henry (1774-1836) was the first to study the deactivation of platinum-based catalysts. Henry discovered that certain substances (for example, hydrogen sulfide and carbon disulfide) inhibited the combustion of hydrogen and that platinum catalysts were less active for the combustion of methane and ethylene than for hydrogen and carbon monoxide. As catalyst he used platinum sponge or balls made of clay and platinum, as Döbereiner had done previously (Henry, 1824, 1825).

With this new discovery Henry developed procedures for separating and analyzing combustible gases based upon their reactivity in the presence of platinum-based catalysts. To ascertain this possibility and others, Henry prepared synthetic mixtures of combustible gases in known volumes and submitted them, mixed with oxygen. The results allowed Henry to devise a method for obtaining carburetted hydrogen gas perfectly free from olefiant gas, hydrogen and CO (Henry, 1824, 1825).

In his study of the phenomenon of decomposition Henry Sainte-Claire Deville (1818-1881) did also work in the field of catalysis. For example, he found that when heating a mixture of potassium cyanide in contact with wet air, at 500 to 600°C, under vacuum, the pressure increased to about ½ atmosphere and maintained itself for many hours. But if the potassium cyanide was first mixed with sponge platinum large amounts

of hydrogen were generated and a double cyanide of potassium and platinum formed (Deville and Debray, 1876).

In spite of having been determined that many metals were capable of catalytic action, the most interesting one continued to be platinum and centralized most of the research work. In his book about catalysis, Paul Sabatier (1854-1941; 1912 Nobel Prize for Chemistry) summarized the known facts about platinum as follows (Sabatier, 1913): "Platinum did not behave in this manner only when made as a sponge; it did also when finely divided as filings, wire, or turnings, as long as it was first heated slightly. Many experiments led to think that this activity increased the more the platinum was divided; it even increased more if before calcination the aqueous solution of chloroplatinate was boiled with a little of sodium carbonate and sugar. The chloroplatinate was completely decomposed and the metal precipitated as a black powder. This powder was much more active than the sponge; it absorbed hydrogen rapidly and the smallest particle led to the instantaneous ignition of a mixture of hydrogen and air. Thenard then found that black platinum decomposed hydrogen peroxide rapidly and with violence into oxygen and water, without absorbing the gas releasing or loosing its activity (Thenard, 1818-1819ab)". By 1900 this property of platinum was found also in other metals (such as copper and iron), metallic oxides (such as manganese dioxide), carbon, certain acids, etc. (Bertrand, 1955).

Intensive research in the area of catalysis, particularly by Sabatier and his students, led to the discovery that many metals, particularly nickel and the platinum group elements, alone or supported, possessed a unique catalytic activity, especially for hydrogenation reactions, that ultimately would become the base for the fast development of the petrochemical industry. The basic work of Sabatier in this fundamental scientific and industrial subject forms the basis of our modern theories about catalysis and catalysts, as well as many of the processes used today in the petrochemical industry. Sabatier and Jean-Baptiste Senderens (1856-1937) discovered catalytic hydrogenation, a finding that gave Sabatier the 1912 Nobel Prize in Chemistry: the hydrogenation metal catalysts (and particularly nickel) make it possible, by their only presence, to fix hydrogen on the most various molecules.

Today, the most important catalysts are of the type Pt-γ-Al_2O_3. The application of supported noble metal catalysts for the treatment of exhaust gases from automobiles has been introduced in recent years in all industrialized countries. Combinations of metals that have a catalytic action of exhaust gases include Pt-Rh, Pt-Pd and Pt-Pd-Rh. The demand for these materials amounts to more than one-third of the annual production of platinum and to more than four-fifths of the annual production of rhodium (Robertson, 1975; Wisniak, 2005).

