Chapter 12 Summary
Introduction to catalysis

Catalysis is very important

- 90% of all chemical processes use catalysts
- Changes in catalysts have a giant influence on rates and selectivity's of reactions. More than anything else
- Most real reactor design associated with optimizing performance of catalyst

Ostwald defined a catalyst as a substance which changed the rate of reaction without itself being consumed in the process

Reaction occurs via a catalytic cycle:

$$\text{reactants} + \text{catalyst} \Rightarrow \text{complex}$$

$$\text{complex} \Rightarrow \text{products} + \text{catalyst}$$

$$CH_3OH + CO \Rightarrow CH_3COOH$$

(12.1)

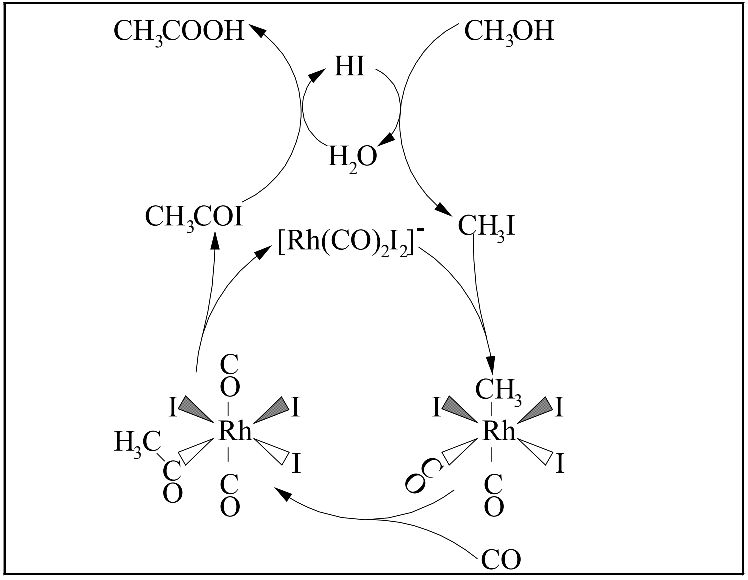


Figure 12.1 A schematic of the catalytic cycle for Acetic acid production via the Monsanto process.

Printing press analogy

Table 12.1 The rate enhancement of a number of reactions in the presence of a catalyst

Reaction	Catalyst	Rate Enhancement	Temperature
Ortho $H_2 \Rightarrow$ Para H_2	Pt (solid)	10^{40}	300°K
$2NH_3 \Rightarrow N_2 + 3H_2$	Mo (solid)	10^{20}	600°K
$C_2H_4 + H_2 \Rightarrow C_2H_6$	Pt (solid)	10^{42}	300°K
$H_2 + Br_2 \Rightarrow 2HBr$	Pt (solid)	1×10^8	300°K
$2NO + 2H_2 \Rightarrow N_2 + 2H_2O$	Ru (solid)	3×10^{16}	500°K
$CH_3COH \Rightarrow CH_4 + CO$	I_2 (gas)	4×10^6	500°K
$CH_3CH_3 \Rightarrow C_2H_4 + H_2$	NO_2 (gas)	1×10^9	750°K
$(CH_3)_3COH \Rightarrow (CH_3)_2CH_2CH_2 + H_2O$	HBr (gas)	3×10^8	750°K

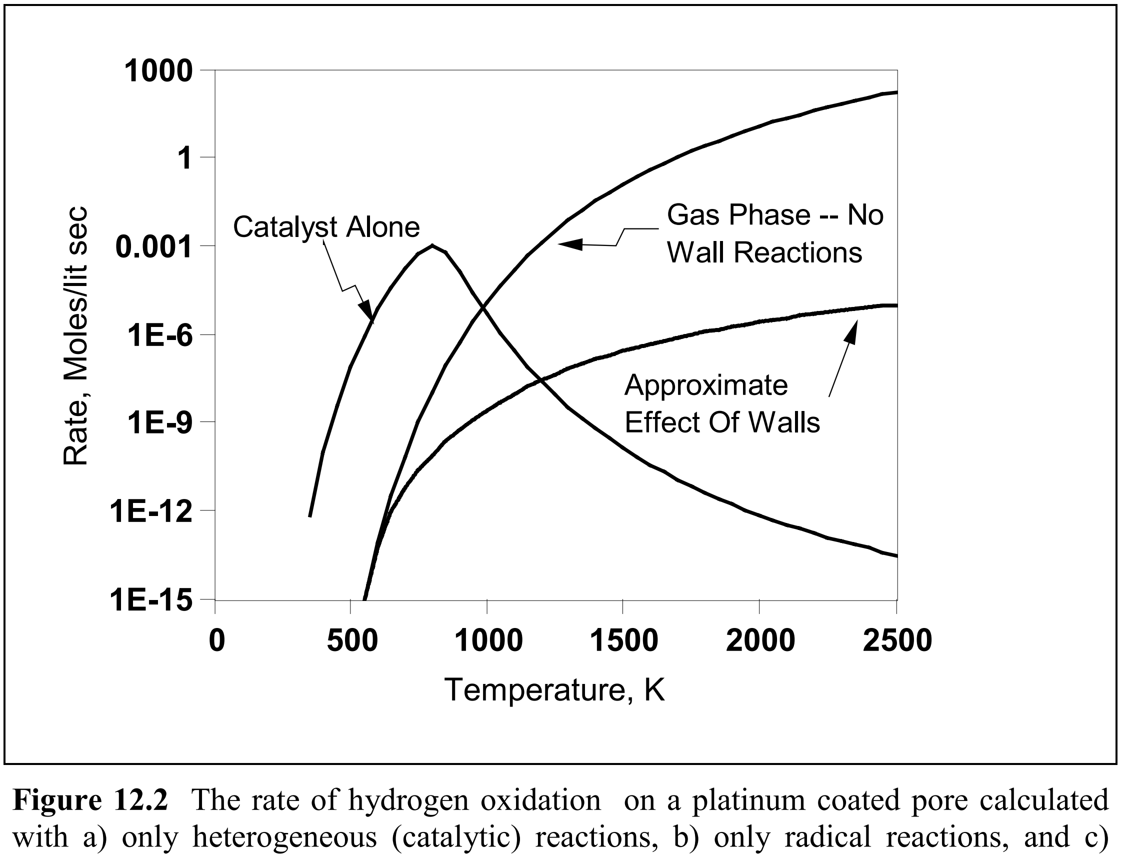


Figure 12.2 The rate of hydrogen oxidation on a platinum coated pore calculated with a) only heterogeneous (catalytic) reactions, b) only radical reactions, and c) combined radical, homogeneous reactions

Types of catalysts:

Homogeneous Catalysts
Heterogeneous Catalysts

Homogeneous catalysts:

- Acids or Bases
- Metal salts
- Enzymes
- Radical initiators

Table 12.2 - Some reactions commonly catalyzed by acids and bases

Reaction	Example	Typical Application
Isomerization (Rearranging the structure of a molecule)	$CH_2{=}CHCH_2CH_3 \Rightarrow CH_3CH{=}CHCH_3$	Octane Enhancement Monomer Production Paraxylene Production
Alkylation (Making too little molecules into a bigger one)	$CH_3CH{=}CHCH_3 + CH_3CH_2CH_2CH_3 \Rightarrow (CH_3CH_2)CH(CH_3)(C_4H_9)$	Pharmaceutical Production Monomer Production Fine Chemicals Butane + olefin⇒ octane
Cracking (Taking a big molecule and making it into two littler ones).	$C_{12}H_{24} \Rightarrow C_7H_{14} + C_5H_{10}$	Crude Oil Conversion Digestion

