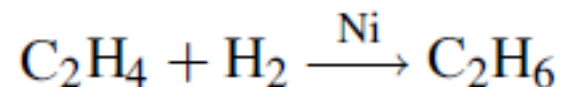


# Catalysis-Science and Technology

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### **What does this mean?**

We see many such “qualified” arrows, often without any explanation or rationale.

What does a catalyst do in a reaction?

Catalysis is an action by which a catalyst takes part in a chemical reaction process and alters the rate of reactions.

Yet, itself will return to its original form without being consumed or destroyed at the end of the reactions

### **Three key aspects of catalyst action**

1. Taking part in the reaction

It will change itself during the process by interacting with other reactant/product molecules

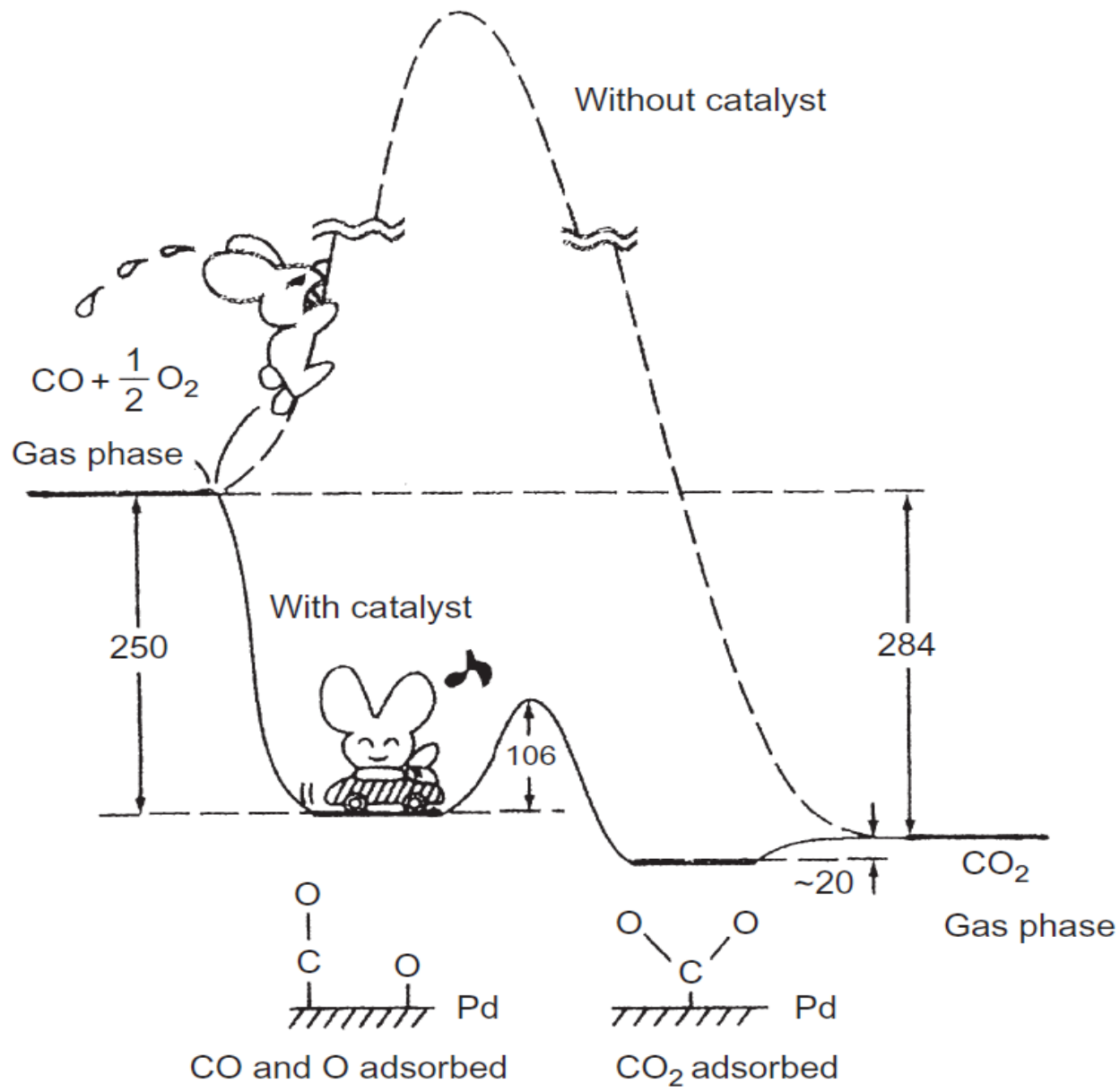
2. Altering the rates of reactions

In most cases the rates of reactions are increased by the action of catalysts; however, in some situations the rates of undesired reactions are selectively suppressed

3. Returning to its original form

After reaction cycles a catalyst is 'reborn'

In practice a catalyst has a lifespan - it deactivates gradually



Three essential points of catalytic functions – Did you notice?

