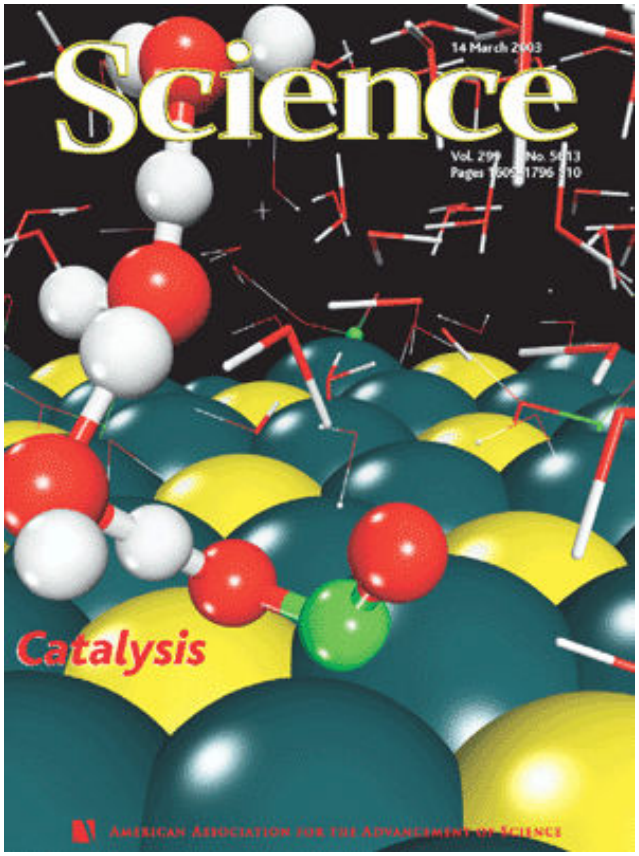
Catalysis (Part 1)



Science 299 **(14 March 2003) cover: The transition state for the catalytic oxidation of carbon monoxide (CO) by a hydroxyl intermediate over a model platinum/ruthenium surface in solution, as determined by quantum mechanical calculations. This path removes CO from the anode of a proton exchange membrane fuel cell. Platinum, ruthenium, carbon, oxygen, and hydrogen atoms are colored turquoise, yellow, green, red, and white, respectively. [Image: Matthew Neurock]**

CATALYSIS What's required?

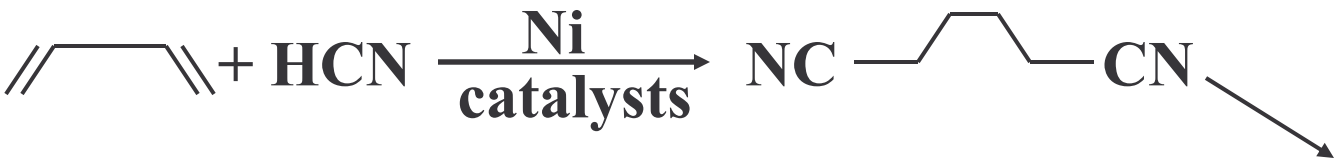
Catalyst --- A substance which increases the rate of a chemical reaction without being consumed in the reaction

1. **Catalyst binds the reactants for the catalytic process**
2. **Catalyst mediates the desired reaction**
3. **Reaction products are released to regenerate the catalyst.**

Some key advantages of catalytic processes:

- catalyst is not consumed
- can bring about transformations under milder conditions
- can control selectivity for a desired product