In 1858 Morris Traube (1826-1894) discussed the phenomena of fermentation and decay and concluded that the pertinent agents were definite chemical compounds arising from the reaction of the protein substances with water, in the same manner that ferments present in the organism had arisen. "All these ferments had the power of transferring to other bodies the oxygen taken up in one or the other manner…to become again reduced…and to be put into the state to take up new quantities of oxygen, again to transfer it and so on. In this way all ferments may transfer free or bound oxygen to other substances in almost endless amounts… (Traube, 1858).

In 1896 Henri Moissan (1852-1907; 1906 Nobel Prize for Chemistry) and Moureu tried the fixation of acetylene by passing a current of acetylene on slivers of iron, nickel, or cobalt freshly reduced from their oxides by hydrogen, and observed a brilliant incandescence. According to Moissan and Moureu "this reaction is due to a physical effect": reduced iron, nickel, or cobalt being extremely porous, absorbed the acetylene with production of enough heat to cause its spontaneous destruction (Moissan, 1904-1906).

Sabatier and Senderens repeated the experiments but using ethylene instead of acetylene, a hydrocarbon less violent in its reactions. But they also found methane almost pure. Sabatier and Senderens concluded that an unstable combination between nickel and ethylene had formed, analogous to nickel carbonyl, which doubled itself into carbon, methane and nickel, which could then repeat an identical process (Sabatier, 1897a). It seemed that reduced nickel had the property of hydrogenating ethylene. This result, they believed "ought certainly to be attributed to the temporary formation of a direct and specific combination of nickel and ethylene" (Sabatier, 1897b).

Sabatier and Mailhe found that some metal oxides were catalysts not for hydrogenation and dehydrogenation, but instead for hydration and dehydration (Sabatier, 1910ab). They also observed that amorphous oxides were more active catalysts for dehydrogenation or dehydration than the crystalline oxides ones (Sabatier, 1911). Calcination reduced the active surface by modifying the nature and distribution of the active centers. This was the first example of the sintering effects, which were later used to graduate the activity of catalysts (Wisniak, 2005).

Explanation of the phenomena

As discussed below, Thenard, for lack of a more plausible reason, attributed the action of catalysts to the action of the "electric fluid". Döbereiner believed that it was due to an effect of the crystalline nature of the agent and Angelo Bellani (1776-1852) even in 1824, laid the foundations of the absorption theory (Bellani, 1824). In any case, abstraction made of the explanations given Clément and Désormes for the homogeneous oxidation of sulfur dioxide by oxides of nitrogen; the opening hypotheses on the mechanism of catalysis contain the first ideas of a physical explanation (surface effects). These limited the catalytic effect to a physical action on the course of the reaction only and thus, emphasized that any chemical change of the reagents takes place according to the laws of stoichiometry.

Désormes and Clément were the first to propose a rational theory for the homogeneous catalytic effect of nitrogen oxides in the lead chamber process for the manufacture of sulfuric acid. They did so by establishing for the first time a quantitative relation between the sulfurous acid, oxygen and oxides of nitrogen that participates in the process. There were different opinions on the advantages of using potassium nitrate in the fabrication of sulfuric acid. Some believed that it was the high temperature that its deflagration produced, which determined the formation of sulfuric acid; others thought that the nitrate contributed the complementary amount of oxygen for the combustion started initially by air; while others believed that it could decompose water, etc. Désormes and Clément decided to look only at the first two hypotheses, which seemed the most plausible. The first hypothesis was discarded immediately because the addition of potassium nitrate and sulfur was followed by the addition of clay and water, which resulted in a diminution of the temperature, clay by making the combustion slower, and water by generating vapor. It was also known that sulfur that burned at least at 1000°C did not generate sulfuric acid at all. The second hypothesis was also unacceptable because it presupposed that the oxygen disengaged from potassium nitrate was sufficient for converting all the sulfur dioxide produced into sulfuric acid, but a simple mass balance proved that this was not true. Although the precise amounts in which every substance participated in the reaction were unknown, it was easy to see that the potassium nitrate employed could hardly provide more than 10% of the oxygen required for converting sulfur dioxide into sulfur trioxide. In addition, a visual observation of the burning of a mixture of sulfur, potassium nitrate, and wet clay indicated that the nitric acid did not decompose completely and that an important part of NO gas went into the lead chamber with the sulfur dioxide; its typical color was clearly visible (Désormes and Clément, 1806).