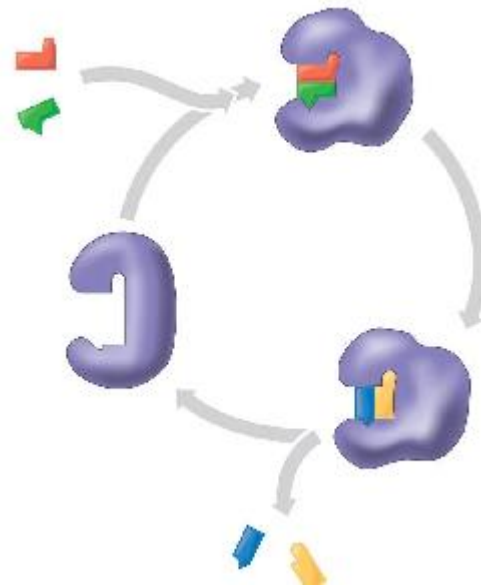
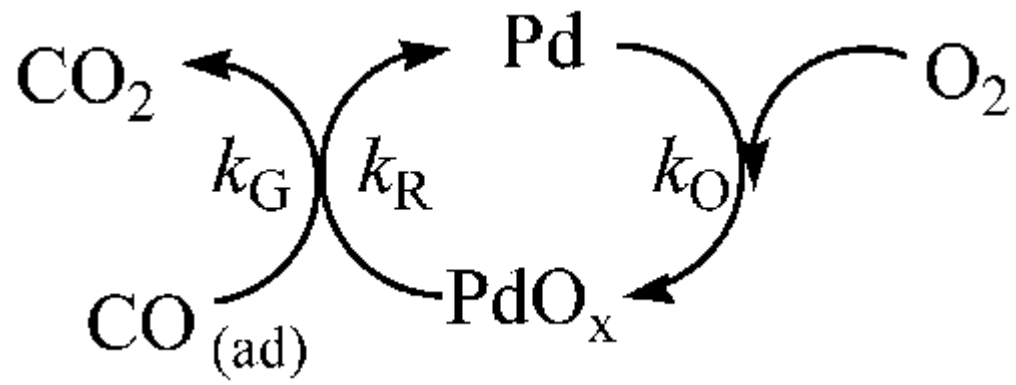
First, the oxygen molecule in which two oxygen atoms are strongly bonded (494 kJ/ mol) dissociates into two oxygen atoms on the surface of palladium with a very low energy barrier.

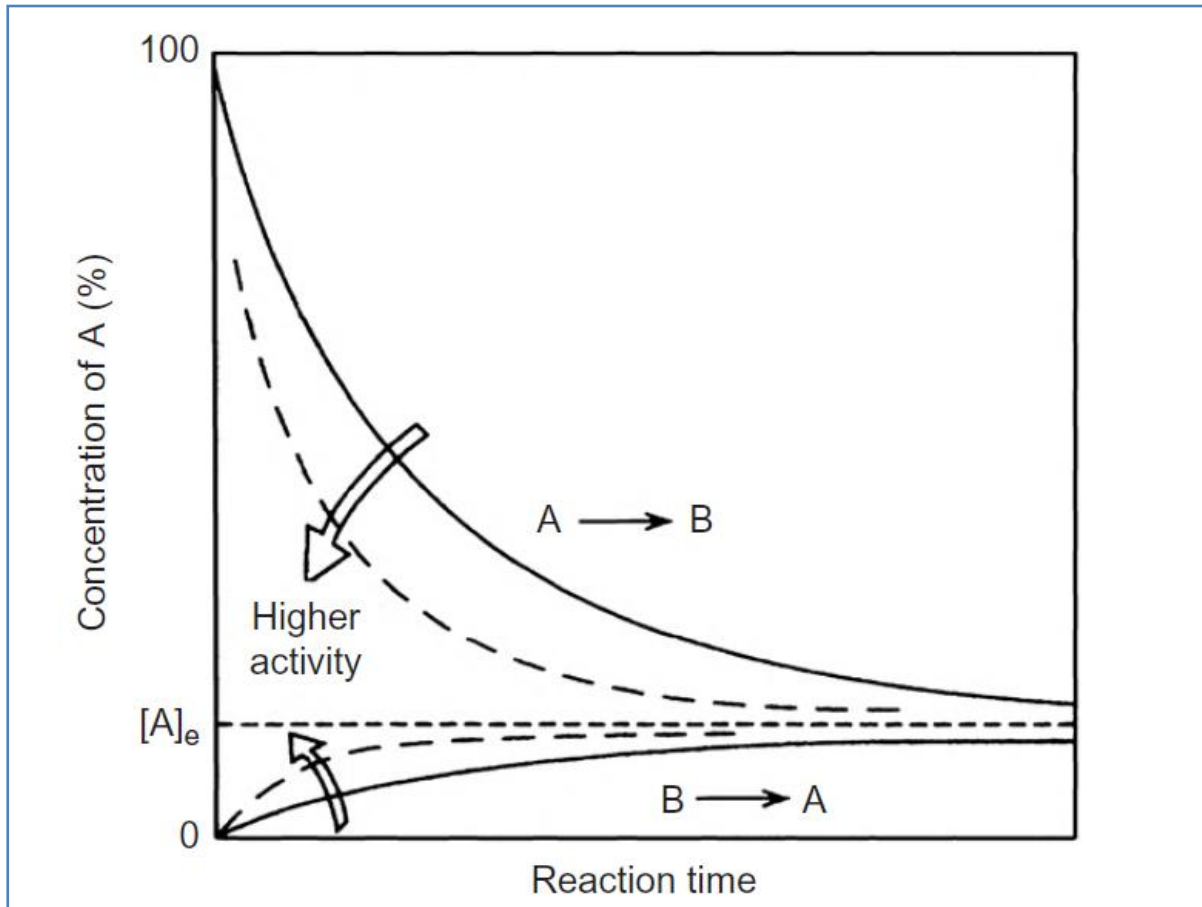
This is due to the formation of two oxygen-palladium bonds that occurs simultaneously with the bond breaking of O<sub>2</sub>.