Table 12.2 - Some reactions commonly catalyzed by acids and bases

Reaction	Example	Typical Application
Esterfication (Attaching an acid to a base eliminating water)	$CH_3CH_2OH + CH_3COOH \Rightarrow CH_3COOCH_2CH_3 + H_2O$	Soap Production Fragrance Production
Aldol Condensation Reactions (combining two aldehydes by eliminating water)	$2\ CH_3CH_2CH_2CHO \Rightarrow CH_3CH_2CH_2CH{=}C(CHO)CH_2CH_3 + H_2O$	Fine Chemicals Pharmaceutical production
Alcohol Dehydration (removing a hydrogen and an OH from an alcohol, producing a double bond)	$CH_3CH_2OH \Rightarrow CH_2{=}CH_2 + H_2O$	Alternative fuels
Cationic Polymerization	Propylene ⇒ polypropylene	Polymer Production

Acids and Bases as catalysts

$$\text{Benzene} + \text{ethylene} \Rightarrow \text{ethylbenzene} \tag{12.2}$$

a proton reacts with the ethylene to form an ethyl ion:

$$H^+ + CH_2CH_2 \rightarrow [CH_3CH_2]^+ \tag{12.3}$$

The ethyl ion reacts with benzene to yield and ethylbenzene ion:

$$[CH_3CH_2]^+ + C_6H_6 \rightarrow [CH_3CH_2C_6H_6]^+$$

(12.4)

Then the ethylbenzene ion loses a proton:

$$[CH_3CH_2C_6H_6]^+ \rightarrow CH_3CH_2C_6H_5 + H^+$$

(12.5)

Metal atoms:

$$H_2 + 2S \rightarrow 2H(ad)$$

(12.6)

$$C_2H_4 + S \rightarrow C_2H_4(ad)$$

(12.7)

$$C_2H_4\ (ad) + H(ad) \rightarrow C_2H_5\ (ad) + S$$

(12.8)

$$C_2H_5(ad) + H(ad) \rightarrow C_2H_6 + 2S$$

(12.9)

Table 12.3 – Examples Of Reactions Catalyzed By Homogeneous Transition Metal catalysts

Reaction	Catalyst
Olefin Polymerization	$[TiCl_2(C_5H_5)_2]^{2+}$ or $TiCl_2/Al(C_2H_5)_3$ (Ziegler-Natta Catalyst)
Olefin Hydrogenation	$Rh(P(C_6H_5)_3)_3Cl$ Wilkinson Catalyst
C_2H_4+H_2O→Acetaldehyde (Wacker Process)	$PdCl_2(OH)_2$
C_2H_4+H_2 +CO →propylaldehyde (Hydroformylation)	$HCo(CO)_4$
$CH_3OH + CO \rightarrow CH_3COOH$ (Monsanto Carbonylation Process)	$[Rh(CO)_2I_2]^{1-}$
$H_2O_2 + CH_3CH_2OH \rightarrow CH_3CHO + 2\ H_2O$	Fe^{2+}

Table 12.4 Some Examples Of Enzymes Listed In The Brookhaven National Labs’ Protein Data Base

Oxidoreductases (promote oxidation reduction reactions)		Transferases (promote transfer of functional groups)	
NADH peroxidase (Oxidizes NADH with peroxides)	NADH + H_2O_2 ⇒ NAD(+) + 2 H_2O.	Dimethylallylcis-transferase (Transfer dimethylallyl groups)	Dimethylallyl diphosphate + isopentenyl diphosphate ⇒ diphosphate + dimethylallylcis-isopentenyldiphosphate
Ferroxidase (Oxidizes Iron)	$4\ Fe^{2+} + 4\ H^{+} + O_2 \Rightarrow 4\ Fe^{3+} + 2\ H_2O$	Glycoaldehyde transferase (Transfer’s Glucoaldeydes) Also called Transketolase	Sedoheptulose 7-phosphate + D-glyceraldehyde 3-phosphate ⇒ D-ribose 5-phosphate + D-xylulose 5-phosphate
Glucose oxidase (oxidizes Glucose)	β-D-Glucose + O_2 ⇒ D-glucono-1,5-lactone + H_2O_2	Alanine aminotransferase (Transfer amino groups from alanine)	L-Alanine + 2-oxoglutarate ⇒ pyruvate + L-glutamate
Hydrolases (Promote hydrolysis/cleavage reactions)		Lyases (promote addition of CO_2, H_2O and NH_3 to double bonds or formations of double bonds via elimination of CO_2, H_2O or NH_3)	

Table 12.4 Some Examples Of Enzymes Listed In The Brookhaven National Labs’ Protein Data Base

Carboxylesterase (Promotes hydrolysis of ester linkages)	A carboxylic ester + H_2O ⇒ an alcohol + a carboxylic anion	Carbonate dehydratase (Dehydrates carbonates)	$H_2CO_3 \leftrightarrow CO_2 + H_2O$
1,4-ALPHA-D-Glucan glucanohydrolase (also called ALPHA-Amylase)	Hydrolysis of 1,4-ALPHA-glucosidic linkages in oligosaccharides and polyasaccharides.	Citrate dehydratase	Citrate ↔ CIS-aconitate + H_2O
Interleukin 1-beta converting enzyme	Release of interleukin 1-beta by specific hydrolysis at 116-ASP-|-ALA-117 and 27-ASP-|-GLY-28 bonds	Pyruvate decarboxylase	A 2-OXO acid ↔an aldehyde + CO_2
Isomerases (promote isomerization reactions		Ligases (promotes formation of bonds - generally used to catalyze endothermic reactions requiring ATP)	
Maleate isomerase (promotes cis-trans isomerization of Maleate)	Maleate ⇒ Fumarate	Leucine--trna ligase	ATP + L-leucine + t-RNA(leu) ⇒ AMP + diphosphate + L-leucyl-t-RNA(leu).

Table 12.4 Some Examples Of Enzymes Listed In The Brookhaven National Labs' Protein Data Base

Cholestenol DELTA-isomerase	5-Alpha-cholest-7-en-3-beta-ol ⇒5-Alpha-cholest-8-en-3-beta-ol	Pyruvate carboxylase	ATP + pyruvate + (HCO_3) ⇒ ADP + phosphate + oxaloacetate
Mannose isomerase	D-Mannose ⇒ D-fructose	Aspartate--ammonia ligase	ATP + L-aspartate + NH_3 ⇒ AMP + diphosphate + L-asparagine

Radical initiators

$$C_2H_6 \Rightarrow C_2H_4 + H_2$$

(12.10)

$$X + I_2 \rightarrow 2I + X$$

(12.11)

Then the iodine can react with ethane to start the reaction:

$$I + CH_3CH_3 \rightarrow HI + CH_2CH_3$$

(12.12)

Free radical initiators are most important for polymerization reactions. Molecules like ethane are hard to decompose into radicals, and you need radicals or ions to start free radical polymerization. Consequently one adds a molecule that is easy to decompose, like benzoyl peroxide. The benzoyl peroxide decomposes into radicals:

$$R-\mathrm{O}-\mathrm{O}-R \rightarrow 2R\mathrm{O}\bullet$$

(12.13)

Then the radical reacts with the ethylene to start the polymerization process:

$$R\mathrm{O}\bullet + \mathrm{CH_2CH_2} \rightarrow R\mathrm{OCH_2CH_2}\bullet$$

(12.14)

Free radical processes are also important to atmospheric chemistry. Chlorine atoms produced from photolysis of chlorocarbons catalyze the destruction of ozone via the process:

$$\mathrm{Cl + O_3 \rightarrow ClO + O_2}$$

(12.15)

The ClO can then react via a number of processes to reduce the ozone layer. One particular reaction is:

$$\mathrm{ClO + O_3 \Rightarrow Cl + 2O_2}$$

(12.16)

Table 12.5 Some examples of reactions initiated or catalyzed by free radicals and similar species

Reaction	Initiator	Reaction	Catalyst
Olefin Polymerization	Peroxides, $(Ph)_3CC(Ph)_3$	$2SO_2 + O_2 \Rightarrow SO_3$ (Lead Chamber Process)	NO/NO_2
Hydrocarbon Dehydrogenation	Iodine, NO_2 chlorine atoms	Ozone Depletion	Cl
Hydrocarbon Oxidations	$[(CH_3CH_2)_4N][I]$, $[(CH_3CH_2)_4N][C_6H_5COO]$		