DUPONT PROBLEM



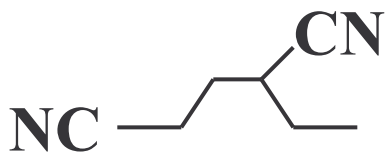
hexamethylene diamine

adipic acid

6,6 Nylon

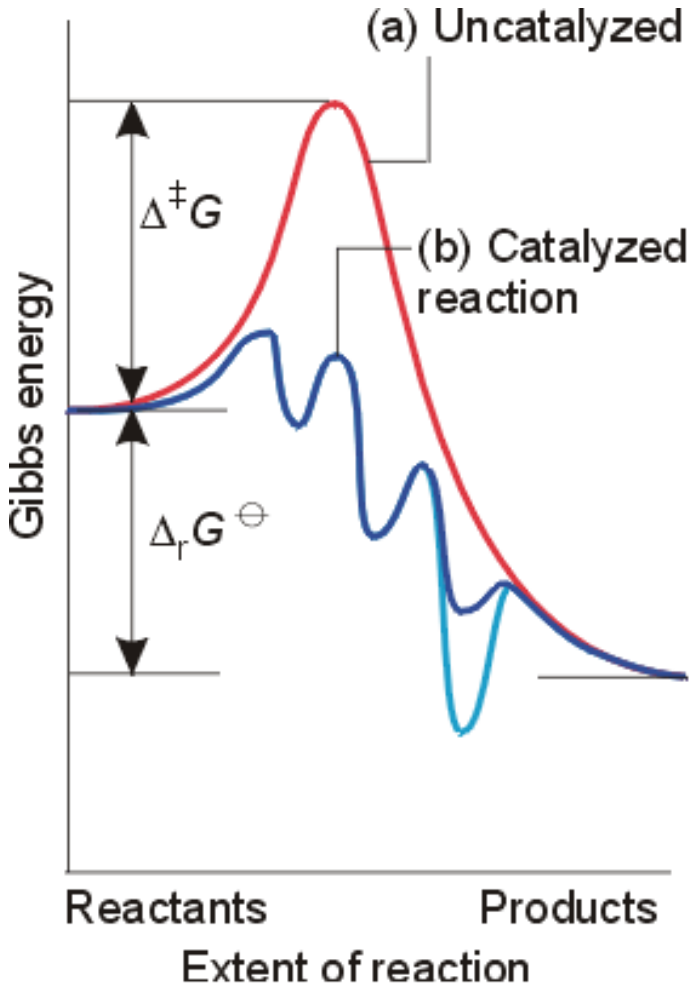
~10^9 lbs/yr

wonderful catalyst -- 90% selective, high turnover frequency..***but***

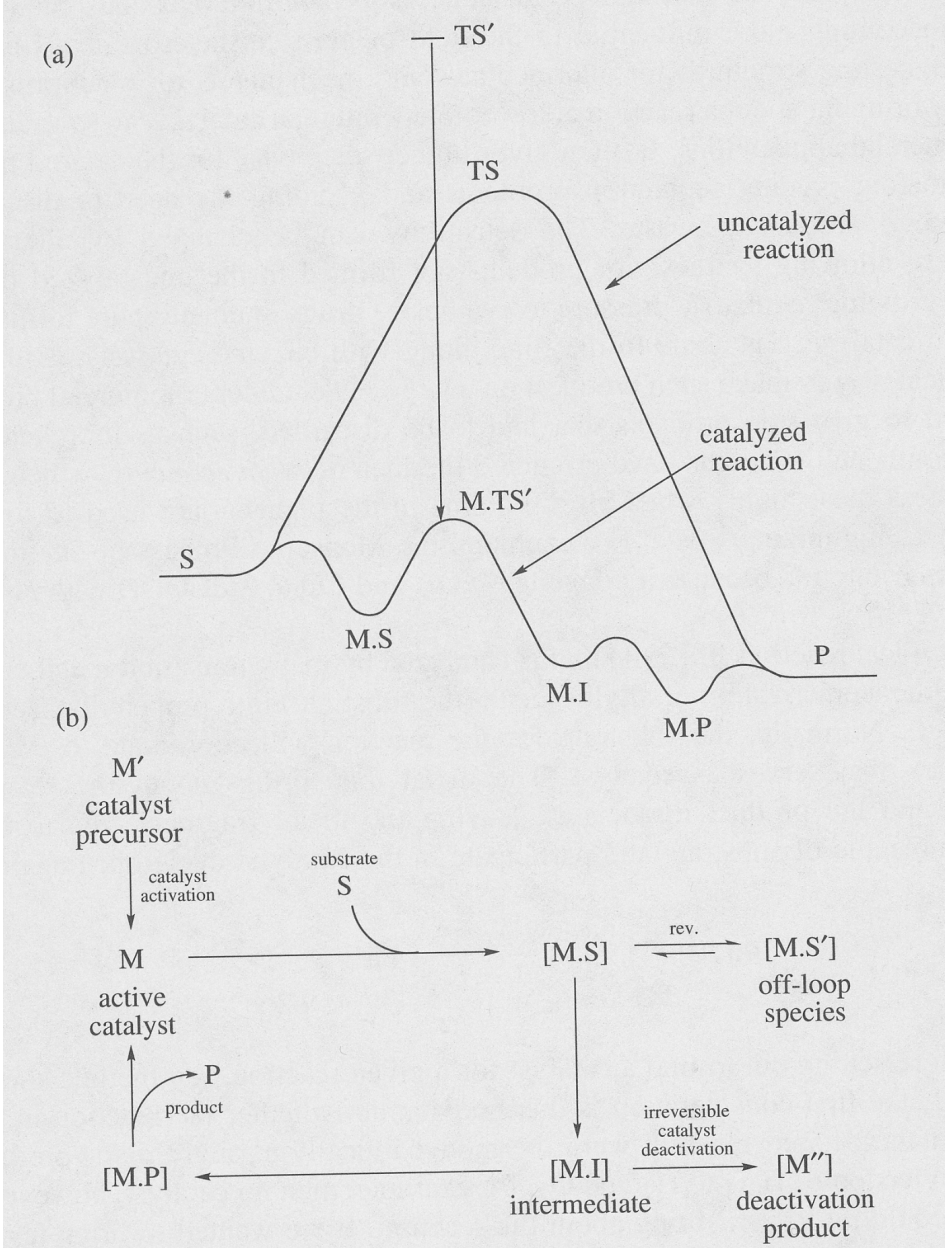
10% 

get 100 million lbs of wrong isomer!

current solution: burn it!



At the molecular level, a catalyst lowers the activation energy by participating in a cyclical series of reactions, each of which has a low activation energy.



The catalytic rate is usually given in terms of turnover frequency (TOF) measured in turnovers per unit time (10^2-10^6 are typical values)

Industrial Importance of Catalysis

Table 17.1 The top 20 synthetic chemicals in the USA

Synthetic chemical	Rank†	Catalytic process
Ethene	1	Hydrocarbon cracking, heterogeneous
Sulfuric acid	2	SO_2 oxidation, heterogeneous
Propene	3	Hydrocarbon cracking, heterogeneous
1,2-Dichloroethane	4	$C_2H_4 + Cl_2$; heterogeneous
Calcium hydroxide	5	Not catalytic
Ammonia	6	$N_2 + H_2$; heterogeneous
Urea	7	NH_3 precursor catalytic
Phosphoric acid	8	Not catalytic
Chlorine	9	Electrolysis
Ethylbenzene	10	Alkylation of benzene; homogeneous
Sodium carbonate	11	Not catalytic
Sodium hydroxide	12	Electrolysis
Styrene	13	Dehydrogenation of ethylbenzene; het
Nitric acid	14	$NH_3 + O_2$; heterogeneous
Ammonium nitrate	15	Precursors catalytic
Hydrogen chloride	16	Precursors catalytic
Acrylonitrile	17	$HCN + C_2H_2$, homogeneous
Ammonium sulfate	18	Precursors catalytic
Potassium oxide	19	Not catalytic
Titanium dioxide	20	Not catalytic

† Based on mass, from *Chemical and Engineering News* survey of US industrial chemicals, June 2
production in 1997.