Second, the oxygen atoms formed are reactive.

If they are too stable, the subsequent reactions would not take place.

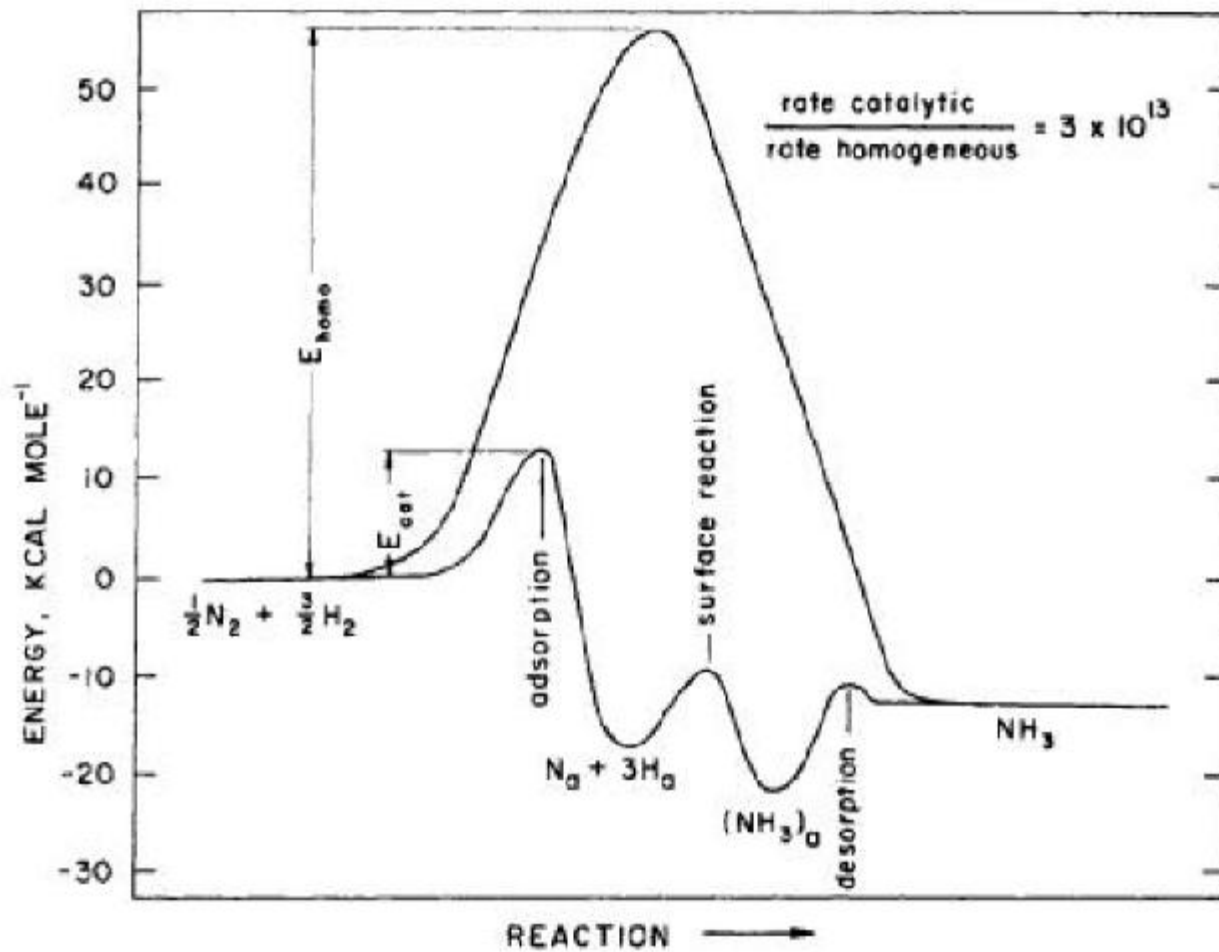
Third, after one cycle of catalytic oxidation of CO to CO<sub>2</sub>, the catalyst surface returns to the initial state. Upon each cycle, one molecule of carbon dioxide is produced



