

Introduction:

# **Catalyst design for synthesis**

**Prof. Xile Hu**

## **Catalysis: some history**

**When is catalysis first mentioned? In what context?**

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The word *catalysis* was introduced by Jöns J. Berzelius in 1835 who first noted that certain chemicals speed up a reaction. He noticed that hydrogen burned rapidly in the presence of platinum and as the surface area of the platinum is increased its catalytic activity increases to a point where the hydrogen can ignite spontaneously.



# What is Catalysis

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Catalysis is the increase in the rate of a chemical reaction due to the participation of an additional substance called a catalyst.

With a catalyst, reactions occur faster and with less energy.

# Catalyst

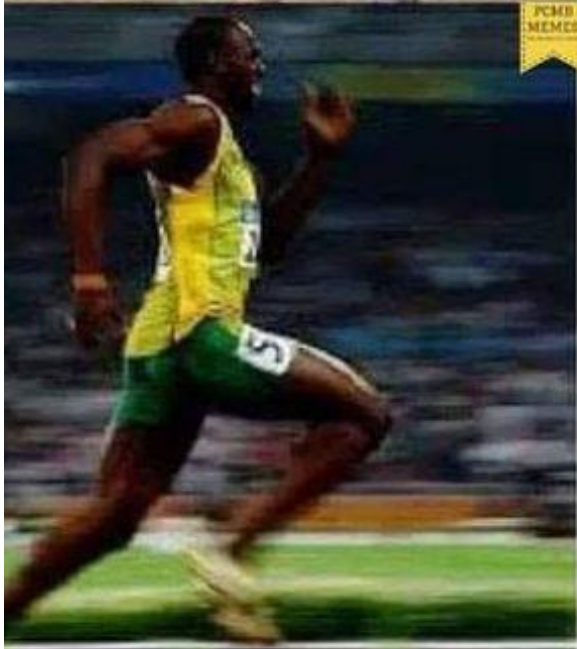
# Catalyst

Catalysts are substances which, when added to a reaction, increase the rate of reaction by providing an alternate reaction pathway with a lower activation energy ( $E_a$ ).

They do this by promoting proper orientation between reacting particles.