Homogeneous Catalysis

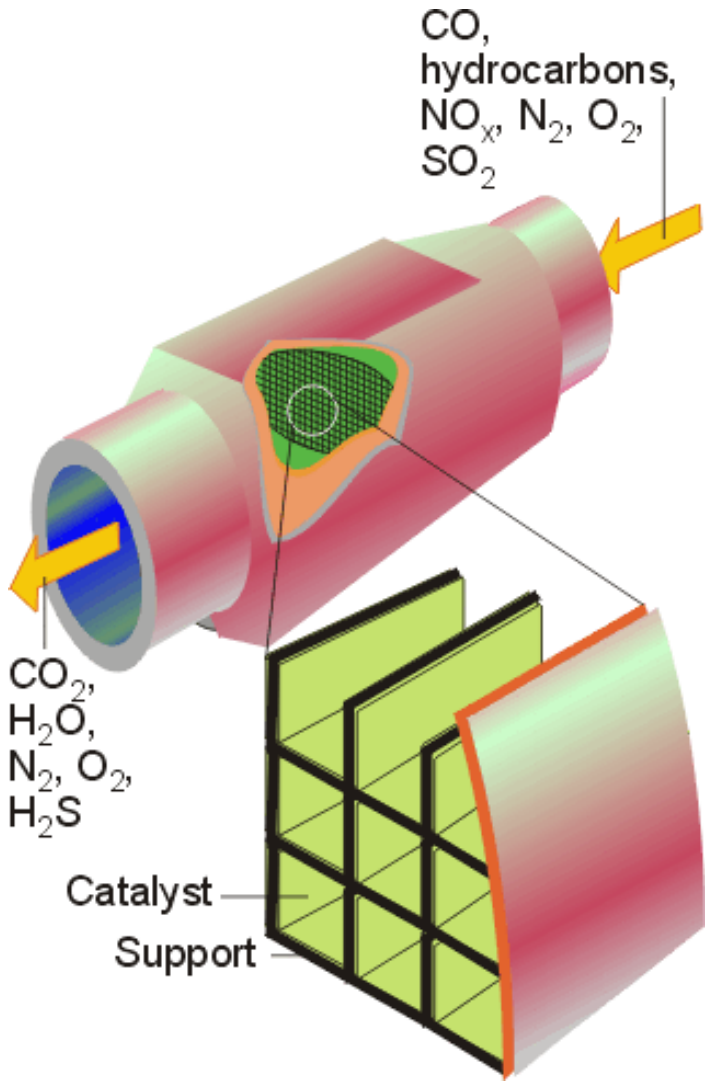
Both the catalyst and the reacting substrate are in the same phase.

Heterogeneous Catalysis

The catalyst and the reacting substrate are in different phases.

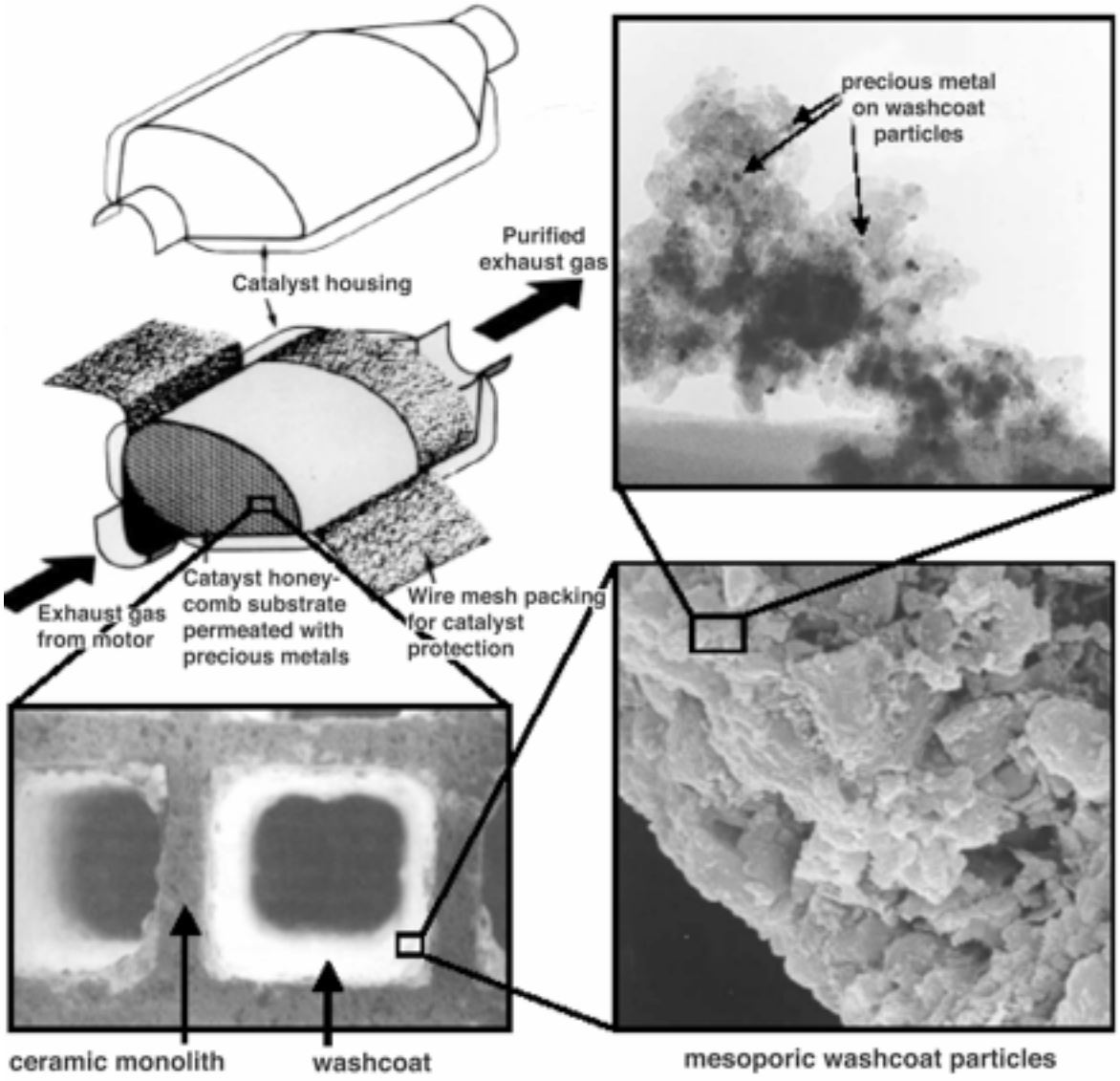
The vacant coordination site on the catalyst is located at a phase boundary (solid/liquid, solid/gas).

