



# Inorganic Molecules, Materials & Medicines

**Instructor: Dr. Prakash Chandra Mondal**

**Department of Chemistry**

**Lecture: 1**

**The topics will be covered in the second half**

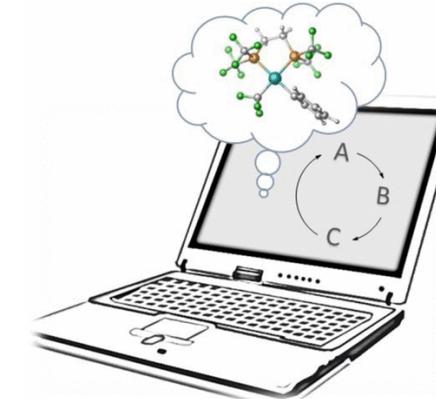
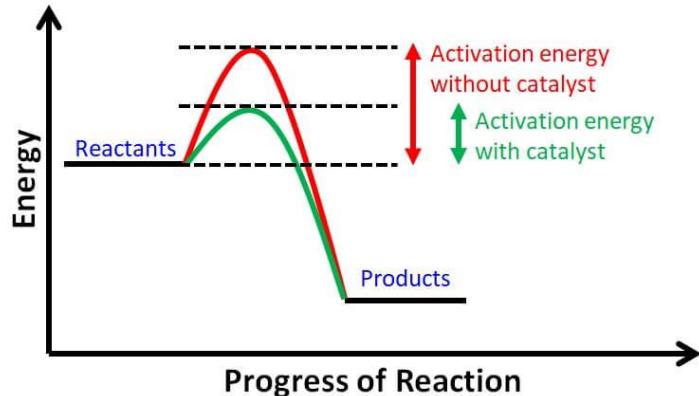
**Module IV: Catalysis and sustainability**

**Module V: Electrochemistry and its applications**

**Module VI: Supramolecular chemistry**

**Module VII: Graphene and carbon nanotubes**

# How does a catalyst work?



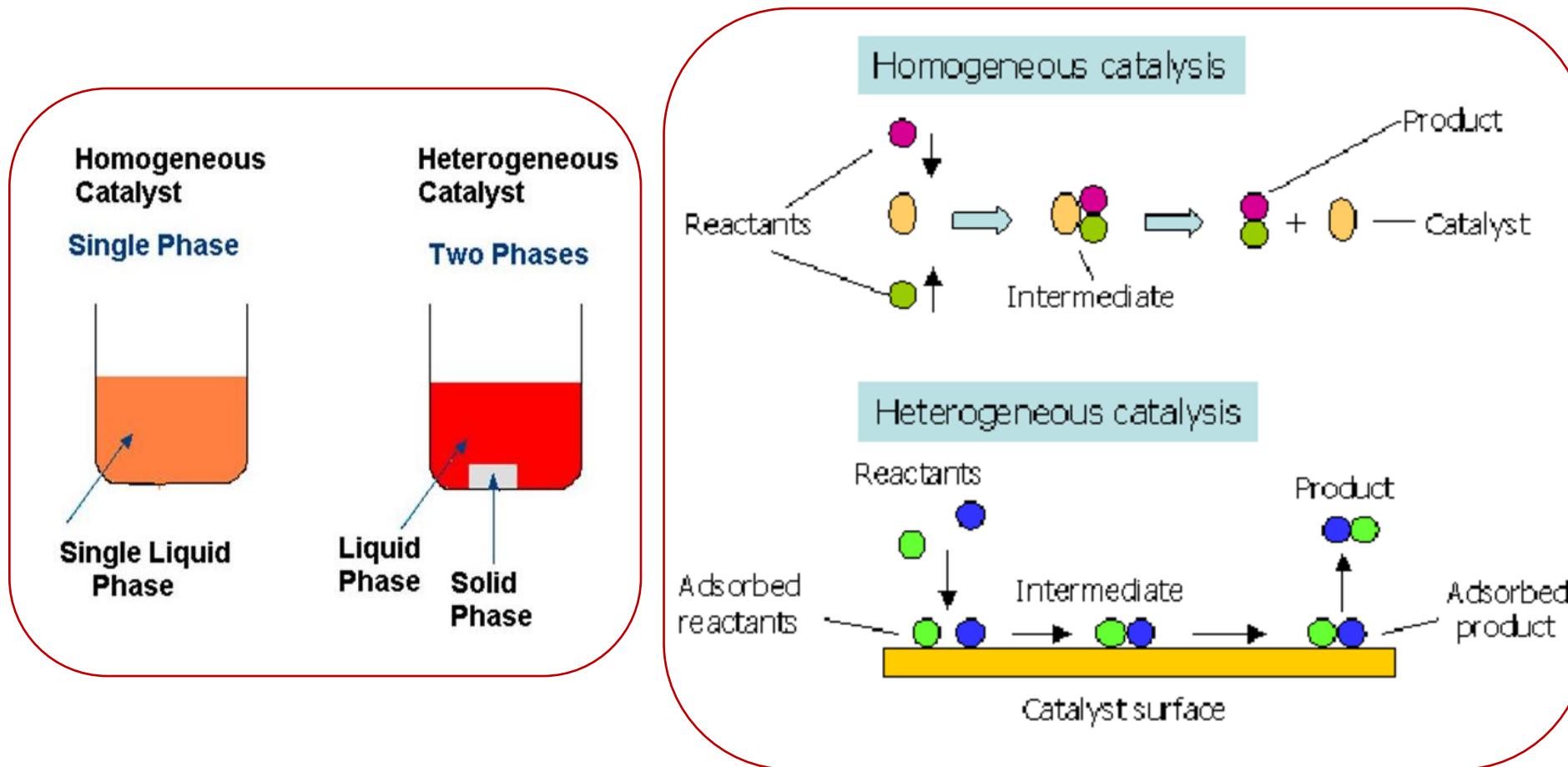
**A catalyst lowers the activation energy,  $E_a$ , thus enhancing the rate of a chemical reaction.**