Solvents:

$$CH_3I + NaCl \rightarrow CH_3Cl + NaI$$

(12.17)

Table.12.6 The rate of reaction (12.17) in several solvents. All measurements have been extrapolated to 25 C

Solvent	Rate const, lit/mole sec
Gas Phase	about 10^{-45}
Water	3.5×10^{-5}
Methol	3×10^{-6}
Methyl Cyanide	0.13
DMF	2.5

Heterogeneous catalysis

Examples of heterogeneous catalysts include:

- Supported Metals
- Transition Metal Oxides and Sulfides
- Solid Acids and Bases
- Immobilized Enzymes and Other Polymer Bound Species

Supported metal catalysts

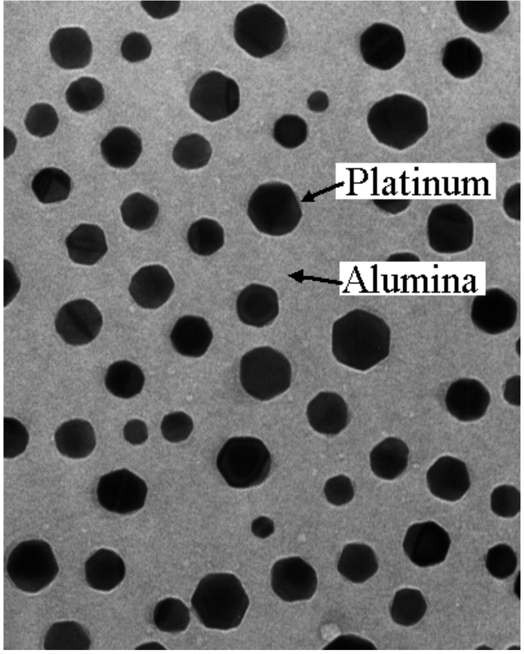


Figure.12.3 A picture of a supported metal catalyst.

Use support because platinum very expensive and only the surface is active.

Spread platinum out on cheap support.

Support also provides strength

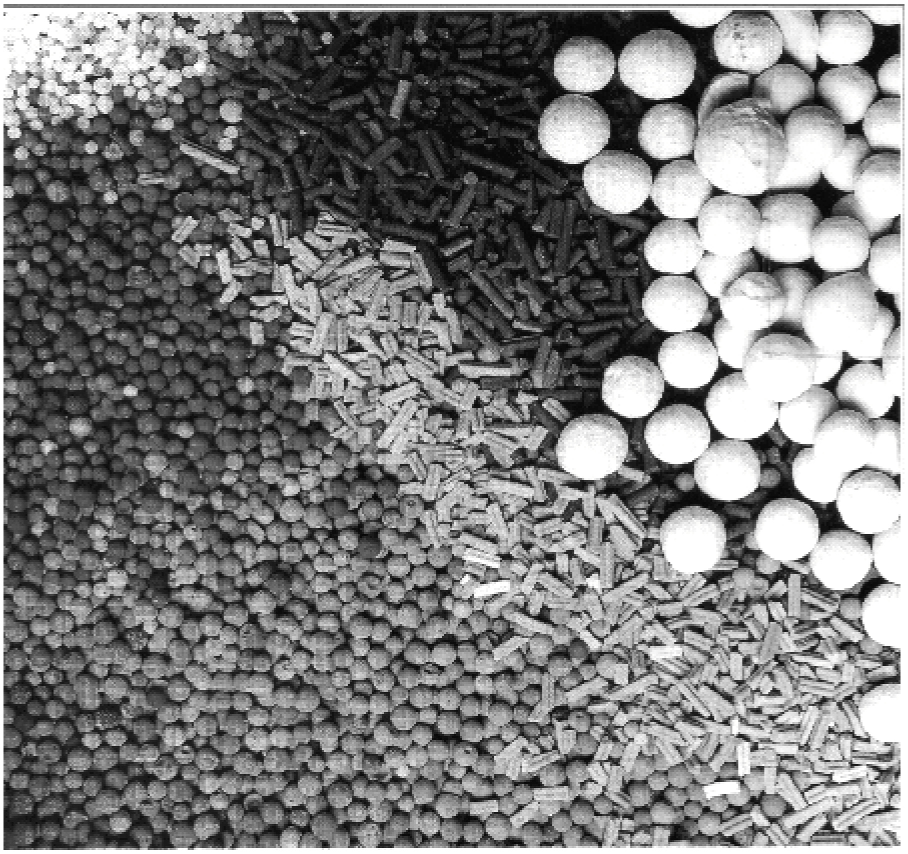


Figure 2.14 Pictures of some heterogenous catalysts. From Wijngaarden et al. Industrial Catalysis, Wiley 1998.

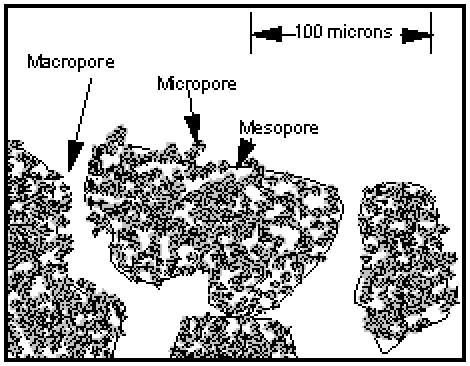


Figure 14.3 A cross sectional diagram of a typical catalyst support.

Advantage of heterogeneous catalysts compared to homogeneous:

- Cheaper separation
- More selective
- Generally cheaper

Disadvantage

- Not quite as active or a per metal atom basis

Table 12.7 A selection of the reactions catalyzed by supported metals

Reaction	Catalyst	Reaction	Catalyst
Hydrocarbon Hydrogenation, Dehydrogenation	Pt, Pd, Ni	$CO + H_2 \Rightarrow$ Hydrocarbons (Fischer-Tropsch)	Fe, Rh
CO oxidation, total oxidation of hydrocarbons	Pt, Pd, Cu, Ni, Fe, Rh, Ru	Steam reforming for production of hydrogen	Ni plus additives
$CO + 2H_2 \Rightarrow CH_3OH$	Cu/ZnO	Reforming (Isomerization of oil)	Pt/Re/Al2O3
$2\ CO + 2NO \Rightarrow 2CO_2 + N_2$	Pt, Rh, Ru (catalytic converter)	$2NH_3 + O_2 \Rightarrow N_2O_5 + 3H_2O$	Pt
$N_2 + 3\ H_2 \Rightarrow 2\ NH_3$	Fe, Ru, Rh	Alcohols + $O_2 \Rightarrow$ Aldehydes + H_2O e.g. $2\ CH_3OH + O_2 \Rightarrow 2\ H_2CO + H_2O$	Ag, Cu
$2\ C_2H_4 + O_2 \Rightarrow$ 2 ethylene oxide	Ag, Cu	$R\text{-}R' + H_2 \Rightarrow RH + HR'$ (Hydrogenolysis)	Ni, Co, Rh, Ru

$$H_2 + 2S \rightarrow 2\ H(ad)$$

(12.18)

$$C_2H_4 + S \rightarrow C_2H_4(ad)$$

(12.19)

$$C_2H_4(ad) + H(ad) \rightarrow C_2H_5(ad) + S$$

(12.20)

$$C_2H_5(ad) + H(ad) \rightarrow C_2H_6 + 2S$$

(12.21)

Table 12.8 A selection of the reactions catalyzed by transition metal oxides, nitrides and sulfides