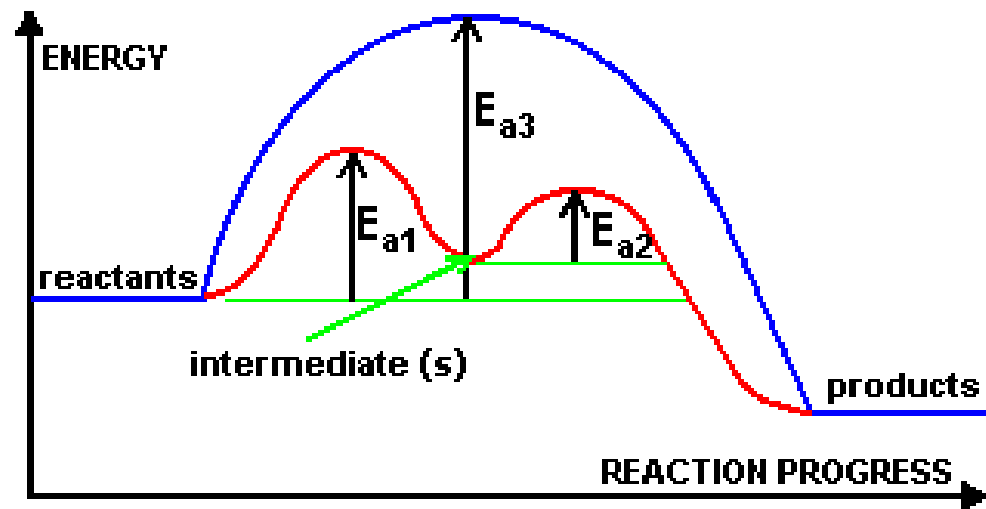


Time course of a reversible reaction,  $A \rightleftharpoons B$ .

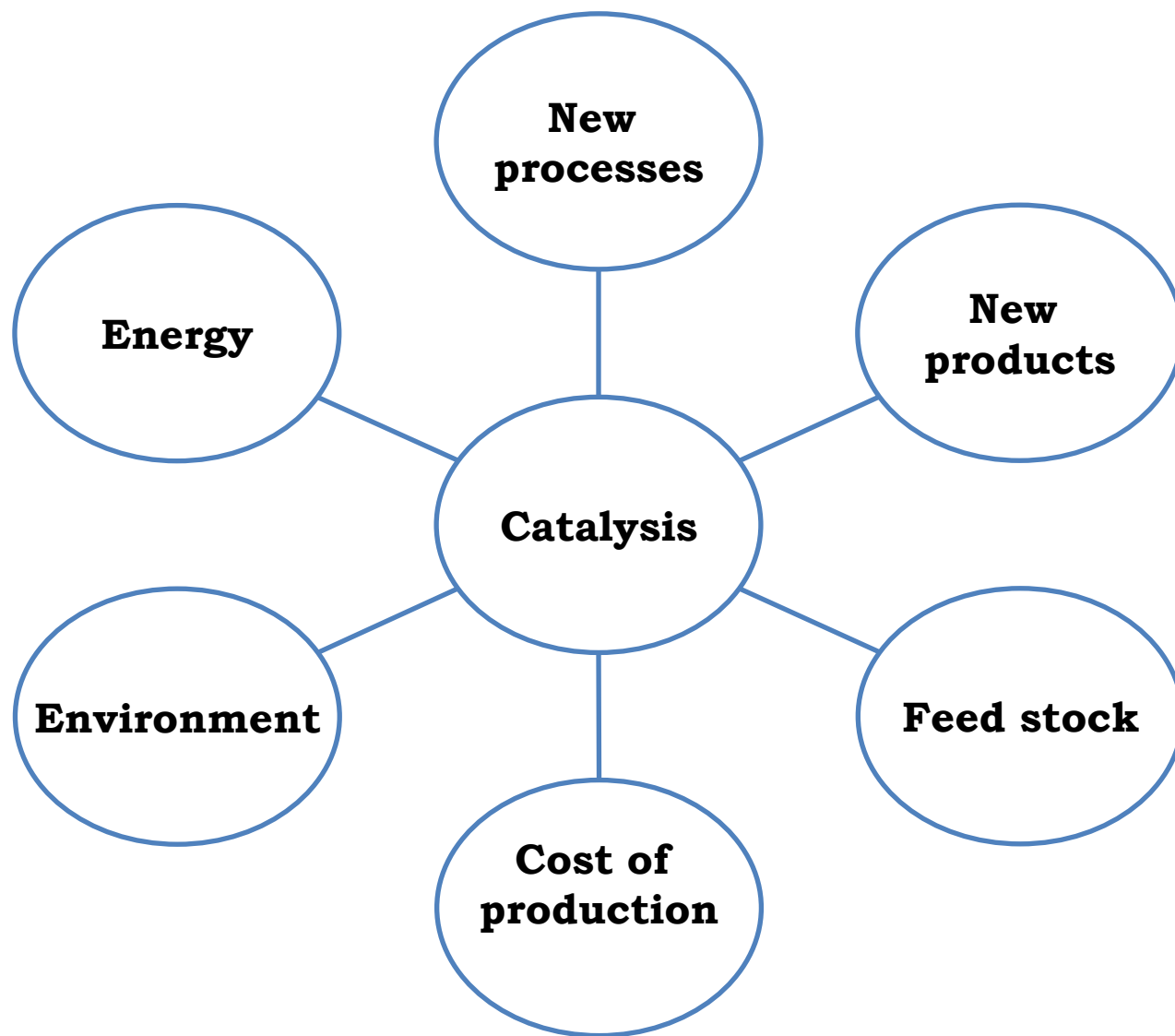
The concentration reaches faster the equilibrium concentration  $[A]_e$  over a catalyst with a higher activity. But the equilibrium concentration is the same..