**A catalyst does not get consumed in the chemical reaction. Its chemical composition and mass remain unchanged.**

**A catalyst provides an alternative reaction pathway with a lower activation energy ( $E_a$ ).**

**$E_a$ : It is the minimum energy required for a chemical reaction to occur. At the cost of  $E_a$ , the reactant molecules are converted into products.**

# Homogeneous Vs. Heterogeneous Catalysis



- **Homogeneous catalysis:** Catalyst and reactants are in the same phase.
- **Heterogeneous catalysis:** Catalyst and reactants are in the different phase (the catalyst is usually insoluble; reaction occurs on its surface).

# Heterogeneous Catalysis

A hot Cu wire catalyzes the oxidation of acetone



# Heterogeneous Catalysis



**Examples of industrial catalysts (metals, metal oxides, zeolites)**

# Terminologies in Catalysis : TON and TOF

- Each time the complete catalytic cycle occurs, we consider one catalytic turnover (one mole of product formed per mole of catalyst) to have been completed.
- TON: The lifetime of the catalyst before its deactivation is measured in terms of turnover number (TON).
- TOF: The catalytic rate can be conveniently given in terms of the Turnover Frequency (TOF) measured in turnovers per unit time.
- How many cycles can a catalyst perform → TON

Example: If **0.1 mole** of catalyst converts **100 moles** of substrates in **5 minutes (100% yield)** then

$$\text{TON} = 100/0.1 = 1,000 \text{ (unitless)}$$

$$\text{TOF} = \text{TON}/\text{time} = 1000/5 \text{ min} = 200 \text{ min}^{-1}$$

# Why are the catalysts so important?

- Apart from speeding up a chemical reaction, they are more energy-efficient.
- They can also reduce unwanted byproducts through a process called ‘selectivity’.
- This allows us to produce new compounds/materials with fewer negative side effects or no harmful effects on the environment.
- We can produce environmentally friendly fuel sources, fertilizers, and even biodegradable plastics.
- Catalysts have profoundly changed modern life and driven evolutionary advances in industrial applications.

# Why are the catalysts important for living organisms?

- Do you know that the human body also runs on catalysts?
- Yes, these are proteins, known as ‘enzymes’ (**biocatalysts, considered as a third category**), which are responsible for helping you move, digest your food, and produce energy. To say that catalysts are the ‘holy grail’.
- Using catalysts for many chemical reactions can help make things greener – they’re also better for living organisms.
- The main reasons for using a catalyst: (i) it makes a faster chemical reaction by lowering Ea, (ii) it reduces the harmful and potentially toxic by-products produced by the uncatalyzed reaction, (iii) it improves yield, (iv) it enhances efficiency (for industrial processes), (v) it is cost effective, (vi) less time-consuming.

# Nobel Prize in catalysis

## Wilhelm Ostwald (1909, Chemistry)

- Awarded “*for his work on catalysis, chemical equilibria, and reaction velocities.*”
- One of the first recognitions of catalysis as a fundamental concept.