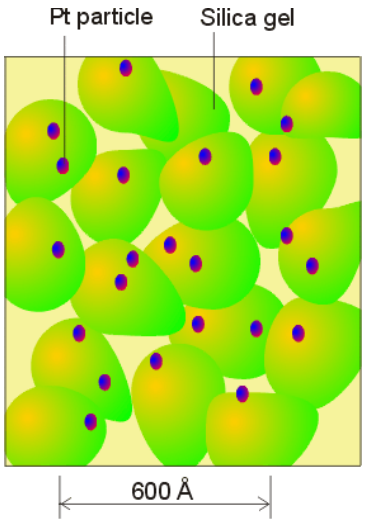
Heterogeneous Catalysis in a Catalytic Exhaust Converter



Catalyst oxidizes CO and hydrocarbons, reduces nitrogen oxides.

Placement of Particles in Catalytic Exhaust Converters

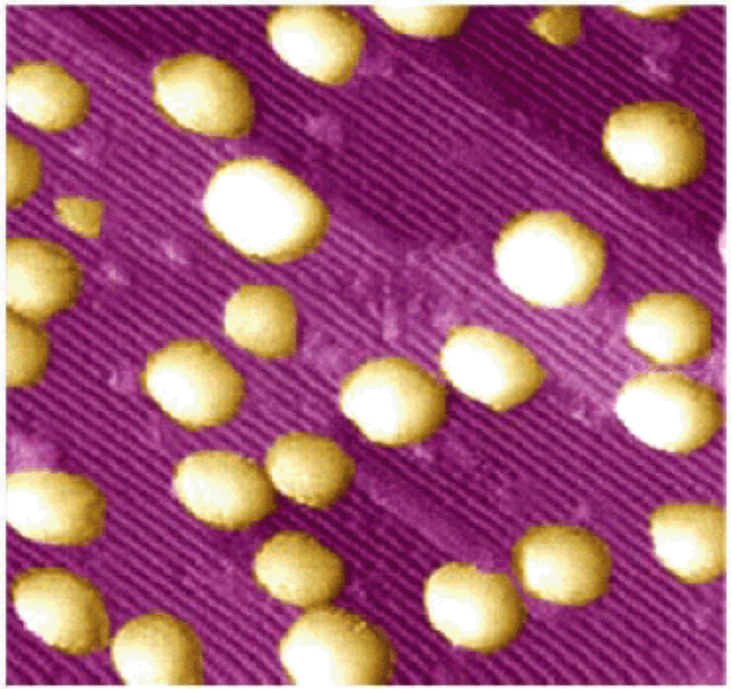


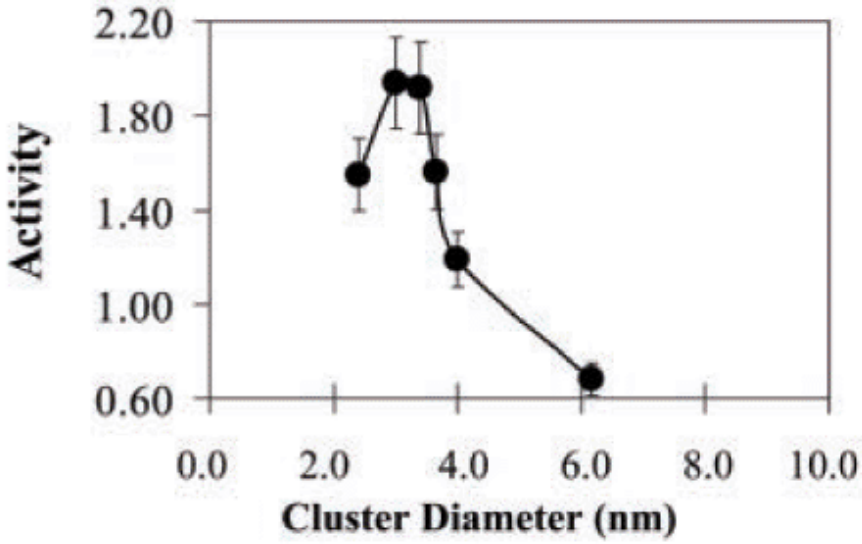


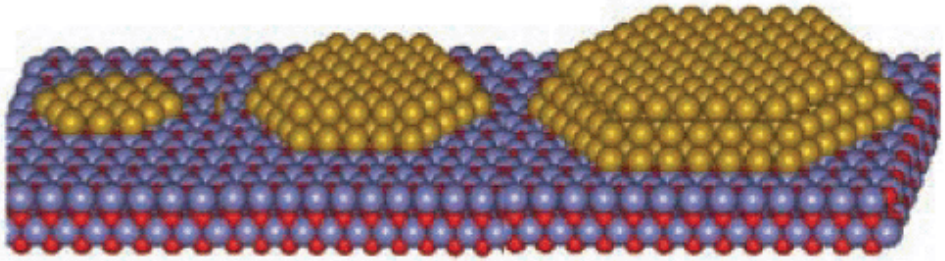