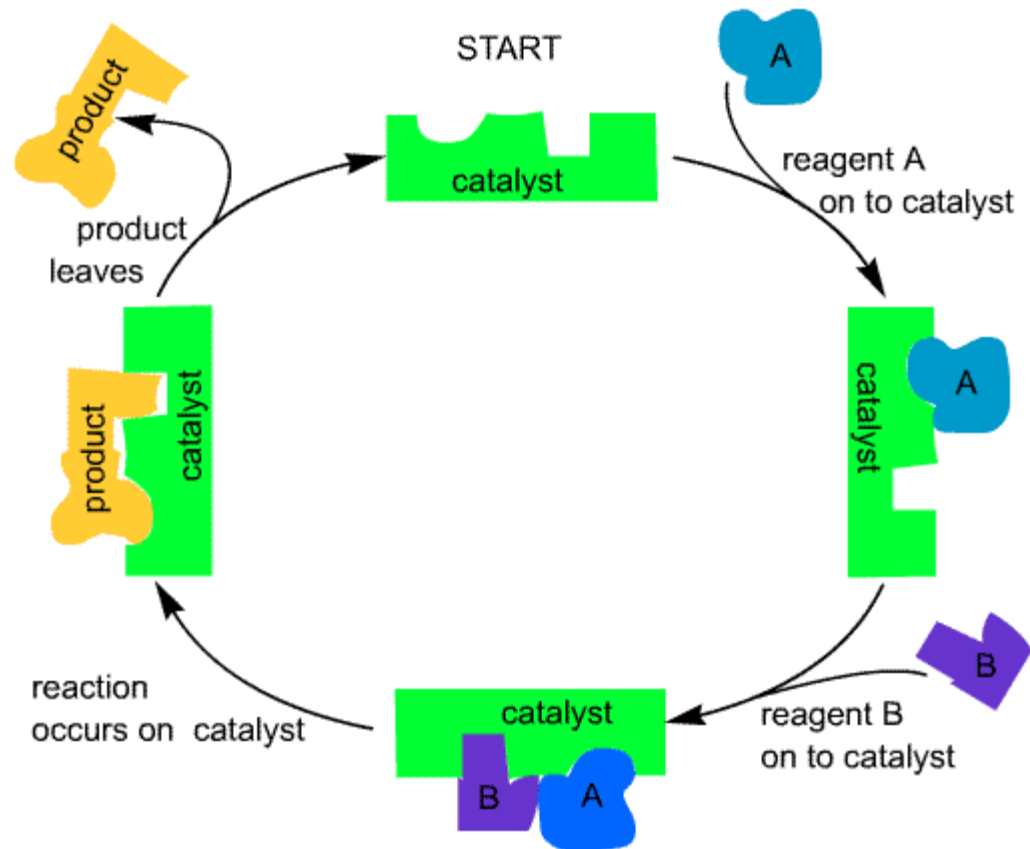


**Normal chemical reaction**

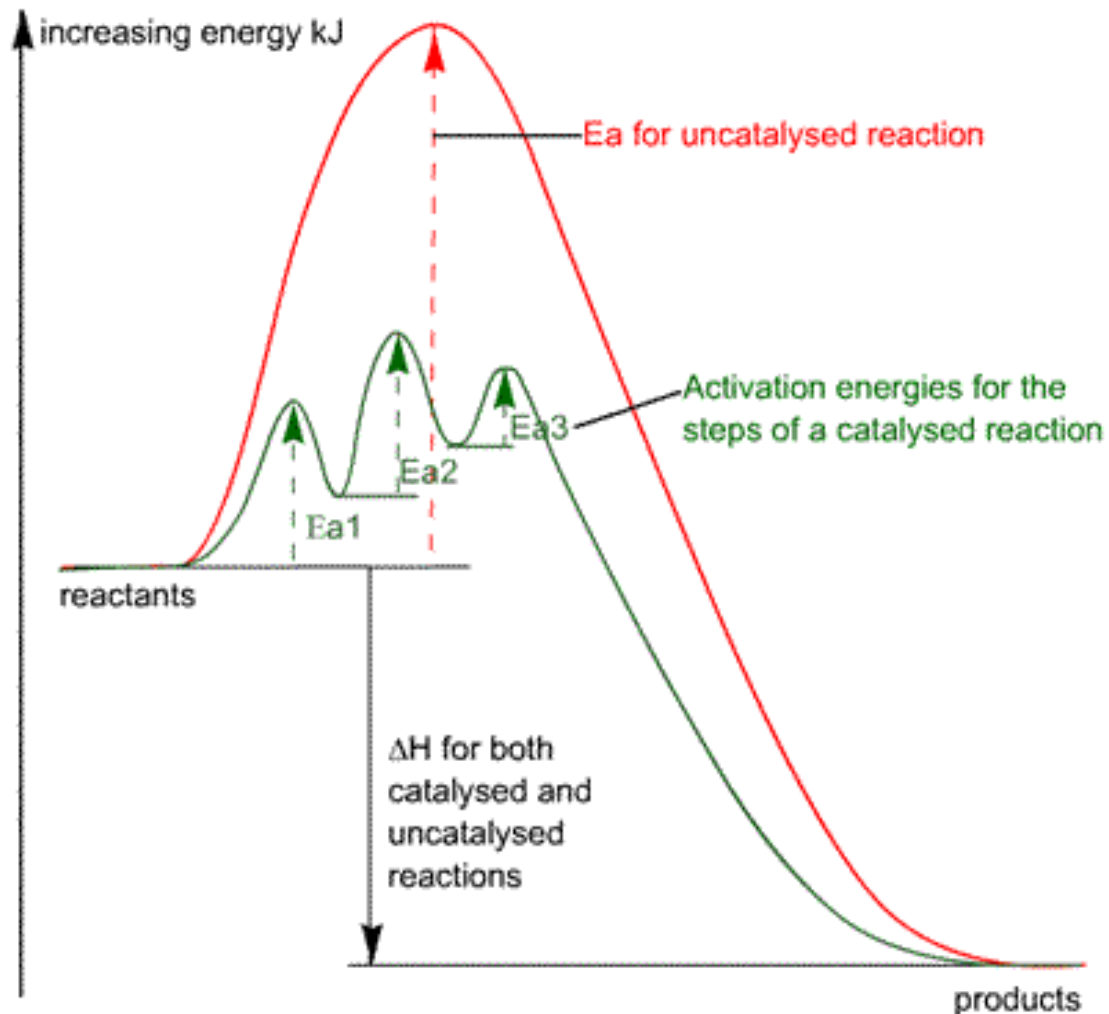


**Chemical reaction on adding catalyst**

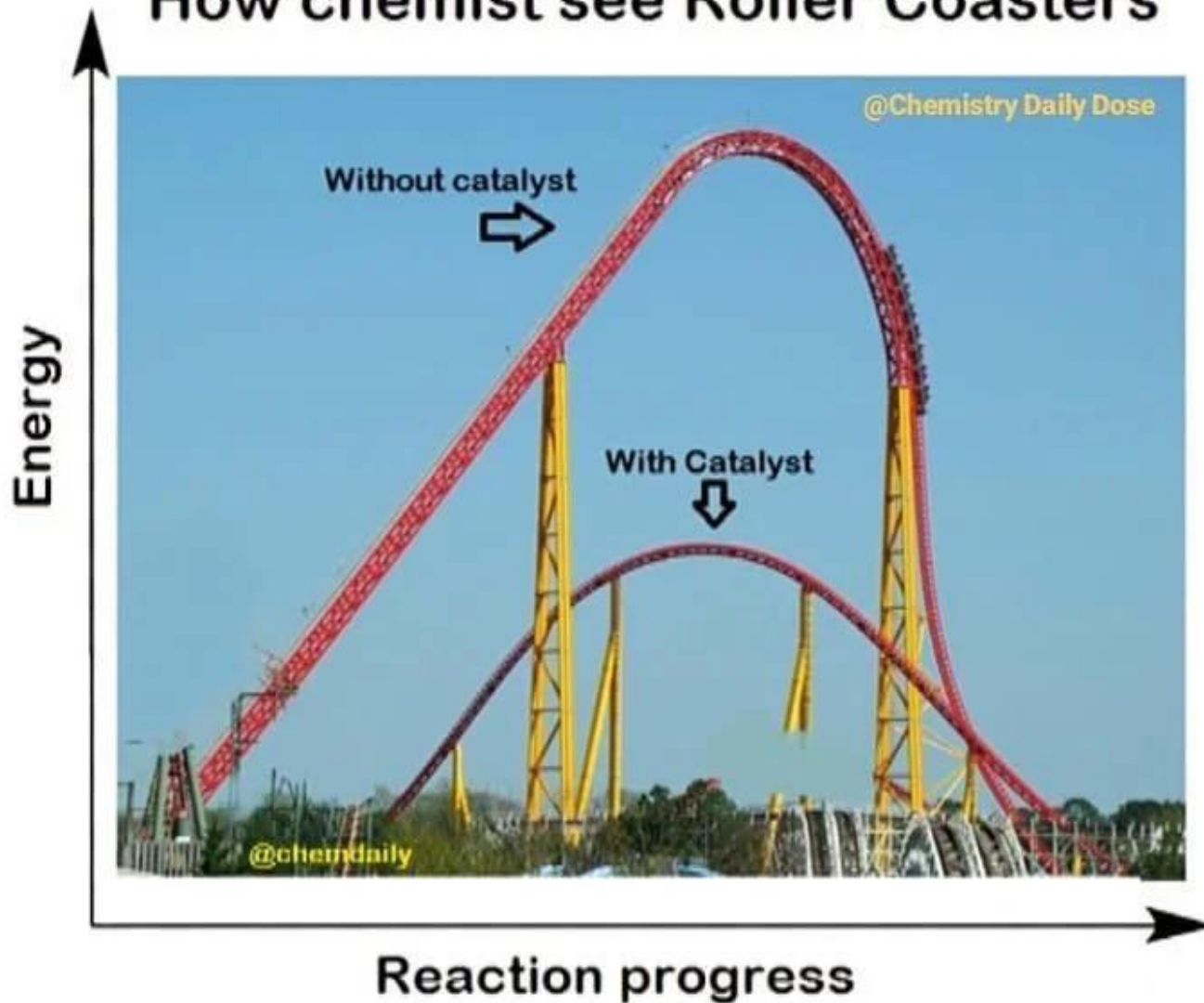
# Catalytic Cycle



# Energy Profile



# How chemist see Roller Coasters



# Nobel Prize in Chemistry for Catalysis Work

1909

Fundamentals of Catalysis

## Wilhelm Ostwald

Born: 2 September 1853, Riga, Russian Empire (now Latvia)

Died: 4 April 1932, Leipzig, Germany

Prize motivation: "in recognition of his **work on catalysis** and for his investigations into the **fundamental principles governing chemical equilibria and rates of reaction**"



Famous students:

(Nobel Laureates)