Wilhelm Friedrich Ostwald was a Baltic German chemist and philosopher.

## Fritz Haber (1918) & Carl Bosch (1931, Chemistry)

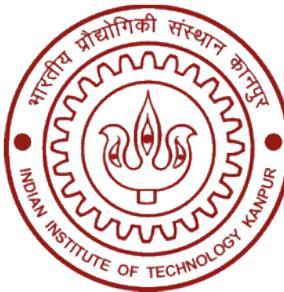
For the Haber–Bosch process, which uses an Fe-based heterogeneous catalyst to synthesize ammonia from N<sub>2</sub> and H<sub>2</sub>.

Carl Bosch: His work enabled the mass production of ammonia

Fritz Jakob Haber, a German chemist



Carl Bosch was a German chemist and engineer



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**Lecture: 2**

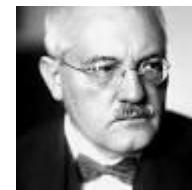
# Haber-Bosch process for NH<sub>3</sub> preparation

Fritz Haber (1918) & Carl Bosch (1931, Chemistry)



For the Haber–Bosch process, which uses an Fe-based heterogeneous catalyst to synthesize ammonia from N<sub>2</sub> and H<sub>2</sub>.

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Carl Bosch: His work enabled the mass production of ammonia

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The process converts atmospheric dinitrogen (N<sub>2</sub>) to ammonia (NH<sub>3</sub>) by a reaction with dihydrogen (H<sub>2</sub>) from natural gas (methane) using finely divided iron metal as a catalyst

# Haber-Bosch process for NH<sub>3</sub> preparation

## The Haber-Bosch Heritage: The Ammonia Production Technology



Haber



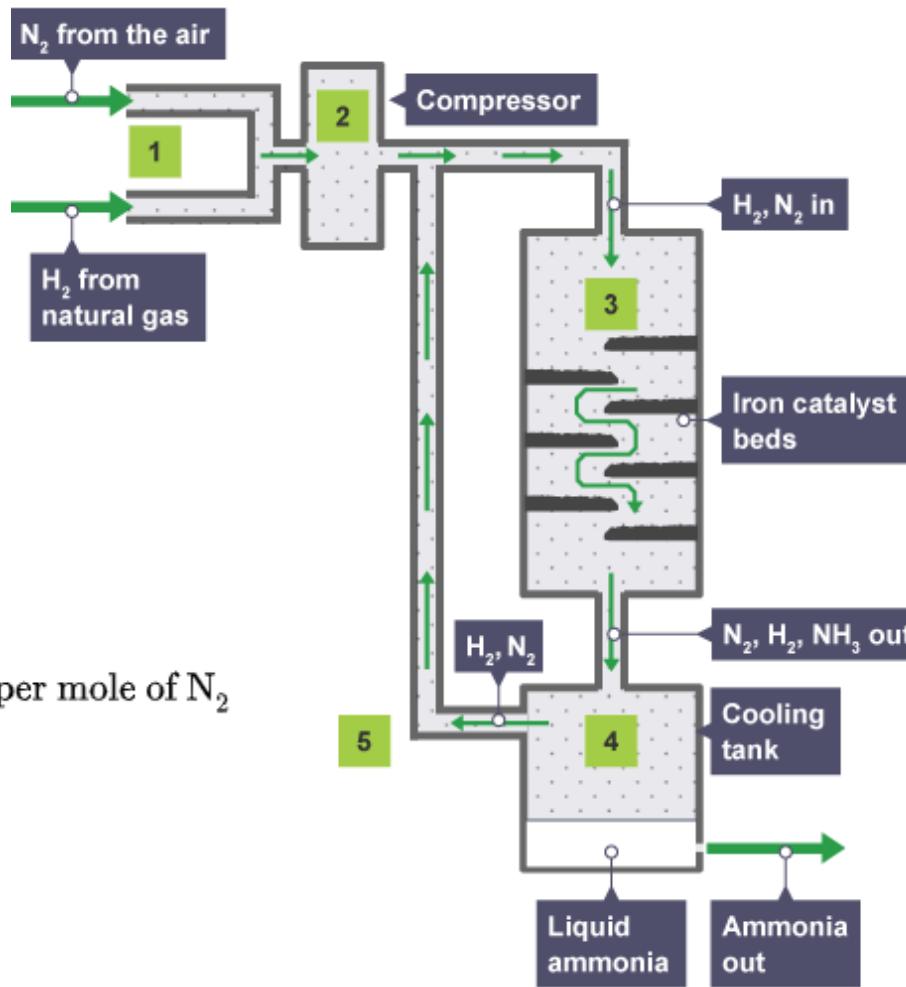
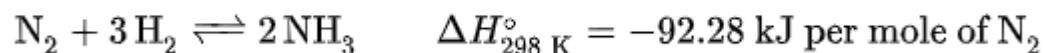
Bosch