# What all can a catalyst do?



## **A catalyst can help in**

- 1. Efficient utilisation of raw materials**
- 2. Development of new materials and chemicals**
- 3. Development of systems for environmental protection**
- 4. Development of new sources of energy**
- 5. Development of new processes and technologies**

# Heterogeneous versus Homogeneous

## Heterogeneous

- Readily separated ✓
- Readily recycled / regenerated ✓
- Long-lived ✓
- Cheap ✓
- Lower rates (diffusion limited) ✗
- Sensitive to poisons ✗
- Lower selectivity ✗
- High energy process ✗
- Poor mechanistic understanding ✗

## Homogeneous

- Difficult to separate ✗
- Difficult to recover ✗
- Short service life ✗
- Expensive ✗
- Very high rates ✓
- Robust to poisons ✓
- Highly selective ✓
- Mild conditions ✓
- Mechanisms often known ✓

Ultimate goal:

To combine the fast rates and high selectivities of homogeneous catalysts with the ease of recovery/recycle of heterogeneous catalysts

# Catalysis in the Chemical Industry

- Hydrogen Industry
- (coal,  $\text{NH}_3$ , methanol, FT synthesis, hydrogenations, fuel cell)
- Natural gas processing
- Petroleum refining
- Petrochemicals
- Fine Chemicals (pharmaceuticals, agrochemicals, fragrance, textile, coating, surfactants)
- Environmental Catalysis

## Historical development of heterogeneous catalysis

### Earliest work



The first scientific reports of the use of heterogeneous catalysts – independently in the year 1800 by Joseph Priestly and Martinus van Marum, both reported work on the dehydrogenation of ethyl alcohol over metal catalysts.

Neither of them had recognized that the metals were acting as catalysts, seemingly thinking that the metals just supplied heat for the reaction.

What seems to have been the first real recognition of the operation of a heterogeneous catalyst was made in 1813 by Louis Jacques The´nard, Professor at the E´cole Polytechnique in Paris. He reported that ammonia was decomposed to give hydrogen and nitrogen when it was passed over red-hot metals



Ten years later, working with Pierre Dulong, The´nard discovered that the reaction occurred over iron, copper, silver, gold and platinum, the rate of reaction decreasing in the order given.

This appears to have been the first report of activity patterns in catalysis.

One of the most important early experiments in the development of heterogeneous catalysis was carried out in the laboratories of the Royal Institution in London in 1817.



Humphrey Davy, assisted by a young Michael Faraday, found that a heated platinum wire could bring about the combination of air and coal gas (largely CO and H<sub>2</sub>) without the action of a flame. This was the first reported example of catalytic oxidation. Davy reproduced the result with palladium but failed to do so with copper, silver, iron, gold and zinc.



The importance of surface area of platinum was demonstrated in 1820 at University College, Cork by Davy's cousin, Edmond Davy. He showed that finely divided platinum could oxidize alcohol at room temperature.

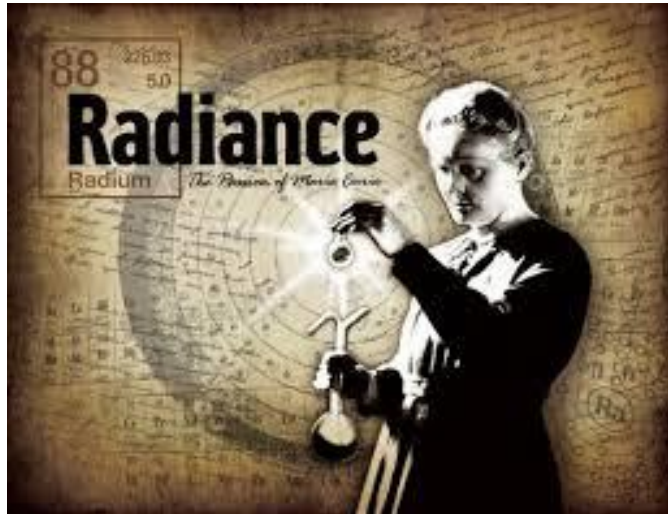
Edmond Davy's technique for making high area platinum was improved in 1823 by J.W. Dobreiner, University of Jena, who produced a spongy material that caused the combination of hydrogen and oxygen at room temperature on finely divided platinum.