Svante Arrhenius

Jacobus Henricus van 't Hoff

Walther Nernst.

But missed:

Albert Einstein

# Nobel Prize in Chemistry for Catalysis Work

1912

## Hydrogenation

**Paul Sabatier**

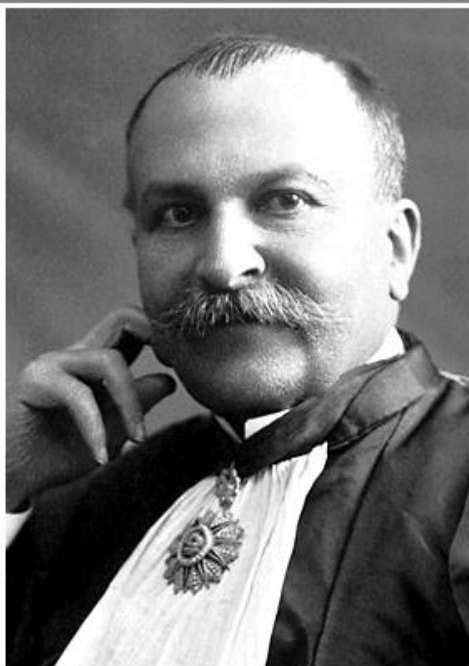
**Born:** 5 November 1854,  
Carcassonne, France

**Died:** 14 August 1941, Toulouse,  
France

**Affiliation at the time of the award:**  
Toulouse University, Toulouse,  
France

**Prize motivation:** "for his method of hydrogenating organic compounds in the presence of finely disintegrated metals whereby the progress of organic chemistry has been greatly advanced in recent years"

**Field:** Organic chemistry



1918