Mittasch

Based on the fundamental research work of **Fritz Haber**, **Carl Bosch** and his engineering team developed industrial-scale ammonia (NH<sub>3</sub>) synthesis using an iron-based catalyst found by Alwin Mittasch and his co-worker.

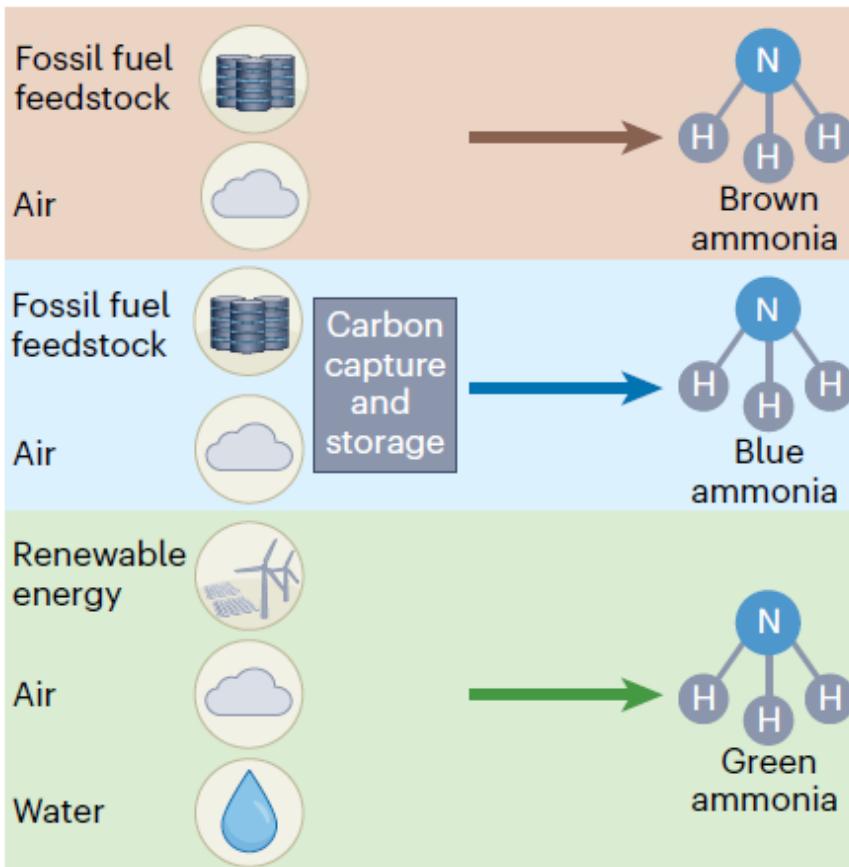
# Haber-Bosch process for NH<sub>3</sub> preparation



Each year, around 170 million metric tons of ammonia are produced globally, with approximately 80% used in fertilizers.

# Green ammonia synthesis

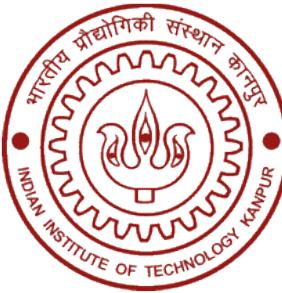
The Haber–Bosch process for synthesizing ammonia has enabled a significant increase in food production over the past century. Haber–Bosch process consumes 1–2% of the total global energy production, 3–5% of the world's natural gas production, and produces 1–3% of our CO<sub>2</sub> emissions.



In 1908, Fritz Haber combined nitrogen from the air with hydrogen from natural gas, over a metal catalyst at high pressure and temperature, to produce (brown) ammonia

The Haber–Bosch process has been modified to make ammonia synthesis cleaner. The inclusion of a carbon capture unit negates emissions from the conventional Haber–Bosch process, producing blue rather than brown ammonia

The use of hydrogen from water electrolysis rather than methane, in combination with the use of renewable energy, produces green ammonia.