Désormes and Clément believed that the true explanation of the production of sulfuric acid was the following: The burner generated a mixture of NO and sulfur dioxide mixed with water vapor and atmospheric nitrogen. Part of the oxygen did not participate in the burning of the sulfur because the gases NO and SO_2 could not exist in contact, without decomposition of the first and conversion of the second to sulfur trioxide. At the exit of the burner the mixture encountered a lower temperature that led to a partial condensation of the steam. The resulting rain entrained with it the sulfur trioxide generated and reduced the pressure of the remaining substances. After production of the first amount of sulfur trioxide, the remaining gas mixture contained NO, sulfur dioxide, and residual air containing less oxygen. The NO would necessarily convert into nitrogen dioxide, which would then decompose again reacting with a second portion of sulfur dioxide, until all of this oxide or the atmospheric oxygen became exhausted. After the sulfur dioxide had been converted totally into trioxide, the remaining gas was composed mainly of a large amount of nitrogen and nitrogen oxides. Hence, it was clear that nitric oxide was only the *instrument* for the total oxidation of sulfur; it was its base, NO, that took the oxygen from the atmospheric air and transferred it to SO_2, *time after time* (Désormes and Clément, 1806). This explanation may be considered the first time that an intermediate compound is assumed to play a part in a catalytic reaction.

In 1818 Thenard concluded his first paper on the decomposition of water peroxide, as follows: "… the vast majority of bodies have upon water peroxide an action that tends to joint oxygen to water more intimately that to separate it. All acids belong to the first group, and metals, metal sulfides, metal oxides, carbon, etc., to the second; facts which show how much the phenomenon is dependent on electricity" (Thenard, 1818-1819a). In another paper of the same year he offered a more definite opinion: "…the cause of these singular results is still hidden from us, only we see that it does not reside in affinity, at least in the manner it is usually conceived, it is probably physical and perhaps linked to electricity" (Thenard, 1818-1819b). In 1819 Thenard recognized that widely different catalysts were capable of decomposing water peroxide and admitted that all these effects were due to the same unidentified force (Thenard, 1818-1819ab; Kilani, Batis and Chastrette, 2001). In 1821 Thenard recognized clearly the generality of catalytic phenomena: "Whichever it be the cause of the phenomena…is it not very probable that it is the same that produces so many other?" He mentions as examples, the detonation of silver ammonia, of the chloride and iodide of nitrogen, fulminating powders, decomposition of ammonia gas by metals, the transformation of starch into sugar by minute amounts of diastase, and the transformation of sugar into alcohol and carbon dioxide by a small amount of ferment (Thenard, 1821). In the sixth edition of his *Traité de Chimie*, published in 1834, Thenard repeated, without change, the summary of his researches on the decomposition of water peroxide, which he had exposed in the 1821 edition. He was very baffled by these facts, as shown by his opinion that "after having exposed all the phenomena presented by water peroxide in its contact with most materials, we have failed in searching for their reason; unfortunately we can only present some conjectures about it…" He then discusses all the possible reasons for the catalytic action and selects again electricity by elimination apparently to the magnetic fluid "We are thus directed to attributing them to the electric fluid" (Kilani, Batis and Chastrette, 2001).

In his book about the safety lamp (Davy, 1825) Davy returned to the catalytic properties of platinum and wrote: "It is probable that the rationale of all these processes is of the same kind…It may be supposed that the spongy platinum absorbs hydrogen, or that it contains oxygen, but neither of these hypotheses will apply to the fact that I first observed, of the ignition of fine wires in different mixtures of inflammable gas and air, at temperatures so far below ignition. A probable explanation of the phenomenon may, I think, be founded upon the electrochemical hypothesis (Davy, 1807)…

and which has seen been adopted and explained, according to their own ideas, by different philosophers".