Reaction	Catalyst	Reaction	Catalyst
$2 SO_2 + O_2 \Rightarrow 2 SO_3$	V_2O_5	$CO + H_2O \Rightarrow CO_2 + H_2$ (Water Gas Shift)	FeO, CuO, ZnO
Hydrodesulfurization	CoS, MoS, WS	$2(CH_3)_3COH \Rightarrow (CH_3)_3COC(CH_3)_3 + H_2O$	TiO_2
$CH_3CH{=}CH_2 + O_2 \Rightarrow CH_2{=}CHCHO + H_2O$	$(Bi_2O_3)_x(MoO_3)_y$ (Bismuth molybate) Uranium Antimonate	$2 CH_3CH{=}CH_2 + 3 O_2 + 2NH_3 \Rightarrow 2CH_2{=}CHC{\equiv}N + 6 H_2O$ (aminoxidation)	$(FeO)_x(Sb_2O_3)_y$
$4 NH_3 + 4 NO + O_2 \Rightarrow 4N_2 + 6 H_2O$ (Selective catalytic reduction)	V_2O_5, TiO_2	benzene+$O_2 \Rightarrow$ maleic anhydride + water naphthylene+$O_2 \Rightarrow$ phthalic anhydride + water	$(V_2O_5)_x(PO_4)_y$
$CH_3CH_2(C_6H_5) + O_2 \Rightarrow CH_2{=}CH(C_6H_5) + H_2O$ (styrene production)	FeO	Selective oxidation of hydrocarbons	NiO, Fe_2O_3, V_2O_5, TiO_2 CuO, Co_3, O_4, MnO_2
Aromatiztion e.g. Heptane⇒Tolvene H_2 or H_2O	Cr_2O_3/Al_2O_3	Hydrodenitrogenation	NiS,MoS

Table 12.9 Some common solid acids and bases

Material	Type	Material	Type
silica/alumina	solid acid	Mordenite	zeolite
alumina	solid acid	ZSM-5	zeolite
Y-zeolite Faugasite	zeolite	VFI	large pore zeolite
Sodalite	zeolite	Offretite	zeolite
$HF\text{-}SbF_5$	superacid	HSO_3F	superacid
$H_2[Ti_6O_4(SO_4)_4(OEt)_{10}]$	superacid	Sulfated Zirconia	superacid
MgO	solid base	Na_2O	base

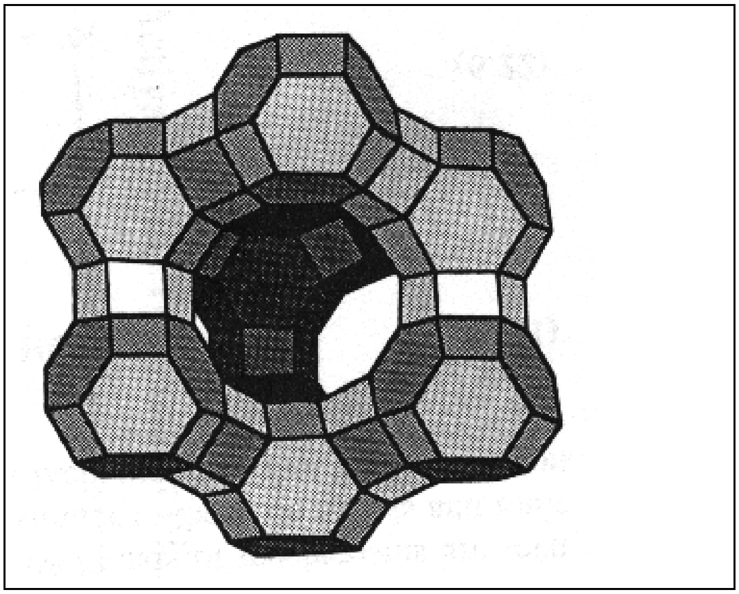


Figure 12.4 A diagram of the pore structure in Faugasite.

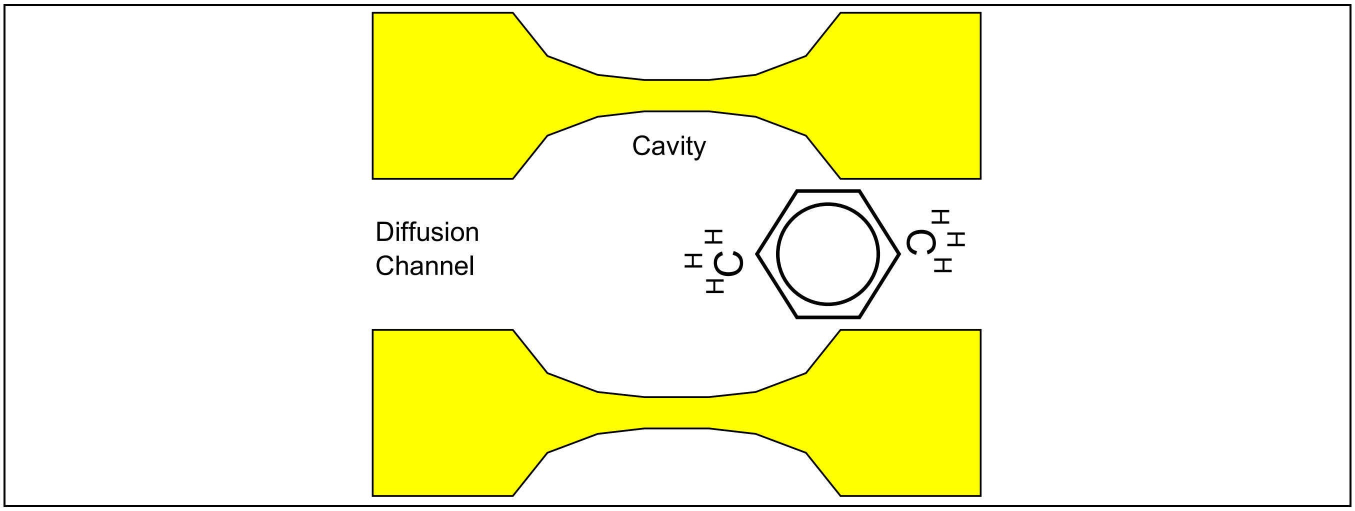


Figure 12.27 An interconnecting pore structure which is selective for the formation of paraxylene.

Next: mechanisms of catalyst action

Catalysts work by:

- Catalysts can be designed to help initiate reactions.
- Catalysts can be designed to stabilize the intermediates of a reaction.
- Catalysts can be designed to hold the reactants in close proximity.
- Catalysts can be designed to hold the reactants in the right configuration to react.
- Catalysts can be designed to block side reactions.
- Catalysts can be designed to sequentially stretch bonds and otherwise make bonds easier to break.
- Catalysts can be designed to donate and accept electrons.
- Catalysts can be designed to act as efficient means for energy transfer.

It is also important to realize that:

- One needs a catalytic cycle to get reactions to happen.
- Mass transfer limitations are more important when a catalyst is present.

The most important effects are

- Catalysts can be designed to help initiate reactions.
- Catalysts can be designed to stabilize the intermediates of a reaction.

$$H_2+Br_2 \Rightarrow 2HBr \tag{12.39}$$

$$Br_2 \rightarrow 2Br$$
$$Br + H_2 \rightarrow HBr + H$$
$$H + Br_2 \rightarrow HBr + Br$$
$$2\,Br \rightarrow Br_2$$

(12.40)