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**Lecture: 3**

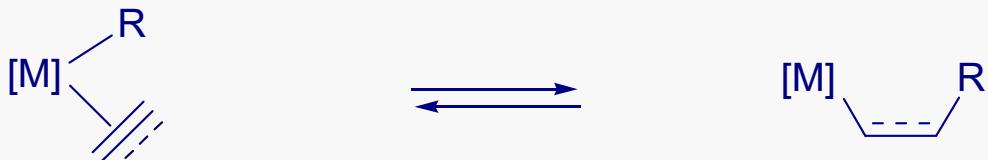
# Types of Organometallic Reactions



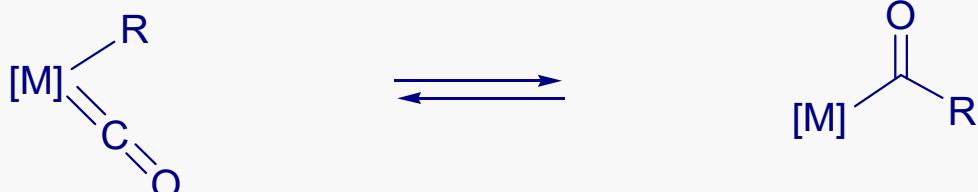
ligand exchange



oxidative addition →  
reductive elimination <



migratory insertion →  
(carbo-, hydro-metalation)  
β-elimination <  
(decarbo-, dehydro-metalation)



(CO) insertion

# Ziegler-Natta catalysts

Nobel Prize in Chemistry  
1963

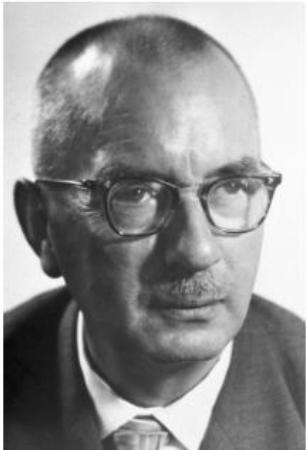


Photo from the Nobel Foundation archive.

Karl Ziegler

Prize share: 1/2



Photo from the Nobel Foundation archive.

Giulio Natta

Prize share: 1/2

The Nobel Prize in Chemistry 1963 was awarded jointly to Karl Ziegler and Giulio Natta "for their discoveries in the field of the chemistry and technology of high polymers"

# Salient features of Ziegler-Natta catalysts

**Ziegler-Natta catalysts are the most common commercial catalysts.**

**The original Ziegler-Natta catalysts were a complex of transition metal halides, such as titanium trichloride ( $TiCl_3$ ), with an organometallic compound, usually triethylaluminum ( $Et_3Al$ ), as cocatalyst to initiate the polymerization.**

**The yield of isotactic polypropylene in these original catalysts was lower (30–40%), but was rapidly increased to more than 80% with further development.**

**The low surface areas of early  $TiCl_3$  catalysts resulted in low catalyst activity.**

**Catalyst improvements have led to increased stereospecificity.**

# Ziegler-Natta catalysts with enhanced surface areas

**Supported heterogeneous Ziegler-Natta catalysts were developed in the 1960's, with magnesium chloride ( $MgCl_2$ ) used as the inert support material.**

**A Z-N catalyst is an excellent platform to polymerize  $\alpha$ -olefins with high linearity and stereoselectivity**

**A Z-N catalyst usually contains two components: (i) a transition metal (Group IV metals, like Ti, Zr, Hf) compound and (ii) an organoaluminum compound (co-catalyst).**

**The common examples of Z-N catalysts include  $TiCl_4 + Et_3Al$  and  $TiCl_3 + AlEt_2Cl$ .**

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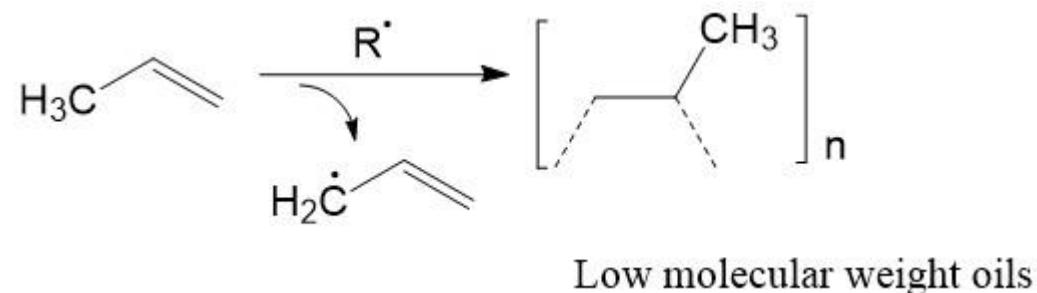
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# Advantages over traditional polymerization method