Döbereiner's numerous experiments on platinum and platinum black led to a slow change in his ideas about the way the material acted. He claimed that platinum black "was not a simple but a mechanical combination of this metal with compressed oxygen gas…the platinum reduced or isolated by the wet method has the property of absorbing and then compressing a large amount of oxygen gas and that it becomes capable of combining chemically with diverse readily oxidisable substances…In the process of oxidation and acidification of alcohol, platinum plays a role corresponding to the function of the nitrous gases in the process of sulfuric acid formation" (Döbereiner, 1828). He also referred to the effect being caused entirely by an electric action, "whereby hydrogen forms an electrical chain with the platinum" (Döbereiner, 1823b). In a book on the phenomenon that he published in 1823 he considered that it was "probably of a quite special nature, i.e., neither mechanical nor electrical nor magnetic (Döbereiner, 1823a; Kauffman, 1999).

The first attempt to give a detailed theoretical discussion of heterogeneous catalytic oxidation on platinum was made by Ambrogio Fusinieri (1775-1852) in a paper published in 1824 (Fusinieri, 1824, 1825). He discussed the effects discovered by Döbereiner and others and also explained in full his own experimental observations remarking that these would dispel all confusion and doubt (Farinelli, Gale and Robertson, 1974; Robertson, 1975). Fusinieri contended, in opposition to Davy, that combustion of ether on platinum occurred with flame, which was either invisible or probably hidden by light from the platinum. He further argued that during the oxidation of ether "concrete sheets" of the combustible substance could be seen with the naked eye, the sheets running over the platinum surface and then disappearing by burning. Fusinieri thought that the ether forming the sheets was solidified, although he noted a relation between the appearance and disappearance of the sheets and capillary action of liquids, that is, in contact with platinum the gases lost their elastic state and became solid. The platinum catalyst acted like a candlewick with the sheets burning like candle wax. He justified the formation and burning of the concrete sheets, on the existence of *native caloric*. Michael Faraday (1791-1867) reviewed Fusinieri's views at some length, but confessed that he could not understand the concept of native caloric, probably because of his imperfect knowledge of Italian (Faraday, 1834; Farinelli, Gale and Robertson, 1974; Robertson, 1975).

In 1834 Faraday published a very thorough analysis of the phenomena observed with solid platinum and added the results of extensive experimentation when using platinum in a voltaic cell (Faraday, 1834). Faraday wrote: "These experiments reduced the phenomena to the consequence of a power possessed by the platina, after it had been the positive pole of a voltaic pile, of causing the combination of oxygen and hydrogen at common…This effect is…altogether new, and was immediately followed out to ascertain whether it was really of an electric nature…the continuance of the action greatly depended upon the purity of the gases used (poisoning)… These experiments led to the expectation that the power of causing oxygen and hydrogen to combine, which could be conferred upon any piece of platina by making it the positive pole of a voltaic pile, was not essentially dependent upon the action of the pile, or upon any structure or arrangement of parts it may receive whilst in association with it, but belonged to the platina *at all times*, and was *always effective* when the surface was *perfectly clean*…These experiments are abundantly sufficient to show that the mere mechanical cleansing of the surface of platina is sufficient to enable it to exert its combining power over oxygen and hydrogen at common temperatures…There can be no doubt that the property of inducing combination, which can be conferred upon masses of platina and other metals by connecting them with the poles of a battery, or by cleansing processes either of a mechanical or chemical nature, is the same as that which was discovered by Döbereiner in 1823, to belong in so eminent a degree to spongy platina…Dulong and Thenard observe that the action is of a kind that cannot be connected with any known theory, and though it is very remarkable that the effects are transient, like those of most electrical actions, yet they state that the greater number of the results observed by them are inexplicable, by supposing them to be of a purely electric origin".