The Impact of Nanoscience on Heterogeneous Catalysis, A. Bell *Science* (2003), 299, 1688

Effect of catalyst particle size on activity

$$CO + \tfrac{1}{2} O_2 \rightarrow CO_2$$



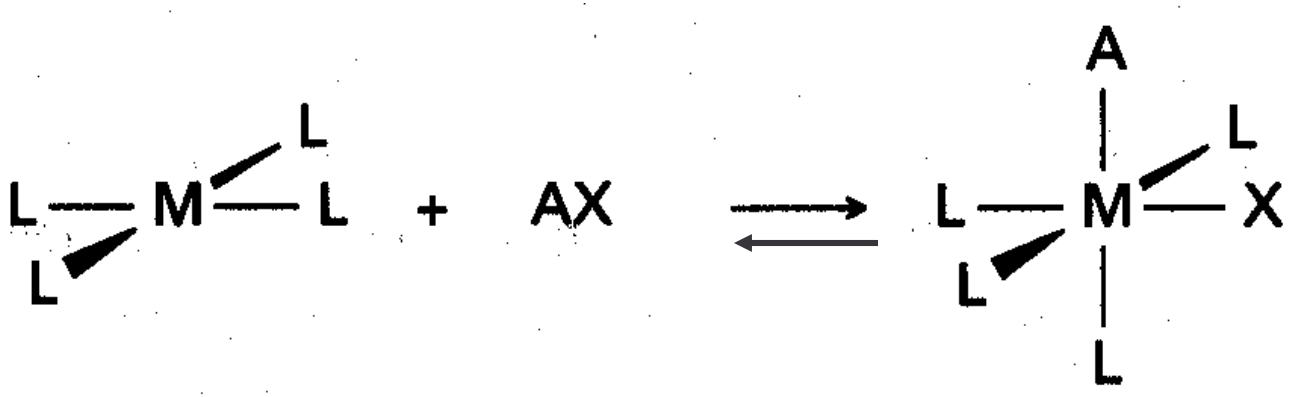




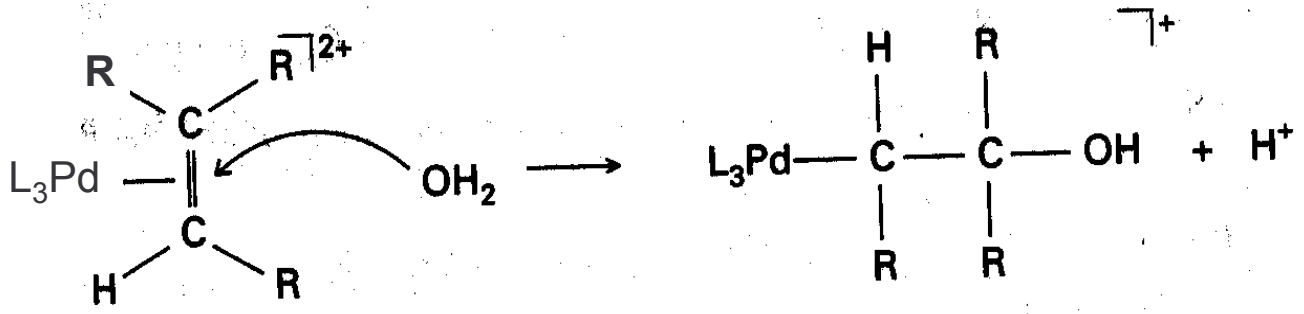
Important Steps in Homogeneous Catalysis:

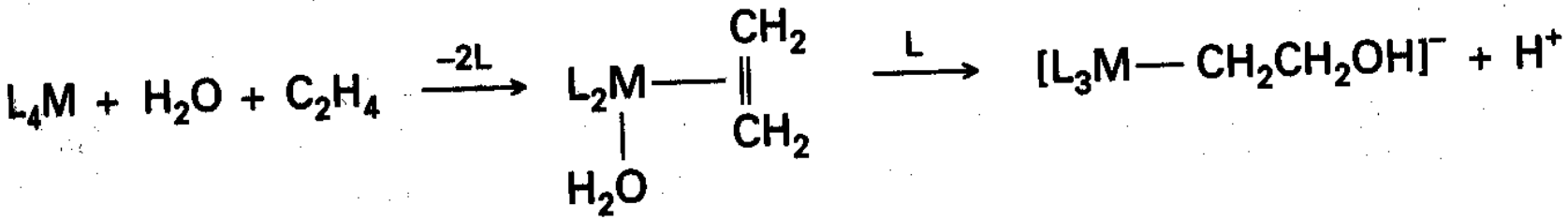
Ligand Coordination & Dissociation

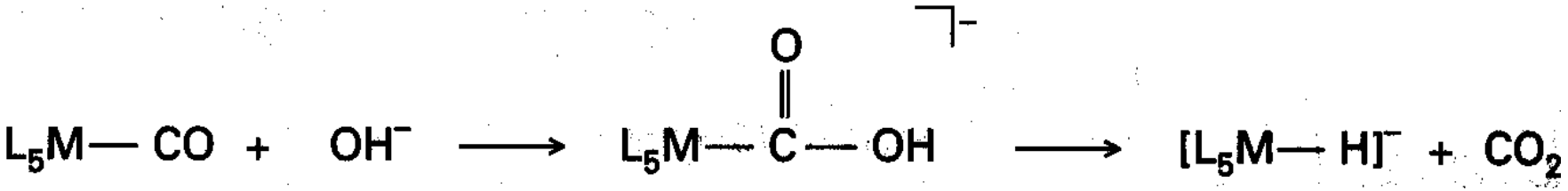
Oxidative Addition & Reductive Elimination



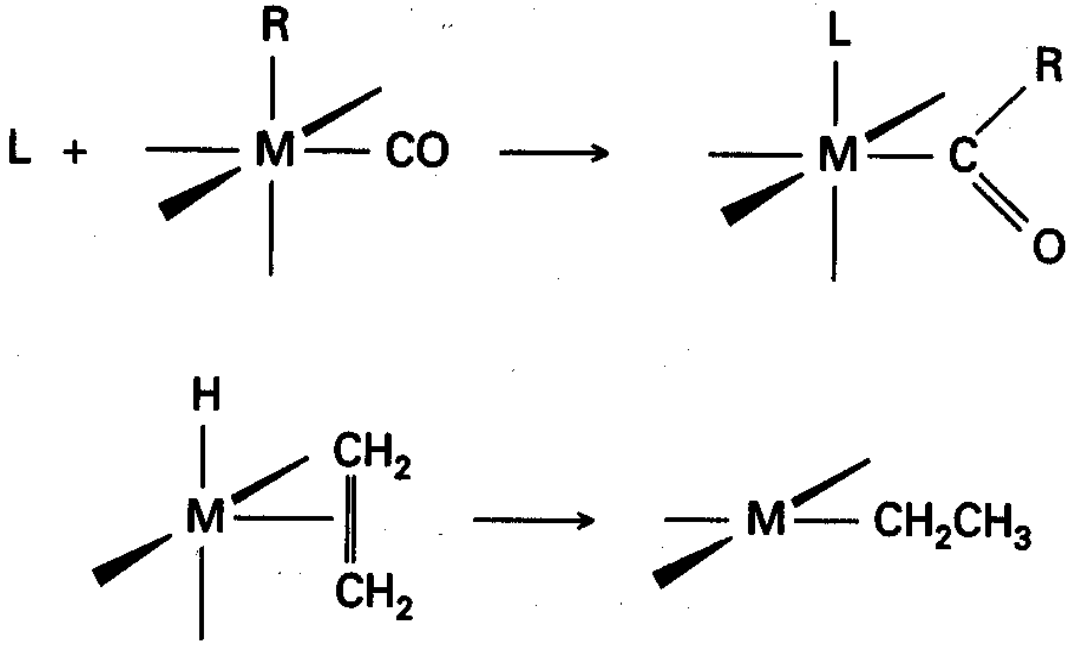
Important Steps in Homogeneous Catalysis: Nucleophilic Attack on Coordinated Ligands



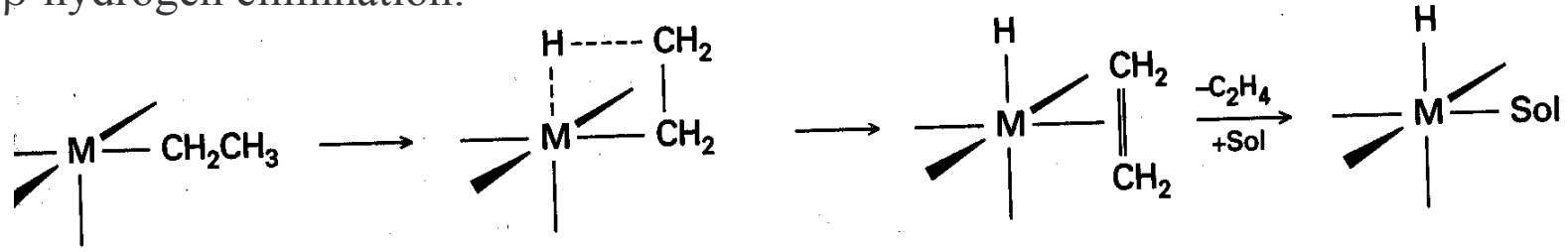




Important Steps in Homogeneous Catalysis: (Migratory) Insertion & Elimination



β-hydrogen elimination:



Important Steps in Homogeneous Catalysis: Oxidation and Reduction

Initiation (In· = radical initiator):

$$In\cdot + RH \longrightarrow InH + R\cdot$$

Propagation:

$$R\cdot + O_2 \longrightarrow R{-}O{-}O\cdot$$

$$R{-}O{-}O\cdot + R{-}H \longrightarrow R{-}O{-}O{-}H + R\cdot$$

Termination:

$$R\cdot + \cdot R \longrightarrow R_2$$

$$R\cdot + R{-}O{-}O\cdot \longrightarrow R{-}O{-}O{-}R$$

$$R{-}O{-}O\cdot + \cdot O{-}O{-}R \longrightarrow R{-}O{-}O{-}O{-}O{-}R \longrightarrow O_2 + \text{nonradicals}$$