## Ammonia Synthesis

**Fritz Haber**

**Born:** 9 December 1868, Breslau  
(now Wroclaw), Prussia (now  
Poland)

**Died:** 29 January 1934, Basel,  
Switzerland

**Affiliation at the time of the award:**  
Kaiser-Wilhelm-Institut (now Fritz-  
Haber-Institut) für physikalische  
Chemie und Electrochemie, Berlin-  
Dahlem, Germany

**Prize motivation:** "for the synthesis  
of ammonia from its elements"

**Field:** Inorganic chemistry, industrial  
chemistry

*Fritz Haber received his Nobel  
Prize one year later, in 1919.*



# Nobel Prize in Chemistry for Catalysis Work

1931

## Ammonia Synthesis

**Carl Bosch**

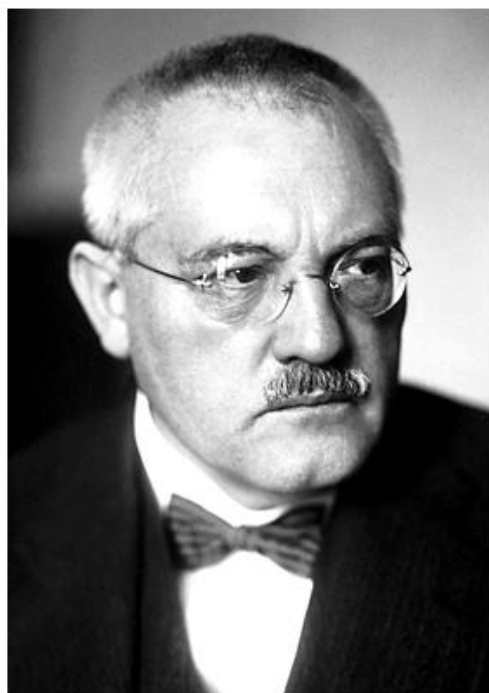
**Born:** 27 August 1874, Cologne, Germany