Faraday went on to express his opinion that catalytic action was due to *physical forces*: "All the phenomena connected with this subject…are connected upon the natural conditions of gaseous elasticity (pressure) combined with the exertion of that attractive forces…by which they are drawn into association more or less close, without at the same time undergoing chemical combination…Bodies which become wetted by fluids with which they do not combine chemically, or in which they do not dissolve, are…well known instances of this kind of attraction…. the gases are those which…might show some mutual action, whilst jointly under the influence of the platina or other solid acting substance…it would seem that the particles of hydrogen or any other gas or vapor which are next to platina…much be in such contact...*as if they were in the liquid state*….The course of events when platina…combines oxygen and hydrogen…is as follows: …the deficiency of elastic power and the attraction of the metal for the gases, the latter, when they are in association with the former… The consequence of their combination is the production of the vapor of water and an elevation of temperature…But as the attraction of the platina for the water formed is not greater than for the gases, if so great (for the metal is scarcely hygrometric), the vapor is quickly diffused through the remaining gases. The platina is not considered as causing combination of any particles with itself but only associating them closely around it…" (Faraday, 1834).

Faraday went on to describe what today we call catalyst poisoning: …"some very extraordinary interferences with this phenomenon, dependent, not upon the nature or condition of the metal, or other acting solid, but upon the presence of

certain substances mingled with the gases acted upon.... It is perfectly clear from these experiments, that olefiant gas, even in small quantities, has a very remarkable influence in preventing the combination of oxygen and hydrogen under these circumstances, and yet without at all injuring or affecting the power of the platina" (Faraday, 1834).

In the section of vegetable chemistry of his 1835 Jahres-Bericht (Annual Survey) (Berzelius, 1835) Berzelius summarized the findings of different scientists on the formation of ether from alcohols; on the enhanced conversion of starch to sugar by acids; the hastening of gas combustion by platinum, of the stability of hydrogen peroxide in acid solution but its decomposition in the presence of alkali and such metals as manganese, silver, platinum, and gold, and the observation that the oxidation of alcohol to acetic acid was accomplished in the presence of finely divided platinum. He repeated this report in French, in a paper published a year later (Berzelius, 1836). He wrote: "Until 1800 no one suspected that any factor other than the degree of affinity could be of importance, with the exceptions of heat and light in certain cases. Then the influence of electricity was discovered…electrical and chemical relationships are the same…preferential affinity is nothing other than the result of strong opposite electrical forces that are intensified by heat or light…Then Kirchhoff discovered that starch, dissolved in dilute acids at a certain temperature, first turns into gum and then into grape sugar... nothing had evaporated into gas, nothing had united with the acid, the bases of which were recovered in the same amount as that in which they had been used, and in the liquid only sugar was found, weighing slightly more than the starch". Thenard then discovered hydrogen peroxide, "the component parts of which were rather weakly joined to each other. Under the influence of acids, they remained in unaltered combination; under the influence of alkalis, they showed a tendency to separate…Not only soluble substances were found to hasten this type of decomposition, but also solid inorganic and organic substances, e.g. manganese dioxide, silver, platinum, gold, and the fibrous element from animal blood. The foreign agent causing the conversion of the substances did not itself participate in the new compounds formed but remained unchanged, thus operating by means of an internal power, the nature of which is still unknown…Edmund Davy observed that wetting platinum finely divided with alcohol rendered the platinum incandescent and the alcohol converted into acetic acid and water. Now came the discovery that crowned the foregoing, namely Döbereiner's finding that platinum sponge is able to ignite a stream of hydrogen gas as it escapes into the air…This discovery was soon followed by the mutual investigation of Dulong and Thenard that showed that several single and compound substances have this property…Thus this power was extended from an exceptional property to a more general one possessed by substances to different degrees...Thus it is certain that substances, both simple and compound, in solid form as well as in solution, have the property of exerting an effect on compound bodies which is quite different from ordinary chemical affinity, in that they promote the conversion of the component parts of the body they influence into other states, without necessarily participating in the process with their own component parts, even if this should occasionally occur…This is a new power to produce chemical activity belonging to both inorganic and organic nature…and the nature of which is still concealed from us. I…do not…imply that it is a capacity independent of the electrochemical properties of the substance...I am unable to suppose that this is anything other than a special kind of special manifestation of these, but as long as we are unable to discover their mutual relationship…it will also make it easier for us to refer to it if it possesses a name of its own. I shall therefore…call it the *catalytic power* of the substances and decomposition by means of this power *catalysis*…Catalytic power actually means that substances are able to awaken affinities…by their mere presence and not by their own affinity. By means of these, the elements in a compound body rearrange themselves in another manner so as to achieve a greater degree of electro-chemical neutrality. Thus their over-all effect resembles that of heat, and here the question may arise as to whether the different degrees of catalytic power possessed by different substances can produce the same dissimilarity in the products of catalysis as is often caused by heat or different temperatures, and thus whether different catalytic substances are able to produce dissimilar products from a given compound body…On this occasion it is sufficient that the existence of catalytic power has been demonstrated with a sufficient number of examples…Turning with this idea to the chemical processes in living nature…we find that the insoluble starch in the tuber is changed to gum and sugar by catalytic power…living tissues" (Berzelius, 1835).