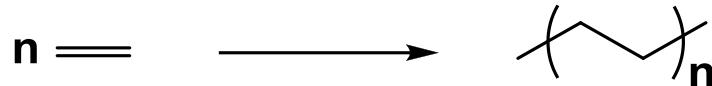
**Polymerization of  $\alpha$ -olefins by free radical method yields undesired branched polymers.**

**Free radical polymerization has no control over stereochemistry.**

**It produces mixtures of linear and unbranched polyethylene and stereoregulated polypropylene cannot be controlled by free radical polymerization. This technique largely limited the potential applications of these polymeric materials.**

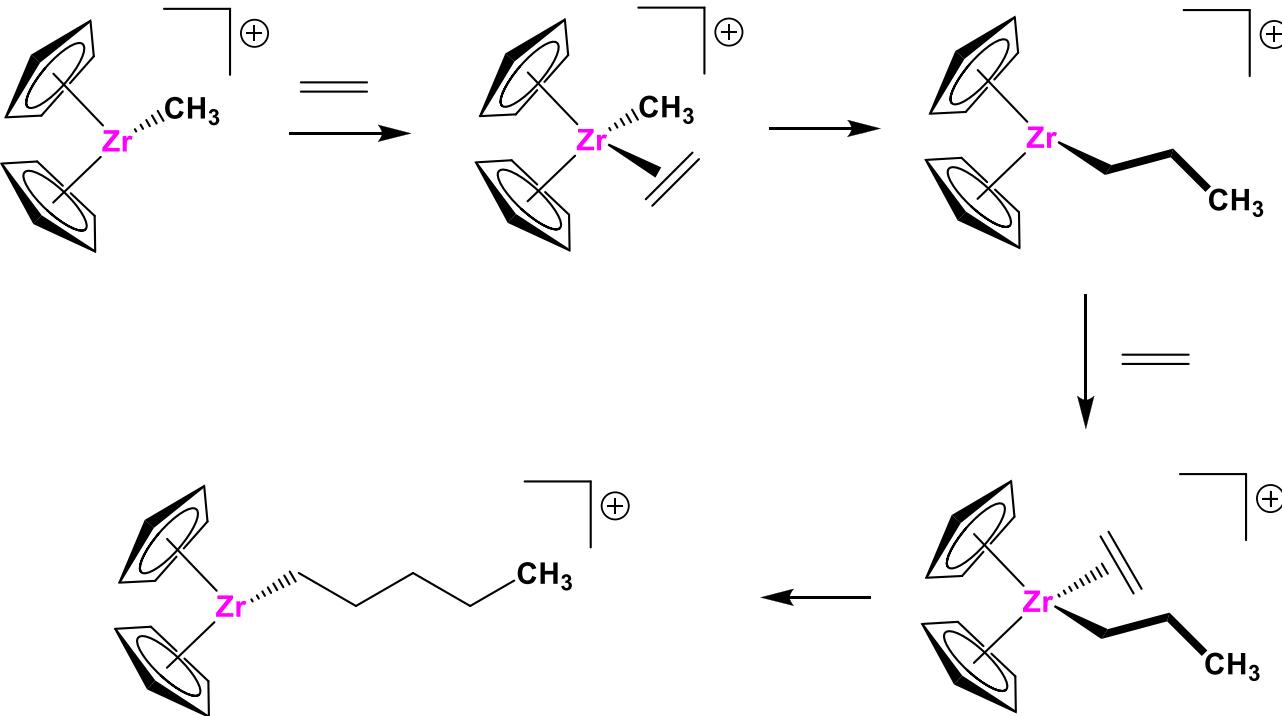


# Alkene Polymerization



	$d^4$
22	Ti
Titanium	
40	Zr
Zirconium	
72	Hf
Hafnium	

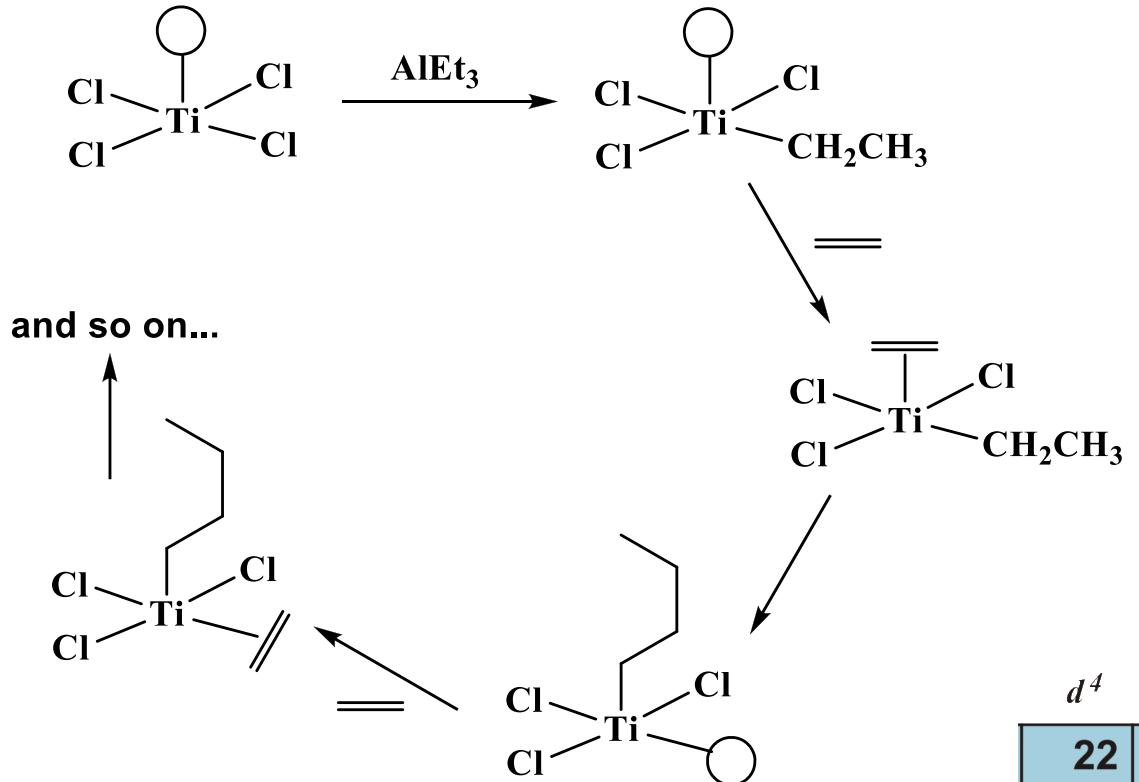
If only a few monomers couple together, the short chains formed are called oligomers.



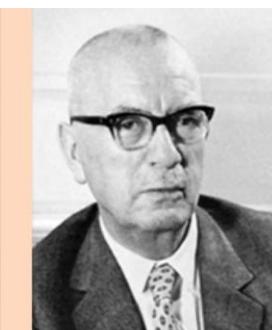
The commonly used catalyst has a tetrahydrofuran molecule occupying the fourth coordination site of zirconium.

# Ziegler-Natta Catalyst

- Karl Ziegler in 1953, discovered a catalyst based on  $TiCl_3$  and  $AlCl_3$  for the polymerization of ethylene.
- Giulio Natta extended the method for the polymerization of other olefins like propylene and made a number of different variations.
- The Ziegler-Natta catalyst family includes halides of titanium, chromium, vanadium and zirconium, typically activated by aluminum halide compounds.
- Ziegler and Natta received the Nobel Prize in Chemistry in the year 1963.