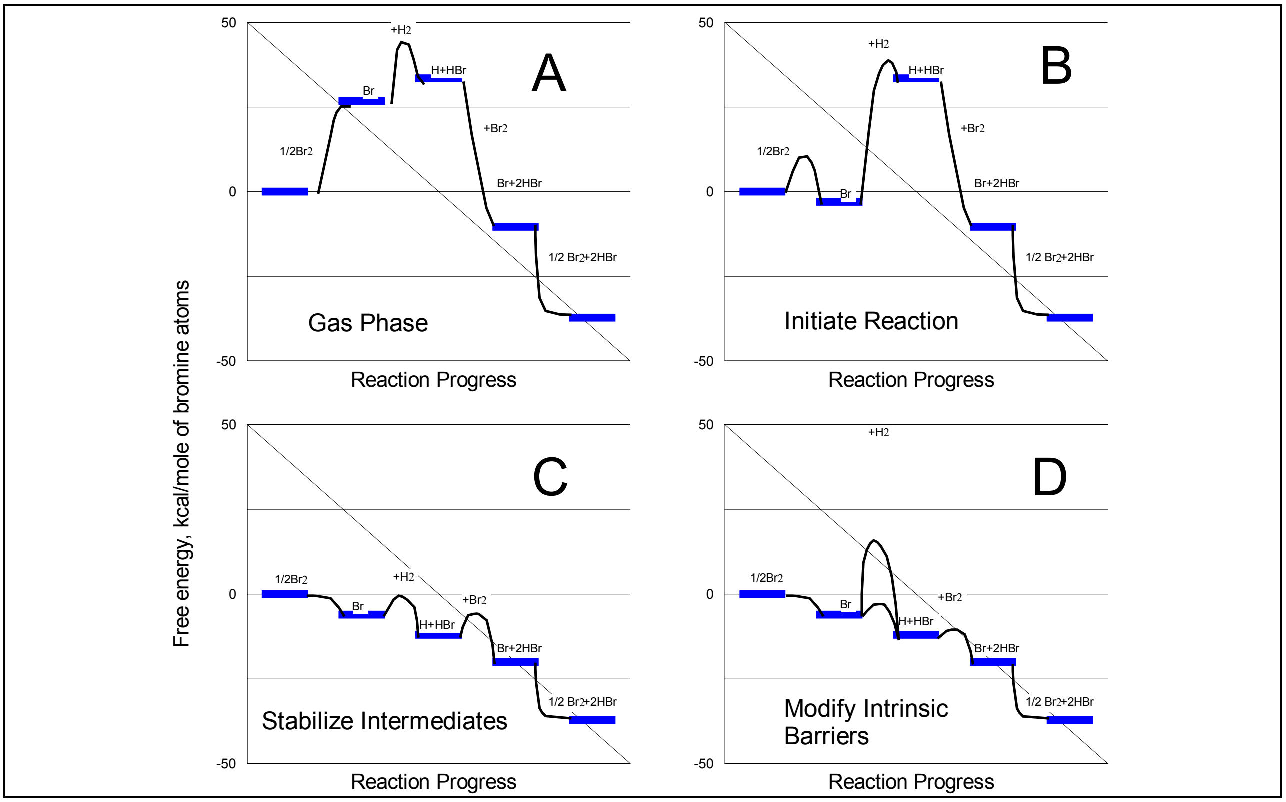


Figure 12.5 An illustration of some of the ways a catalyst can affect the free energy changes during a reaction.

Key principles of catalytic mechanisms

- Catalysts bind intermediates at distinct sites

- Mechanism same as in gas phase & solution
- Initiation much faster - in effect do not need initiation reaction

Catalysts initiate reactions

Example

$$C_2H_6 \Rightarrow C_2H_4 + H_2$$

(12.41)

Gas phase mechanism

$$C_2H_6 \rightarrow 2CH_3$$

(12.42)

$$CH_3 + C_2H_6 \rightarrow C_2H_5 + CH_4$$

(12.43)

$$C_2H_5 \rightarrow C_2H_4 + H$$

(12.44)

$$H + C_2H_6 \rightarrow C_2H_5 + H_2$$

(12.45)

$$2CH_3 \rightarrow C_2H_6$$

(12.46)

$$2C_2H_5 \rightarrow C_4H_{10}$$

(12.47)

$$CH_3 + C_2H_5 \rightarrow C_3H_8$$

(12.48)

Now consider adding NO_2

$$NO_2 + C_2H_6 \rightarrow C_2H_5 + HNO_2$$

(12.50)

Catalysts can initiate reactions. The mechanisms are similar to the mechanisms without a catalyst, but the initiation process is much faster with the catalyst.

Effect 10^9 (small for catalysis)

Table 12.10 Some examples of reactions initiated by catalysts

Reaction	Catalyst	Mechanism of Initiation
$CH_3\ CH_3 \Rightarrow C_2H_4 + H_2$	NO_2	$NO_2 + CH_3CH_3 \rightarrow HNO_2 + CH_3CH_2\bullet$
$CH_3COH \Rightarrow CH_4 + CO$	I_2	$X + I_2 \rightarrow 2I + X$ $I + CH_3COH \rightarrow HI + CH_3CO\bullet$
Ethylene $\Rightarrow$ polyethylene	$ROOR$	$ROOR \rightarrow 2RO\bullet$ $RO\bullet + CH_2{=}CH_2 \rightarrow RO\ CH_2CH_2\bullet$
$H_2 + Br_2 \Rightarrow 2HBr$	metalic platinum	$Br_2 + 2S \rightarrow 2Br\bullet_{ad}$
Propylene $\Rightarrow$ Polypropylene	Ti^+	T_1^+ + propylene $\rightarrow CH_3CHTiCH_2^+$
$C_2H_5OH \Rightarrow C_2H_4 + H_2O$	H^+	$C_2H_5OH + H^+ \rightarrow [C_2H_5OH_2]^+$ $[C_2H_5OH_3]^+ \rightarrow [C_2H_5]^+ + H_2O$ $[C_2H_5]^+ \rightarrow C_2H_4 + H^+$
$2O_3 \rightarrow O_2$	Cl	$O_3 + Cl \rightarrow O_2 + ClO$

$$H_2 + Br_2 \Rightarrow 2HBr$$

(12.51)

$$\begin{aligned}
X + Br_2 &\xrightarrow{1} 2Br + X \\
Br + H_2 &\xrightarrow{2} HBr + H \\
H + Br_2 &\xrightarrow{3} HBr + Br \\
X + 2Br &\xrightarrow{4} Br_2 + X \\
H + HBr &\xrightarrow{5} H_2 + Br \\
X + Br + H &\xrightarrow{6} HBr + X
\end{aligned}$$

(12.52)

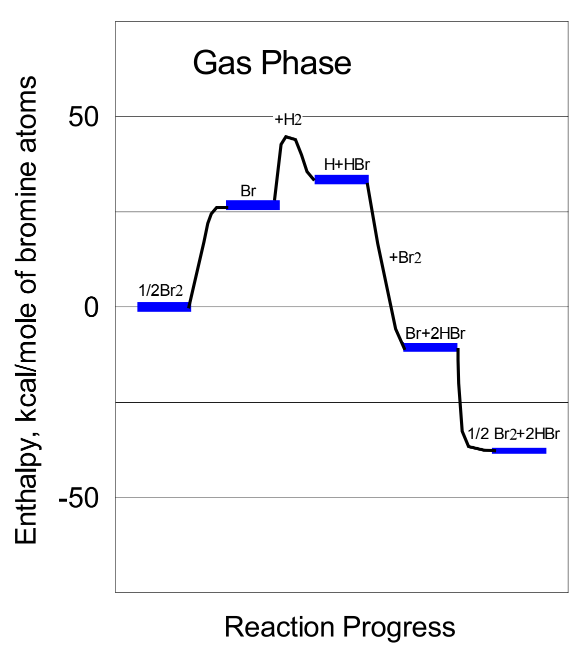


Figure 12.7 The enthalpy changes during the gas phase reaction $H_2 + Br_2 \Rightarrow 2$ HBr assuming that the reaction terminates after one cycle

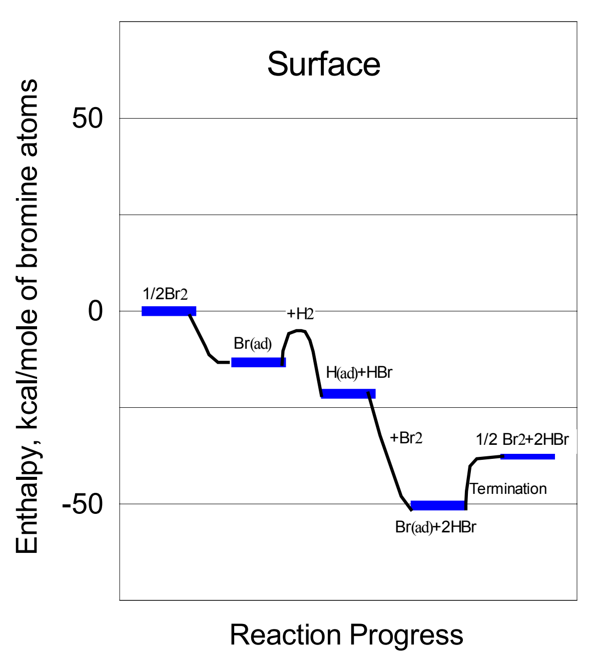


Figure 12.8 The enthalpy changes during the Rideal-Eley surface reaction $H_2 + Br_2 \Rightarrow 2$ HBr on Pt(111) assuming that the reaction terminates after one cycle