In 1843 Berzelius, explained the catalytic force within the frame of his dualistic theory: "it acts primarily on the polarity of the atoms, increasing or decreasing it. In other words, the catalytic force manifests itself by the excitation of the electrical relations that have so far evaded our researches" (Kilani, Batis and Chastrette, 2001).

Further developments

When Sabatier commenced his investigations on catalysis there were two theories of heterogeneous catalysis, a physical and a chemical one. The physical theory was supported by the work of Jacques Duclaux (1877-1978) and Moissan on the absorption of gases by finely divided metals (Moissan, 1904-1906; Duclaux, 1911). Wilhelm Ostwald (1853-1932; 1909 Nobel Prize for Chemistry) and others had also assumed that catalyzed gas reactions resulted from the absorption of gases in the cavities of the porous metal, where compression and local temperature elevation led to chemical combination. Ostwald believed that a catalyst did not induce a reaction but rather accelerated it without formation of intermediate compounds. In other words, a catalyst was a body that modified the reaction a reaction without taking part in it, a position clearly different from that of Désormes and Clé-

ment. Ostwald chose to state his theory of catalysis in the course of an abstract, which he prepared for an article by Friedrich Karl Adolph Stohmann (1832-1897) on the heats of combustion of foodstuffs (Stohmann, 1894). He disagreed with Stohmann's definition that "catalysis is a condition of movement of the atoms in a molecule of a labile body which follows the entrance of the energy emitted from one body into another and leads to the formation of more stable bodies with loss of energy" (Ostwald, 1894). Ostwald had several objections to make to this definition: "First, the assumption of a condition of movement of the atoms in a molecule is hypothetical and therefore not suitable for purposes of definition. Also, that is plainly not a loss of energy. What is more, in describing characteristic conditions of catalysis, a loss of free energy can follow under conditions even of absolute energy uptake… the abstractor (Ostwald)…would consider the following expression as probably most suitable: Catalysis is the acceleration of a chemical reaction, which proceeds slowly, by the presence of a foreign substance…There are numerous substances or combinations of substances, which in them are not stable but undergo slow change and only seem stable to us because their changes occur so slowly that...they do not strike us. Such substances or systems often attain an increased reaction rate if certain foreign substances, that is, substances, which are not in themselves necessary for the reaction, are added. This acceleration occurs without alteration of the general energy relations…after the end of the reaction the foreign body can again be separated from the field of the reaction, so that the energy used up by the addition can once more be obtained by the separation, or the reverse. However, these processes, like all natural ones, must always occur in such a direction that the free energy of the entire system is decreased. It is therefore misleading to consider catalytic action as a force which produces something which would not occur without the substance which acts catalytically; still less can it be assumed that the latter performs work…that time is not involved in the idea of chemical energy…it is only the initial and final states, as well as the whole series of intermediate given states which must be passed through, which must occur…Time is here dependent on conditions, which lie outside the two chief laws of energetics. The only form of energy, which contains time in its definition, is kinetic energy…All cases in which such energies take a fixed part are therefore completely determined in time if the conditions are given; but all cases in which the vibrational energy does not play this role are independent of time, that is, they can occur without violating the laws of energy in any given time. Catalytic processes are empirically found to be of the type in which this last property is observed; the existence of catalytic processes is to me therefore a positive proof that chemical processes cannot have a kinetic nature" (Ostwald, 1894).