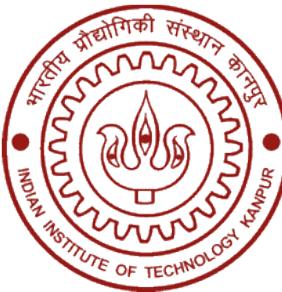


Giulio Natta  
1903-1979, Nobel Prize 1963



Karl Ziegler  
1898-1973, Nobel Prize 1963

$d^4$	
22	Ti
Titanium	
40	Zr
Zirconium	
72	Hf
Hafnium	



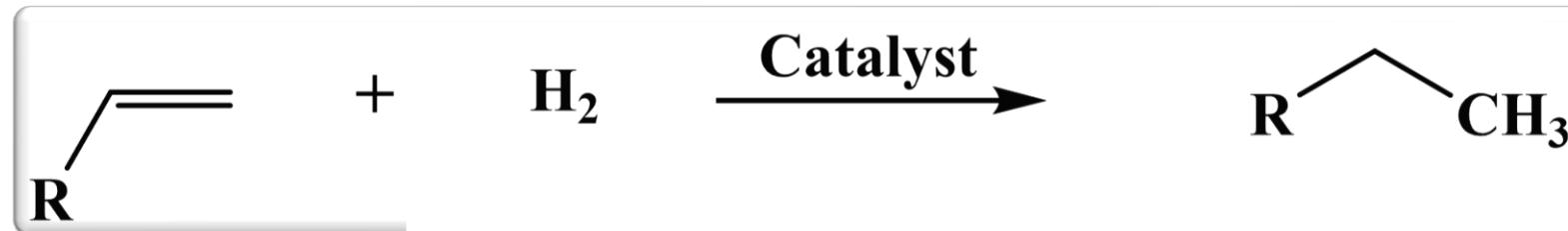
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**Lecture: 4**

# Hydrogenation of Alkenes



Geoffrey Wilkinson, Nobel  
Prize in Chemistry (1973)

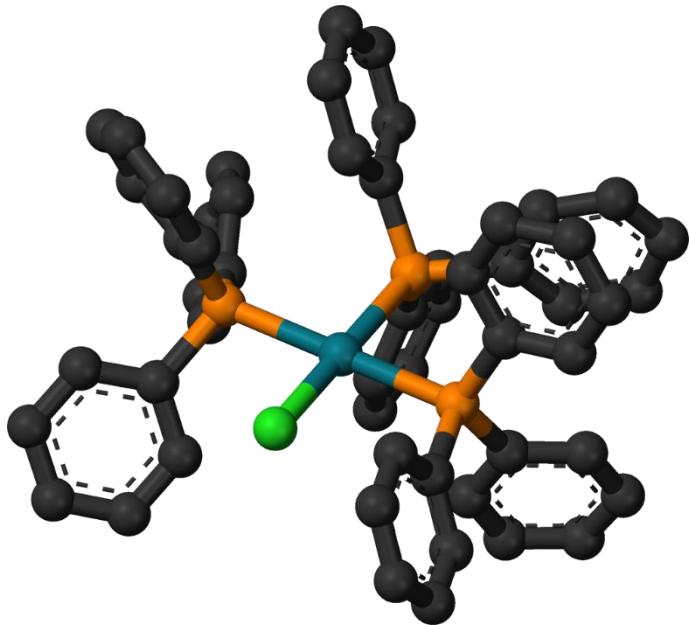


Wilkinson's catalyst

- The most used catalyst is the Wilkinson's Catalyst
- Many alkenes are hydrogenated with hydrogen at 1 atm pressure or less.
- Wilkinson's catalyst is highly sensitive to the nature of the phosphine ligand and the alkene substrate.
- The stereochemistry of H<sub>2</sub> addition is *cis*

$d^9$	
27	Co
Cobalt	
45	Rh
Rhodium	
77	Ir
Iridium	

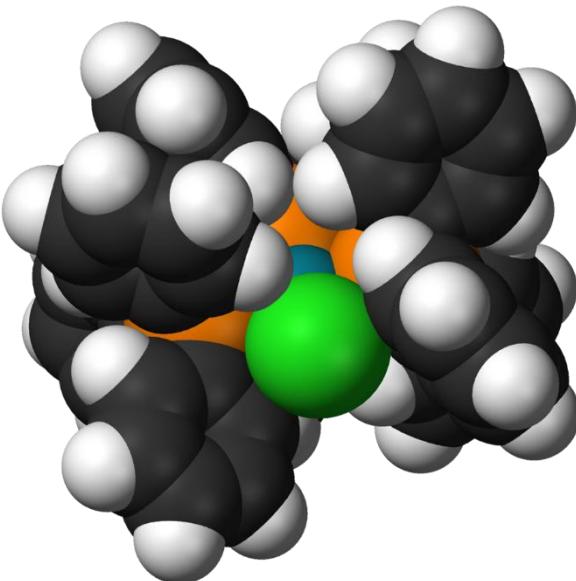
# Wilkinson's catalyst



slightly distorted square planar structure

coordinatively unsaturated

Wilkinson's catalyst performs selective catalytic hydrogenation of unsaturated hydrocarbons (alkenes and alkynes)



Geoffrey Wilkinson, Nobel  
Prize in Chemistry (1973)

# Wilkinson's Catalyst - Mechanism

	$d^9$
27	Co Cobalt
45	Rh Rhodium
77	Ir Iridium