**Died:** 26 April 1940, Heidelberg, Germany

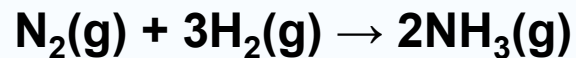
**Affiliation at the time of the award:**  
University of Heidelberg,  
Heidelberg, Germany, I.G.  
Farbenindustrie A.G., Heidelberg,  
Germany

**Prize motivation:** "in recognition of their contributions to the invention and development of chemical high pressure methods"

**Field:** Industrial chemistry

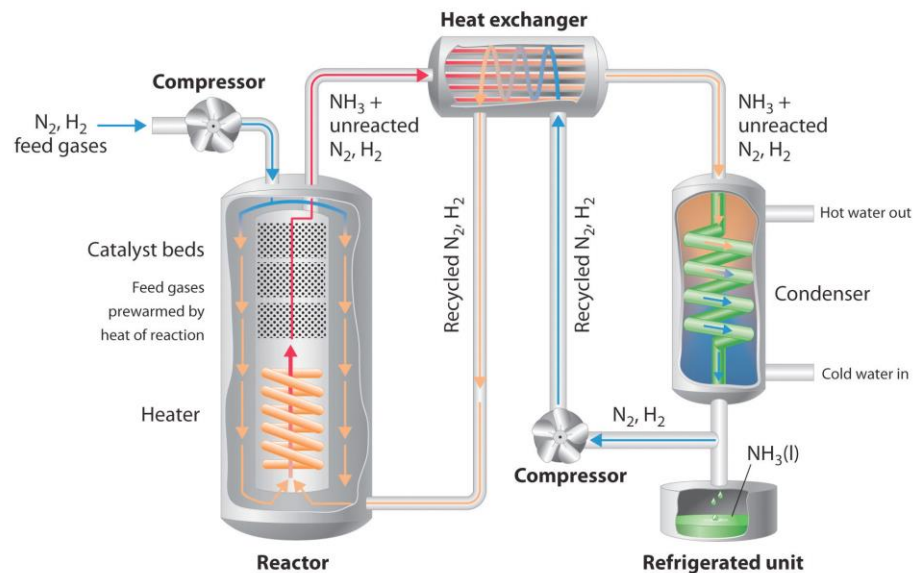


# The Haber-Bosch process - catalysis that changed the world



Heterogeneous iron catalyst ( $\text{Fe}(\text{III})$ ), aluminium oxide ( $\text{Al}_2\text{O}_3$ ) and potassium oxide ( $\text{K}_2\text{O}$ ) promoters. 250 atmospheres (atm), 450-500°C; yield of 10-20%:

The process was patented by Fritz Haber in 1908. In 1910 Carl Bosch, at BASF, commercialized the process.



Fritz Haber



Carl Bosch

# Nobel Prize in Chemistry for Catalysis Work

**1963**

**Polymerization catalysis**

**Karl Ziegler prepared linear polyethylene with a catalyst he discovered and Giulio Natta used similar catalysts to polymerize 1-alkenes.**