Sabatier did not accept the purely physical view of the function of the catalyst, remarking that if it was true then charcoal should be almost a universal catalyst, whereas it proved to be somewhat mediocre except for the formation of carbonyl chloride (Sabatier, 1897a, 1913). While finely divided metals were able to absorb substantial quantities of gas, these absorptions were somewhat specific, being "characterized by a sort of selective affinity". Not only that, some catalytic reactions were extremely specific, for example, zinc oxide decomposed formic acid into hydrogen and carbon dioxide, but at the same temperature titania gave carbon monoxide and water. The physical theory was unable to explain the development of high local pressure and temperature in the cases where the catalyst was held in suspension, and did not account for the specificity of catalysts and the remarkable diversity of effects they produced, depending on the particular metal or oxide used (Sabatier, 1897a, 1913).

Sabatier then formulated a chemical theory of catalysis involving the formation of *unstable chemical compounds* as intermediate stages, which determined the direction and rate of the reaction. He assumed that in hydrogenation various nickel hydrides were involved, whose composition depended on the activity of the nickel. He also argued that the formation and decomposition of intermediate compounds usually corresponds to a diminution of the Gibbs energy of the system (Sabatier, 1913).

Sabatier postulated the formation of different intermediate compounds, each with its own mode of decomposition, and he also clearly established that some organic reactions are reversible. In cases where the intermediate compounds could not be isolated, he assumed the formation of surface compounds, a phenomenon, which he named fixation, thus linking the physical, and the chemical theories of catalysis (Partington, 1954).

The catalysts sensitivity to poisons, discovered by the work of Rudolph Knietsh (1854-1906) on catalysts used for the synthesis of sulfur trioxide, was shown to be a general phenomenon, which could be used to control catalytic reactions. Sabatier, when comparing catalysts to ferments, described poisoning in the following words: "In the same way that organized ferments are killed by infinitesimal amounts of certain toxins, the mineral ferment which is the metal, is killed by traces of chlorine, bromine, iodine, sulfur or arsenic that are carried by the hydrogen or by the substance to be hydrogenated…nickel, a little poisoned, can only provide a first hydride similar to that of copper and capable of acting over the nitro groups or on the ethylenic double bond, only nickel cannot provide a hydride able to completely hydrogenate the aromatic ring" (Sabatier, 1913; Wojtkowiak, 1989). Sabatier and Léo Espil made the interesting discovery that after being used to hydrogenate nitrobenzene, nickel poisoned by chlorine recovered its ability to hydrogenate benzene (Sabatier, 1913, 1914).

During the First World War Langmuir's published a rival theory called "theory of chemisorption" according to which a gas adsorbed over a catalysts was fixed thanks to its unsaturated valences yielding a gas-metal compound of the type M_xG_y (Langmuir, 1916, 1917, 1918). This theory was contrary to Sabatier's hypothesis of distinct, individual intermediates and allowed more importance to physical conditions

(Nye, 1977). Although Langmuir's theory retained the concept of fixation of the reagents on the surface of the catalysts, it assigned a predominant importance to the physical conditions that Sabatier had purposed ignored. For a time, Langmuir's theory of the fixation of a monomolecular layer on the catalyst gave it a certain advantage because it permitted to address quantitatively the problem of heterogeneous catalysis and played a considerable role in experimental studies (Wojtkowiak, 1989). Langmuir's theory became particularly important because it permits a first quantitative analysis of the possible mechanism of a reaction.

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