The metal ions control the reaction by contributing to the formation of the R—O—O· radicals:

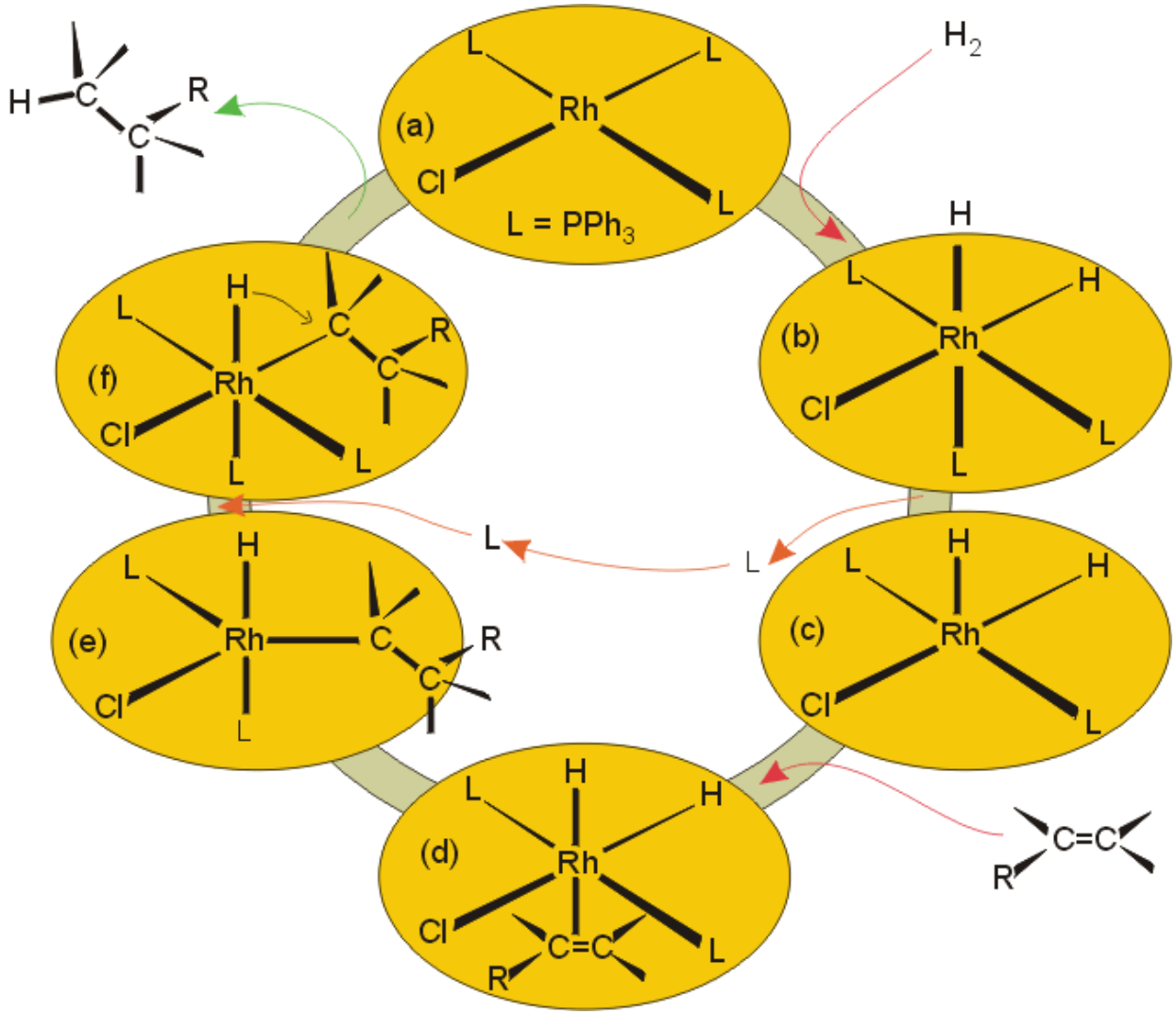
$$Co(II) + R{-}O{-}O{-}H \longrightarrow Co(ROOH) \longrightarrow Co(III)OH + R{-}O\cdot$$

$$Co(III) + R{-}O{-}O{-}H \longrightarrow Co(II) + R{-}O{-}O\cdot + H^+$$

$$ArCH_3 + Co(III) \longrightarrow \cdot ArCH_3^+ + Co(II)$$

With arenes, simple redox process

Hydrogenation of Alkenes with Wilkinson's Catalyst



Mechanism: oxidative addition of H_2, dissociation of L, coordination of alkene, migratory insertion (RDS), reductive elimination, release of alkane product.