Stabilization of ionic intermediates

$$R\mathrm{HC} = \mathrm{C}R\mathrm{H} \Rightarrow RR\mathrm{C} = \mathrm{CHH}$$

(12.63)

Possible gas phase mechanism

$$\mathrm{X} + R\mathrm{HC} = \mathrm{C}R\mathrm{H} \rightarrow R\mathrm{HC} = \mathrm{CH} + R\bullet + \mathrm{X}$$

(12.64)

$$R\bullet + R\mathrm{HC} = \mathrm{C}R\mathrm{H} + \mathrm{X} \rightarrow R_2\mathrm{HCC}R\mathrm{H}\bullet + \mathrm{X}$$

(12.65)

$$R_2\mathrm{HCCH}\bullet + \mathrm{X} \rightarrow R_2\mathrm{C} = \mathrm{CH} + \mathrm{H}\bullet + \mathrm{X}$$

(12.66)

Acid catalyzed reaction

$$R\mathrm{HC} = \mathrm{C}R\mathrm{H} + \mathrm{H}^+ \rightarrow [R\mathrm{HC} = \mathrm{C}R\mathrm{HH}]^+$$

(12.67)

$$[R\mathrm{HC} = \mathrm{C}R\mathrm{HH}]^+ \rightarrow [RR\mathrm{HC} = \mathrm{CHH}]^+$$

(12.68)

$$[RR\mathrm{HC} = \mathrm{CHH}]^+ \rightarrow RR\mathrm{C} = \mathrm{CHH} + \mathrm{H}^+$$

(12.69)

Stabilization of intermediates Can we have too much of a good thing?

If we stabilize intermediates we make them less reactive. Increasing the intermediate concentration good. Decreasing reactivity bad. Which wins?

Experimental evidence

$$\mathrm{HCOOH} \Rightarrow \mathrm{H_2} + \mathrm{CO_2}$$

(12.74)

$$\mathrm{HCOOH} \rightarrow \mathrm{HCOO^{-}_{(ad)}} + \mathrm{H_{ad}}$$

$$\mathrm{H_{(ad)}} + \mathrm{HCOO^{-}_{ad}} \rightarrow \mathrm{CO_2} + \mathrm{H_2}$$

(12.75)

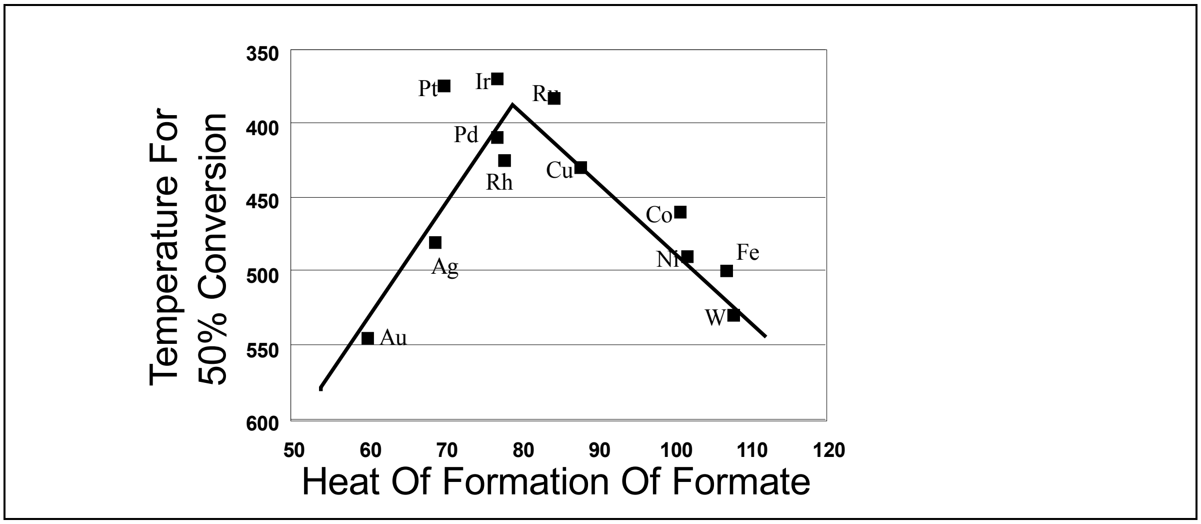


Figure 12.9 The rate of formic acid decomposition changes as a function of the binding energy of the formate intermediate.

Sabatier's principle

The best catalysts are substances which bind the reactants strongly, but not too strongly.

Consider $H_2 + Br_2 \Rightarrow HBr$

Rideal Eley mechanism

$$\begin{aligned} Br_2 + 2S &\rightarrow 2Br_{ad} \\ Br_{ad} + H_2 &\rightarrow HBr \quad + H_{ad} \\ H_{ad} + Br_2 &\rightarrow HBr + Br \end{aligned}$$

(12.76)

Complicated derivation (see classnotes)

$$r_{HBr} = 2\,k_{Br} \exp\left((1-\gamma_{p,2})\Delta H_{ad} / k_B T\right) [H_2][S][Br_2]^{\frac{1}{2}}$$

(12.85)

$$k_{Br} = 2k_2^0 \exp\left(-\left(E_{a,2}^0 - \gamma_{p,2}\Delta H_O + T\Delta S_{ad}\right) / k_B T\right)$$

(12.86)

For unlimited sites

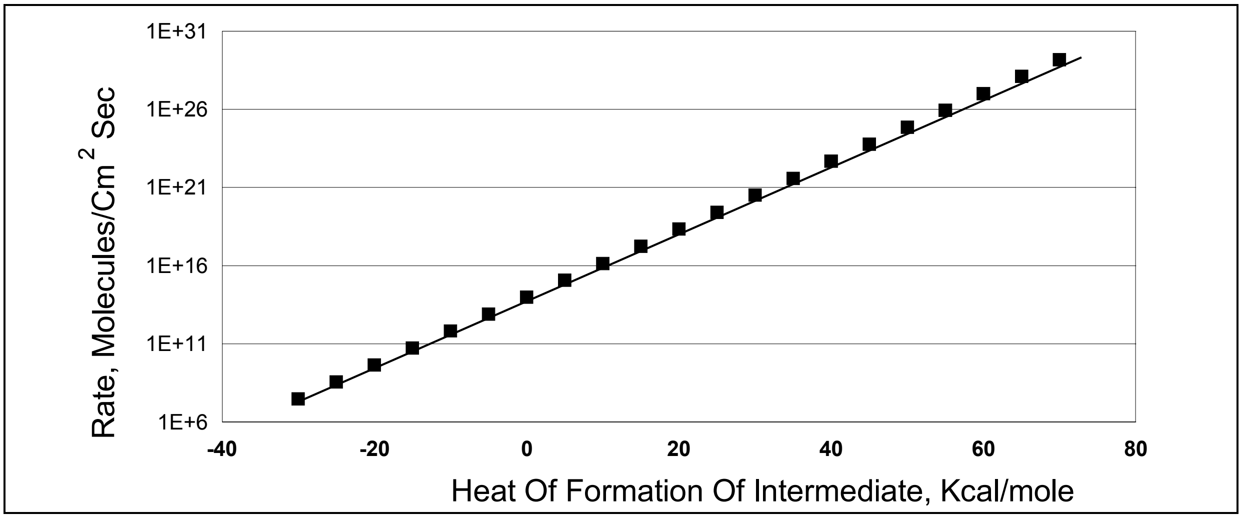


Figure 12.10 The rate of HBr formation as calculated from Equation (12.85), with [S] = 1e14/cm^2 and γ_p= 0.5, T = 500K, $P_{H_2} = P_{Br_2} = 1\text{atm}$.