Later that year, the same reaction was shown by Dulong and The´nard to occur on palladium and iridium at around room temperature and on cobalt, nickel, rhodium, silver and gold when the temperature was increased.

The fact that the platinum brought about the reaction smoothly, without explosion, and yet with the evolution of heat which caused the wire to glow red-hot, was the basis for the development of the miners' safety lamp.

In practice the miners' lamp did not contain Pt but only an iron gauze. This gauze rusted in high water vapour pressures and so the lamp was in fact ineffective.

# CHRONOLOGY

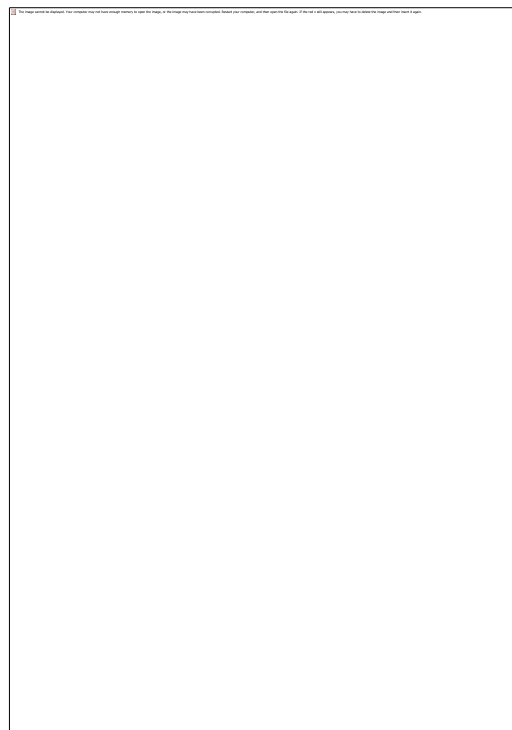
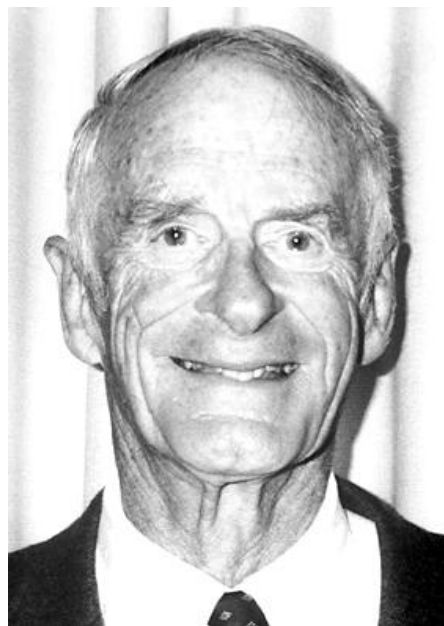


- 1909 – W. Ostwald, for his work on catalysis, and for his investigations into the fundamental principles governing chemical equilibria and rates of reactions.
- 1912 – P. Sabatier, for his method of hydrogenating organic compounds in the presence of finely divided metals whereby the progress of organic chemistry has been greatly advanced in recent years.
- 1918 – F. Haber, for the synthesis of ammonia from its elements.
- 1931 – C. Bosch and F. Bergius, in recognition of their contributions to the invention and development of chemical high-pressure methods.
- 1932 – I. Langmuir, for his discoveries and inventions in surface chemistry.
- 1956 – C. N. Hinshelwood and N. N. Semenov, for their researches into the mechanism of chemical reactions.
- 1963 – K. Ziegler and G. Natta, for their discoveries in the field of chemistry and technology of high polymers.
- 1973 G. Wilkinson and E. O. Fischer for pioneering work on the chemistry of the organometallic so-called sandwich compounds.
- 1983 – H. Taube, for his work on electron transfer reactions, especially in metal complexes.
- 1989 – S. Altman and T. Cech, for their discovery of the catalytic properties of RNA.
- 1993 – K. B. Mullis, for his invention of the polymerase chain reaction.
- 1994 – G. A. Olah, for his contributions to carbocation chemistry.

- 2001 – W. S. Knowles, R. Noyori, and K. Barry Sharpless, for their work on chirally catalyzed hydrogenation reactions and for the work of K. Sharpless on chirally catalyzed oxidation reactions.
- 2005 – Y. Chauvin, R. H. Grubbs, and R. R. Schrock, for the development of the metathesis method in organic synthesis.
- 2007 – G. Ertl, for his studies of chemical processes on solid surfaces.
- 2010 – R. F. Heck, E. Negishi, and A. Suzuki, for palladium-catalyzed cross-couplings in organic synthesis.