# Nobel Prize in Chemistry for Catalysis Work

**1973**

**Organometallic Chemistry**



**E.O. Fischer**

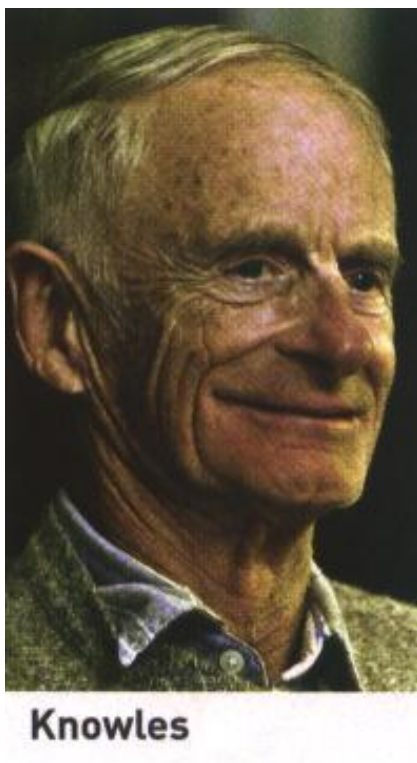


**Geoffrey Wilkinson**

# Nobel Prize in Chemistry for Catalysis Work

2001

Asymmetric catalysis



# Nobel Prize in Chemistry for Catalysis Work

2005  
Olefin Metathesis



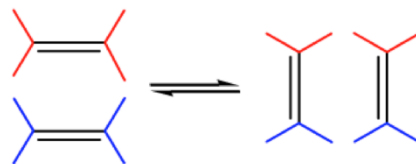
**Yves Chauvin**



**Robert H. Grubbs**



**Richard R. Schrock**



# Nobel Prize in Chemistry for Catalysis Work

2010  
C-C cross-coupling



**Heck**



**Negishi**



**Suzuki**

# Nobel Prize in Chemistry for Catalysis Work

**2018**  
**Directed evolution**  
**(biocatalysis)**



**Francis Arnold**

# Nobel Prize in Chemistry for Catalysis Work

2021  
Organocatalysis



**Benjamin List**

**David W.C. MacMillan**

# Catalyst Parameters

**Catalysts *cannot* make energetically unfavorable reactions possible — they have *no* effect on the chemical equilibrium of a reaction because the rate of both the forward and the reverse reaction are equally affected.**

**The degree of activity of a catalyst can be described by the turnover number (TON) and the catalytic efficiency by the *turnover frequency* (TOF).**

Turnover number: the number of moles of substrate that a mole of catalyst has been converted.

Turnover frequency is used to refer to the turnover number per unit time.

# **Types of catalysis**

## **Homogeneous Catalysis**

The catalyst and reactants are in the same phase, usually liquid.

## **Heterogeneous catalysis**

Catalyst and reactants are in different phases.

## **Enzymatic Catalysis**

Catalyst is an enzyme (macromolecules made of amino acids).

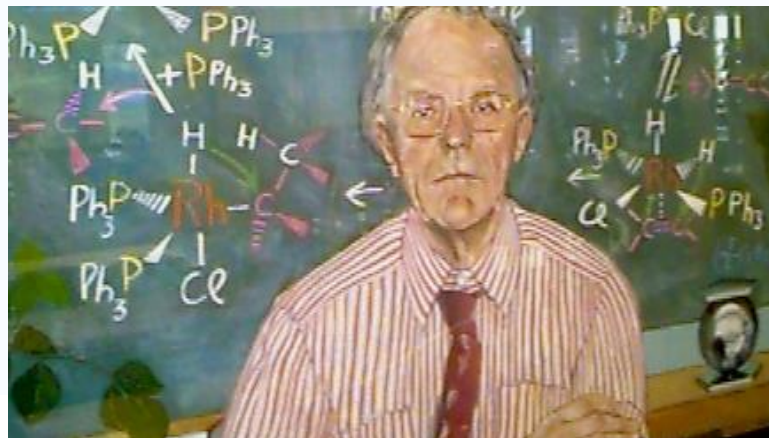
# The origins of homogeneous catalysis

Modern homogeneous catalysis, which has transformed the chemical industry, started in the 1950s.

Ziegler and Natta developed Ti and Zr metallocene catalysts for making polyethylene and related polymers.

Wilkinson made a Rh compound that catalyses the addition of a wide range of substrates across unsaturated bonds.

Within a short time their catalysts were used on an industrial scale.



# Course objectives

**Examples of modern homogeneous catalysis.**

- hydrogenation**
- C-C and C-N coupling**
- Olefin metathesis**

**Understand how homogeneous catalysts work – catalytic cycles.**

**Know how to design/modify a homogeneous catalyst with specific properties – ligands/metals.**