For finite number of sites

$$[S] = \frac{S_o}{1 + K_{Br_2}\sqrt{P_{Br_2}} + K_{H_2}\sqrt{P_{H_2}}}$$

(12.87)

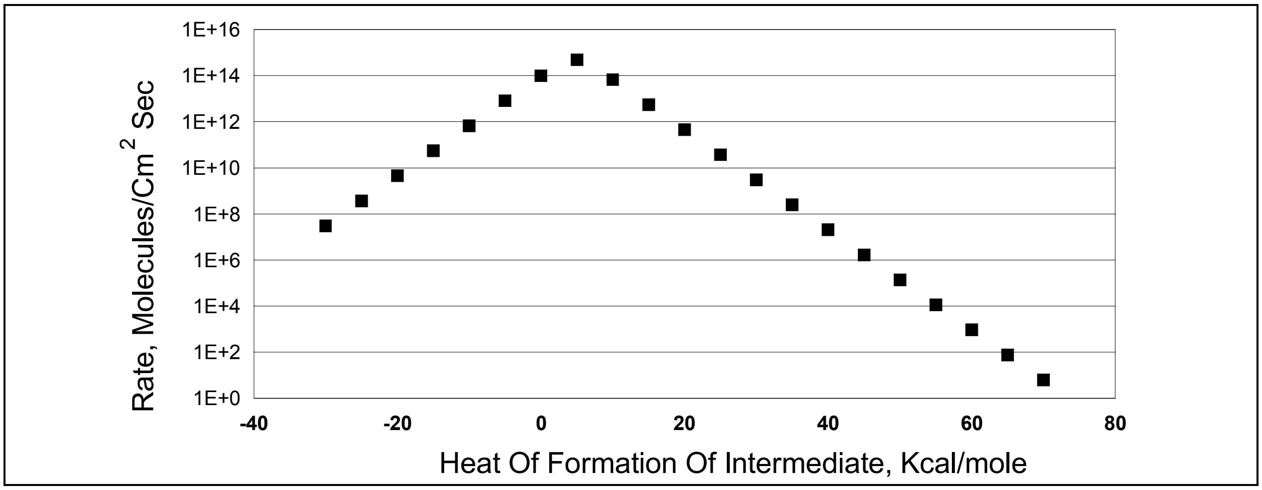


Figure 12.11 The rate of HBr formation calculated from Equation (12.85), with [S] from Equation (12.87) and γ_p= 0.5, T = 500K, $P_{H_2} = P_{Br_2} = 1\,\text{atm}$.

Sachtler-Frahenfort plots

Use heat of oxidation per mole of oxygen as surrogate for heat of formation of product.

Tanaka-Tamaru plots

Use heat of oxidation per mole of metal as surrogate for heat of formation of product.

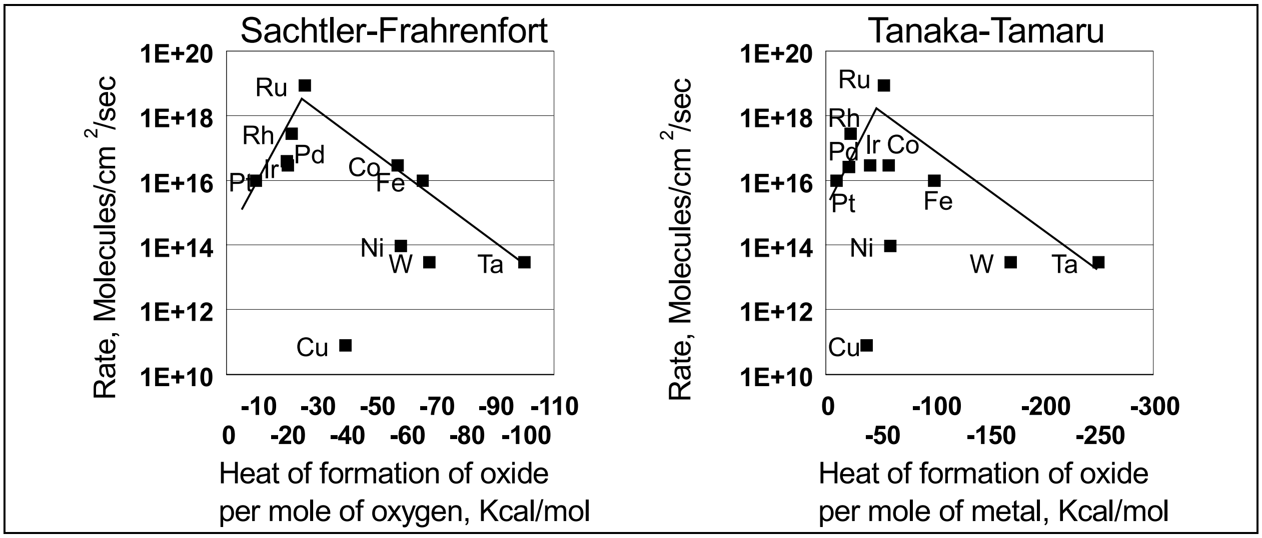


Figure 12.13 A Sachtler-Frahrenfort and Tanaka-Tamaru plot for the hydrogenation of ethylene.

Summary so far

- Catalysts work by initiating reactions, stabilizing intermediates
- Leads to 10^{20} increase in rates
  - need other effects to get to 10^{40}
- Can stabilize too much

- Catalysts can be designed to hold the reactants in the correct configuration to react.

$$3C_2H_2 \Rightarrow C_6H_6$$

(12.91)

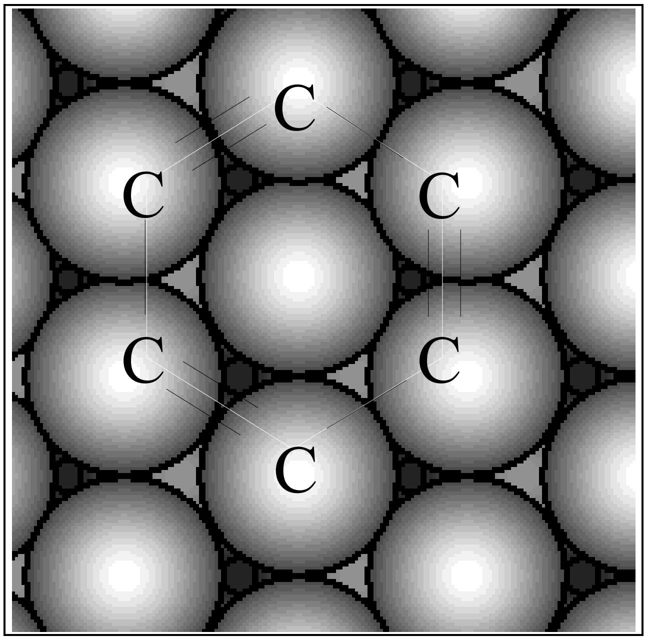


Figure 12.15 The active site for reaction (12.91) on a palladium catalyst.

$$NAD^{+} + CH_3CH_2OH \Rightarrow NADH + [CH_3CHOH]^{+}$$

(12.92)