Before 1963 no research award was given for the use of coordination complexes in catalysis. In biocatalysis.

The first Nobel Prize was in 1946 for crystallization of an enzyme (Sumner, Northrop, and Stanley), followed by Kendrew and Perutz's (1962) Nobel Prize for crystallographic studies of haemoglobin.



The Nobel Prize in Chemistry 2001 was divided, one half jointly to William S. Knowles and Ryoji Noyori *"for their work on chirally catalysed hydrogenation reactions"* and the other half to K. Barry Sharpless *"for his work on chirally catalysed oxidation reactions"*.



The Nobel Prize in Chemistry 2005 was awarded jointly to Yves Chauvin, Robert H. Grubbs and Richard R. Schrock *"for the development of the metathesis method in organic synthesis"*



The Nobel Prize in Chemistry 2007 was awarded to Gerhard Ertl "*for his studies of chemical processes on solid surfaces*".





The Nobel Prize in Chemistry 2010 was awarded jointly to Richard F. Heck, Ei-ichi Negishi and Akira Suzuki *"for palladium-catalyzed cross couplings in organic synthesis"*.

There are many factors that contribute to the recognition of a Nobel Prize award.

It is interesting to ask the question whether for catalysis there are other breakthrough developments that possibly are equivalent at least in impact and originality.

They are important because they often are basic to the development of new industries or new catalytic processes.

- F. Fischer and H. Tropsch (1926). Oligomerization of hydrocarbons from CO – heterogeneous catalysis.
- V. Ipatieff and E. Houdry (1930). Amorphous solid acid catalysts – catalytic cracking.
- (1930) Reducible vanadium oxide catalysts for benzene oxidation, earlier discovered for SO<sub>2</sub> oxidation.
- T. E. Lefort (1931). Silver-catalyzed epoxidation of ethylene – a heterogeneous process.
- H. Pines (1940). Superacid catalysis (liquid phase) – alkylation.
- O. Roelen (1938) and W. Reppe (1941). Hydroformylation, carbonyl chemistry, and homogeneous catalysis.
- V. Haensel (1940). Bifunctional heterogeneous catalysts (catalytic reforming).
- J. Smidt, WACKER (1959). Homogeneous oxidation of ethylene by oxygen by Pd-Cu oxidation redox couple.
- R. K. Graselli, SOHIO (1955). Mixed oxides for selective oxidation and ammoxidation.

- R. L. Banks and G. C. Bailey (1964). Heterogeneous metathesis by supported oxide clusters.
- C. J. Plank and E. J. Rosinski, MOBIL (1968). Zeolite catalytic cracking.
  - H. P. Wulff and F. Wattimena, SHELL (1969). Heterogeneous Ti-catalyzed epoxidation.
  - W. Keim, SHELL (1972). Shell Higher Olefins Process.
  - C. D. Chang, A. J. Silvestri, and W. H. Lang, MOBIL (1972). Methanol to gasoline, ZSM-5 zeolite catalyst.

Before 1900 – two important inorganic chemicals produced by catalytic processes:

- Sulfuric acid by the lead chamber process (NO<sub>x</sub>) or contact process (Pt).
- Chlorine from HCl by the Deacon process (Cu/ZnCl<sub>x</sub>).

The first half of the twentieth century - dominated by the development of heterogeneous hydrogenation processes (NH<sub>3</sub> and hydrocarbon-related chemistry).

Hydrogen was then available from coal. High-pressure continuous processes were developed through the use of this technology. This can be considered to be the origin of reactor engineering.

Note the early discovery of heterogeneous catalytic hydrogenation and the discovery of homogeneous catalytic hydrogenation 60 years later by Wilkinson.

Similarly the early discovery by Banks *et al.* of the heterogeneous catalysis of the metathesis reaction and the 30-years-later discovery of homogeneous metathesis

|                             | Catalyst   | Process  |
|-----------------------------|--|--|
| 1900                        | Noble metal  | Hydrogenation  |
| 1910 World War I            | Promoted iron  | Nitrogen to ammonia<br>Synthesis gas to methanol<br>gasoline |
| 1920                        | Sulfides   | Desulfurization–denitrogenation                              |
| 1930 Automobiles            | Solid acids  | Catalytic cracking   |
| 1940 World War II           | New acid catalysis<br>Superacids<br>Anionic catalysis          | Synthetic kerosene<br>Alkylates<br>Synthetic rubber          |
| 1950                        | Coordination catalysis   | Polymers   |
| 1960 Petrochemical industry | Bifunctional catalysis<br>Zeolites<br>Reducible oxidic systems | Hydrocracking<br>Catalytic cracking<br>Selective oxidation   |
| 1970 Energy crisis          | Methanol to gasoline<br>Synthesis gas to chemicals             | Novel synthetic acidic zeolites<br>Organometallic complexes  |