Wilkinson's Catalyst

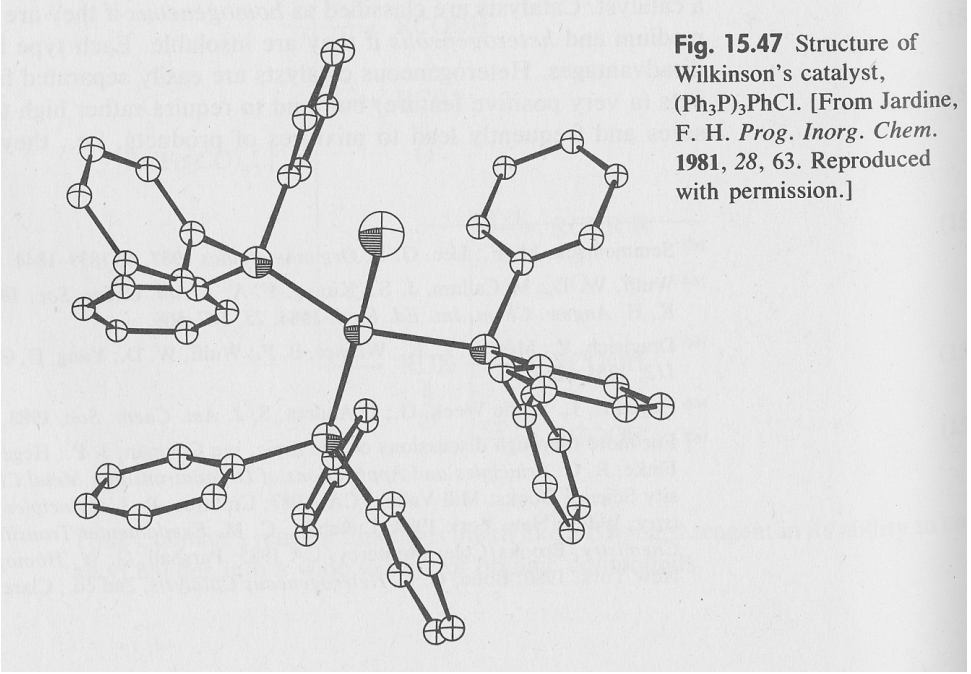
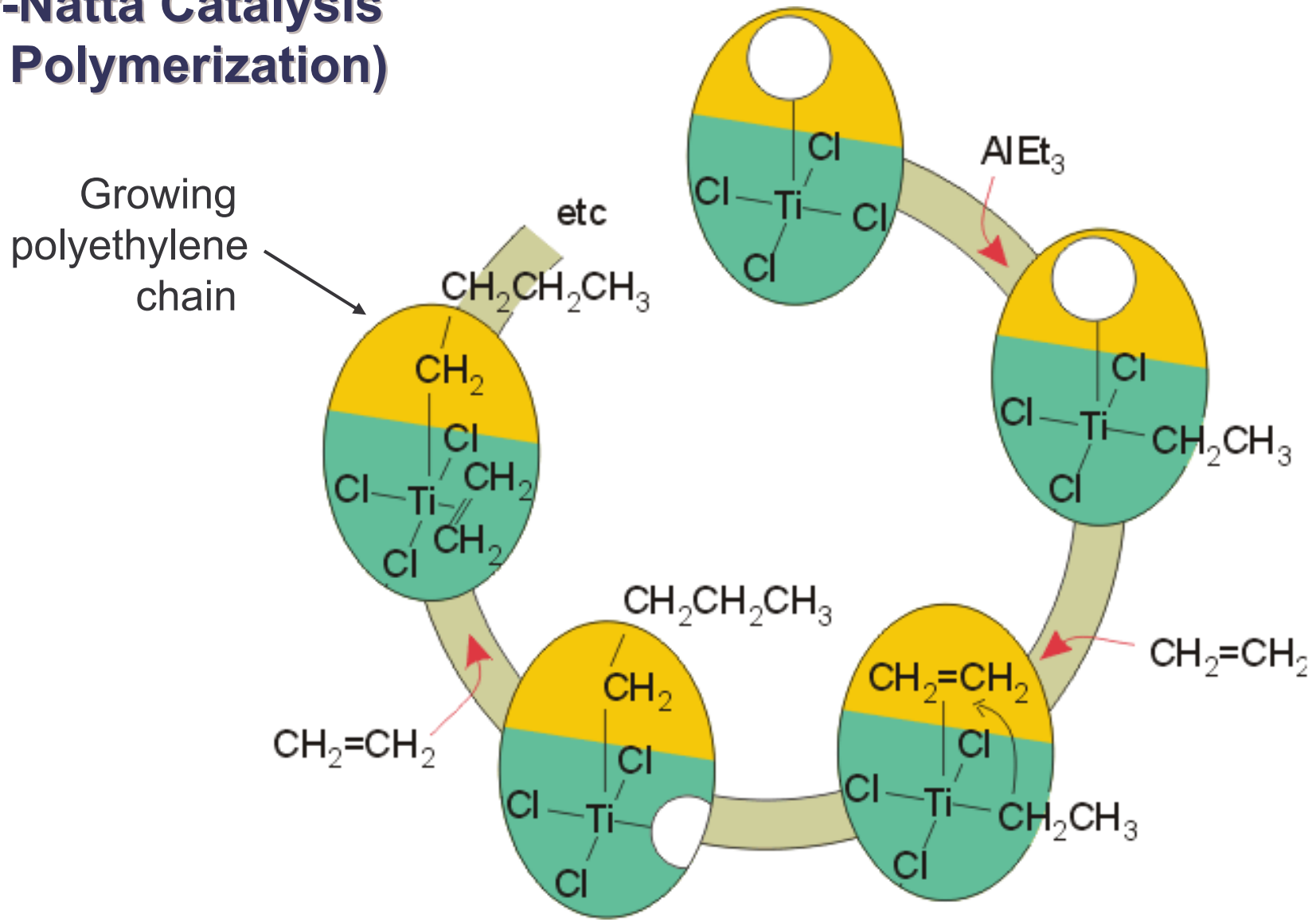


Fig. 15.47 Structure of Wilkinson's catalyst, $(Ph_3P)_3PhCl$. [From Jardine, F. H. *Prog. Inorg. Chem.* **1981**, *28*, 63. Reproduced with permission.]

Ziegler-Natta Catalysis (Olefin Polymerization)



Mechanism: formation of active Ti complex, coordination of alkene, migratory insertion, coordination of new alkene, etc.