## What is the present status?

Chemical Industry

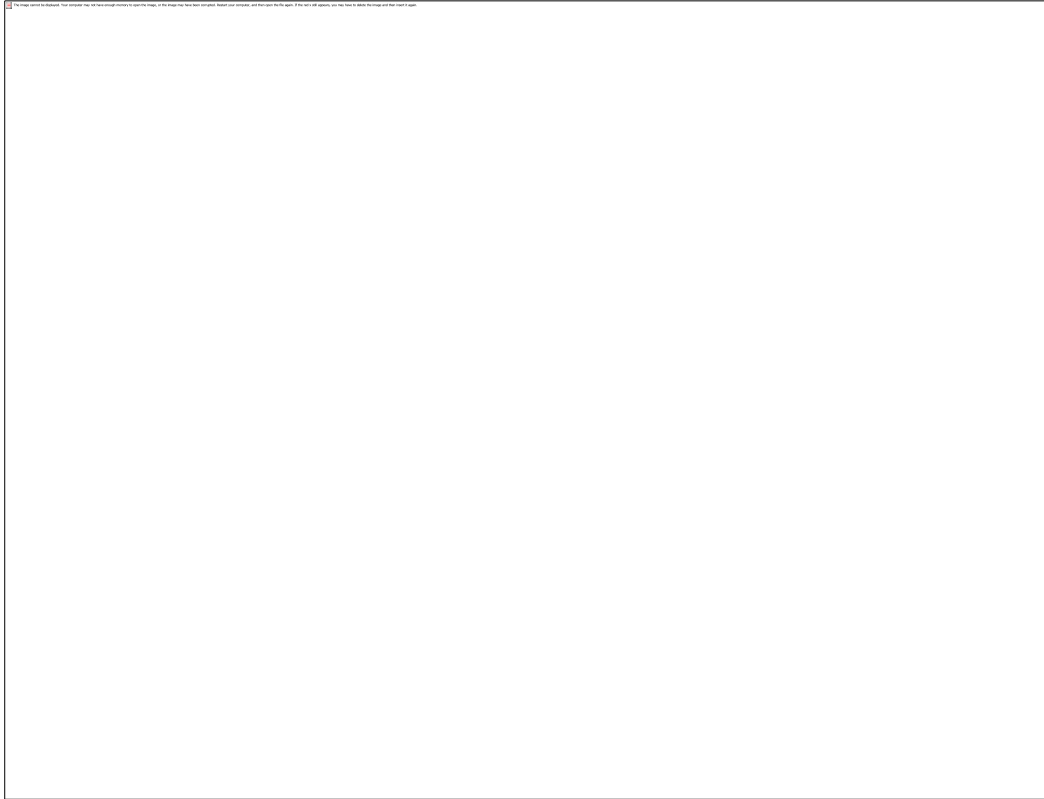
ca. \$2 bn annual sale of catalysts

ca. \$200 bn annual sale of the chemicals that are related products

90% of chemical industry has catalysis-related processes







## The First Industrial Catalytic Processes

The “Contact Process” for the production of sulfuric acid was patented by Peregrine Phillips, Junior, in 1831.

Phillips brought about the oxidation of sulfur dioxide ( $\text{SO}_2$ ) by drawing it with air through tubes of platinum (or similar material) packed with platinum wire or platinum in any finely divided state and heating them to a “strong yellow heat”.

- The foundations for another important catalytic oxidation process, the oxidation of ammonia over platinum to give nitric oxide, a step in the formation of nitric acid and hence nitrate fertilizers, was reported by C.F. Kuhlmann in 1838.
- Kuhlmann recognized that the process(using ammonia from coke-oven gas) would in due course become important even though at that time it was uncompetitive due to the cheap and readily available supplies of nitrogenous fertilizer in the form of Chile saltpeter.
- Towards the end of the nineteenth century, fears began to emerge that it would become impossible to feed the world's population using the available supply of this saltpeter. However, it was only with the threatened approach of war that scientists in various countries started to examine the oxidation of ammonia

- H.L. Le Chatelier, aware that the decomposition of ammonia should be reversible, did experiments in 1901 attempting to bring about the synthesis of ammonia from the elements.
- He carried out his experiments in a bomb at 200 atmospheres pressure and at a temperature of 600 C using a reduced iron catalyst heated by a platinum spiral.
- However, he terminated his experiments after contamination of the reaction mixture with air led to an explosion.
- Le Chatelier is quoted as saying, near the end of his life, “I let the discovery of the ammonia synthesis slip through my hands.
- It was the greatest blunder of my scientific career”.

- Berzelius first introduced the term “catalysis”.
- This word comes from the Greek word loosen.
- Berzelius proposed that there was a catalytic force and that catalysis occurred because of the decomposition of bodies by this force.
- The ideas behind the concept of what we now know as adsorption was introduced a year earlier in 1834 by Michael Faraday who had been working on electrolysis and had observed a spontaneous combustion of hydrogen and oxygen occurring on platinum electrodes.
- Faraday proposed that the two reacting gases were condensed on the surface of the platinum and that “the approximation of the particles to those of the metals may be very great”.