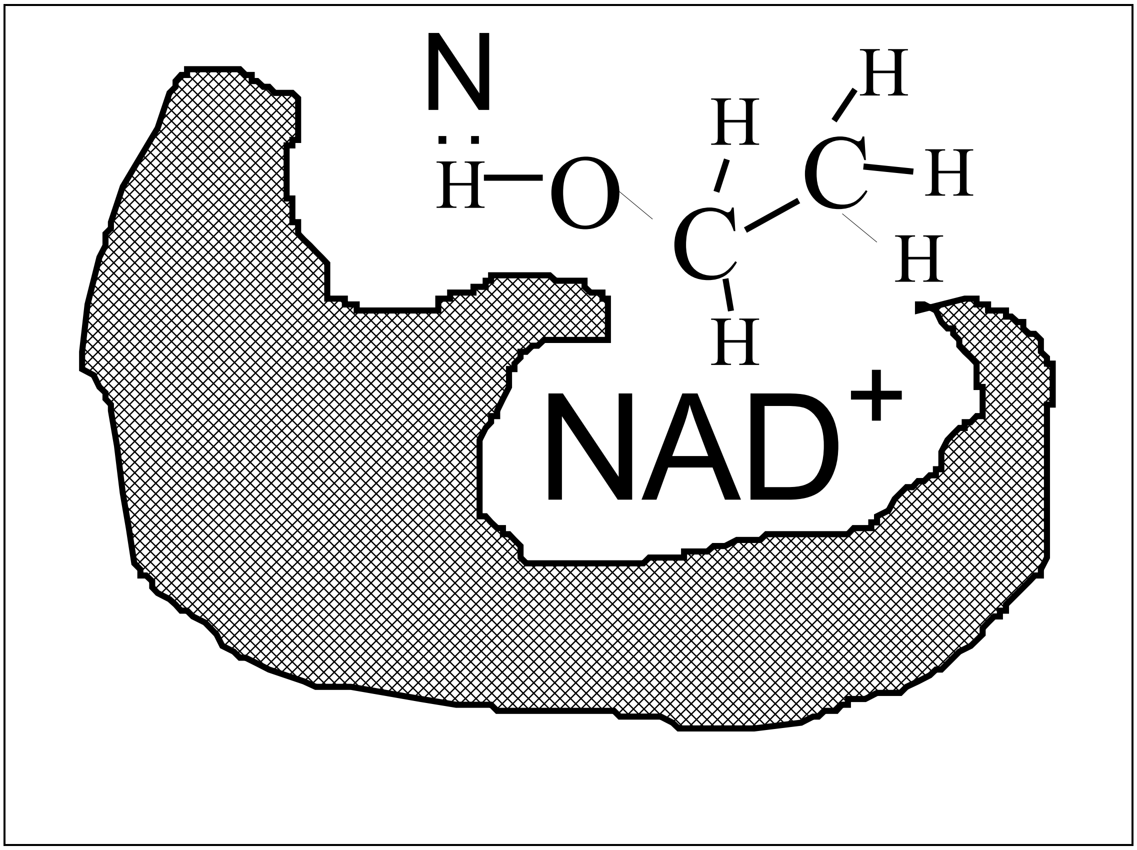


Figure 12.16 A cartoon of the reaction of ethanol and NAD^{+} on the active site of liver alcohol dehydrogenase. Adapted from Oppenheimer and Handlon (1992) (In the Enzyme, vol 20 (1992) 453.

Catalysts make bonds easier to break

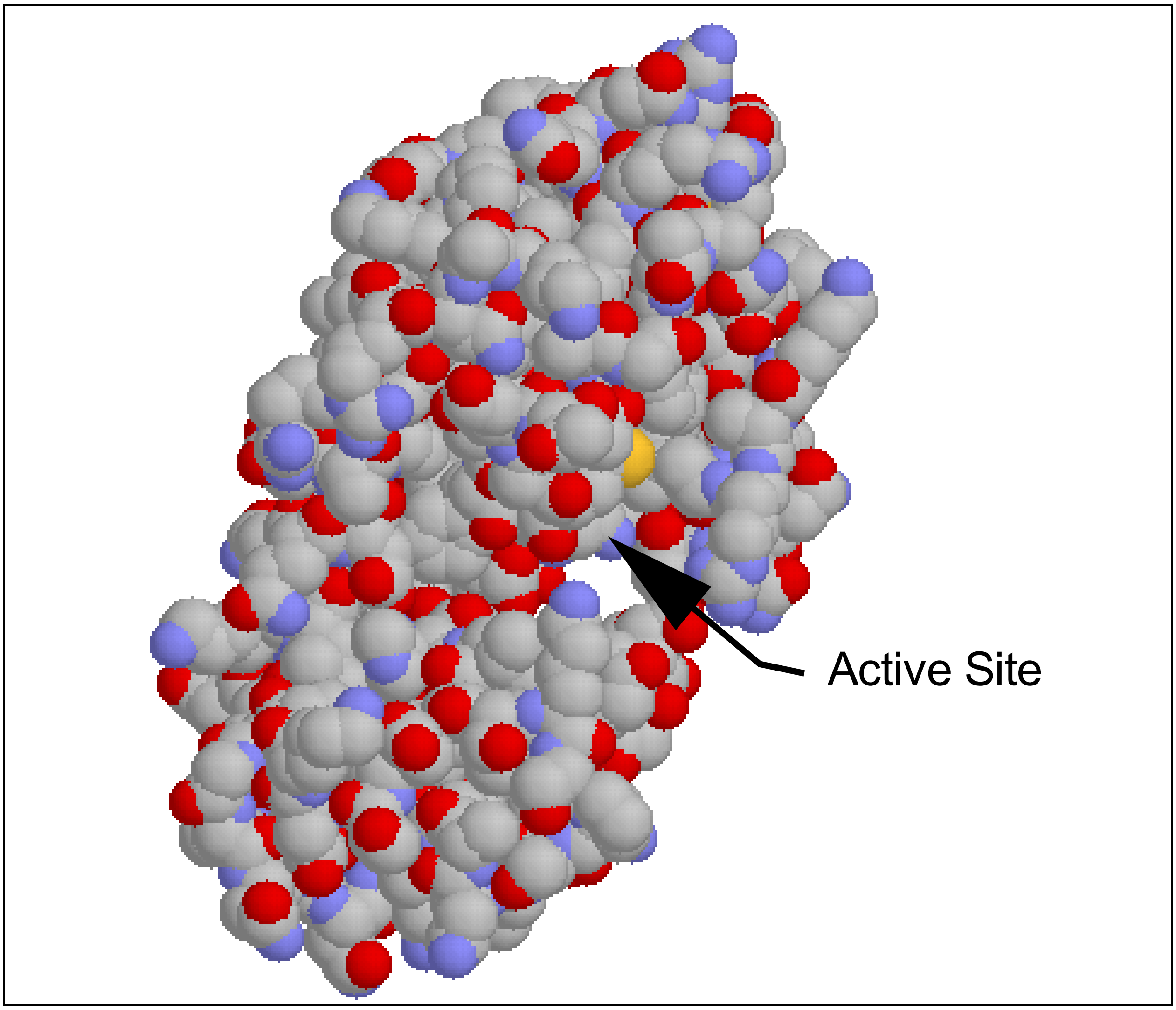
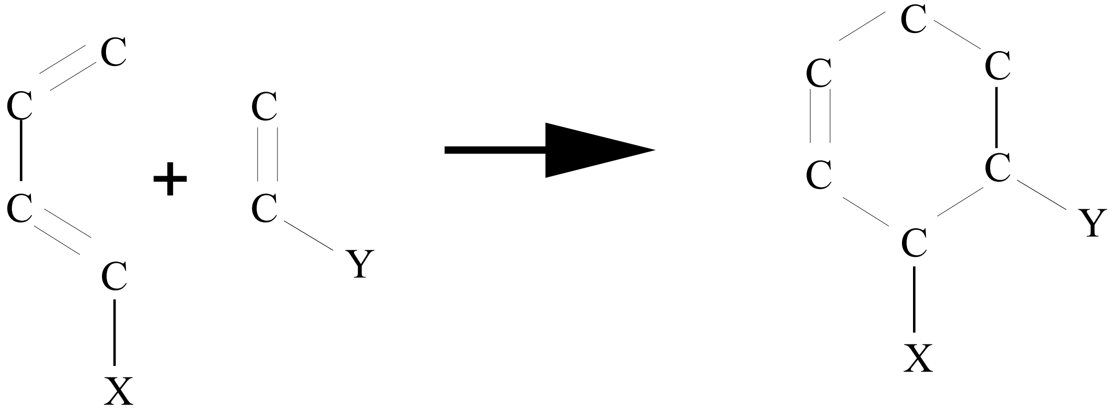


Figure 12.17 A Picture of Lysozyme 161L. This figure was generated using a program called RASMOL, using data in the protein data base from an x-ray diffraction spectrum generated by Weaver and Matthews[1987]

Catalytic antibodies



(12.94)

Transition metals - weaken bond by attaching to antibonding orbitals

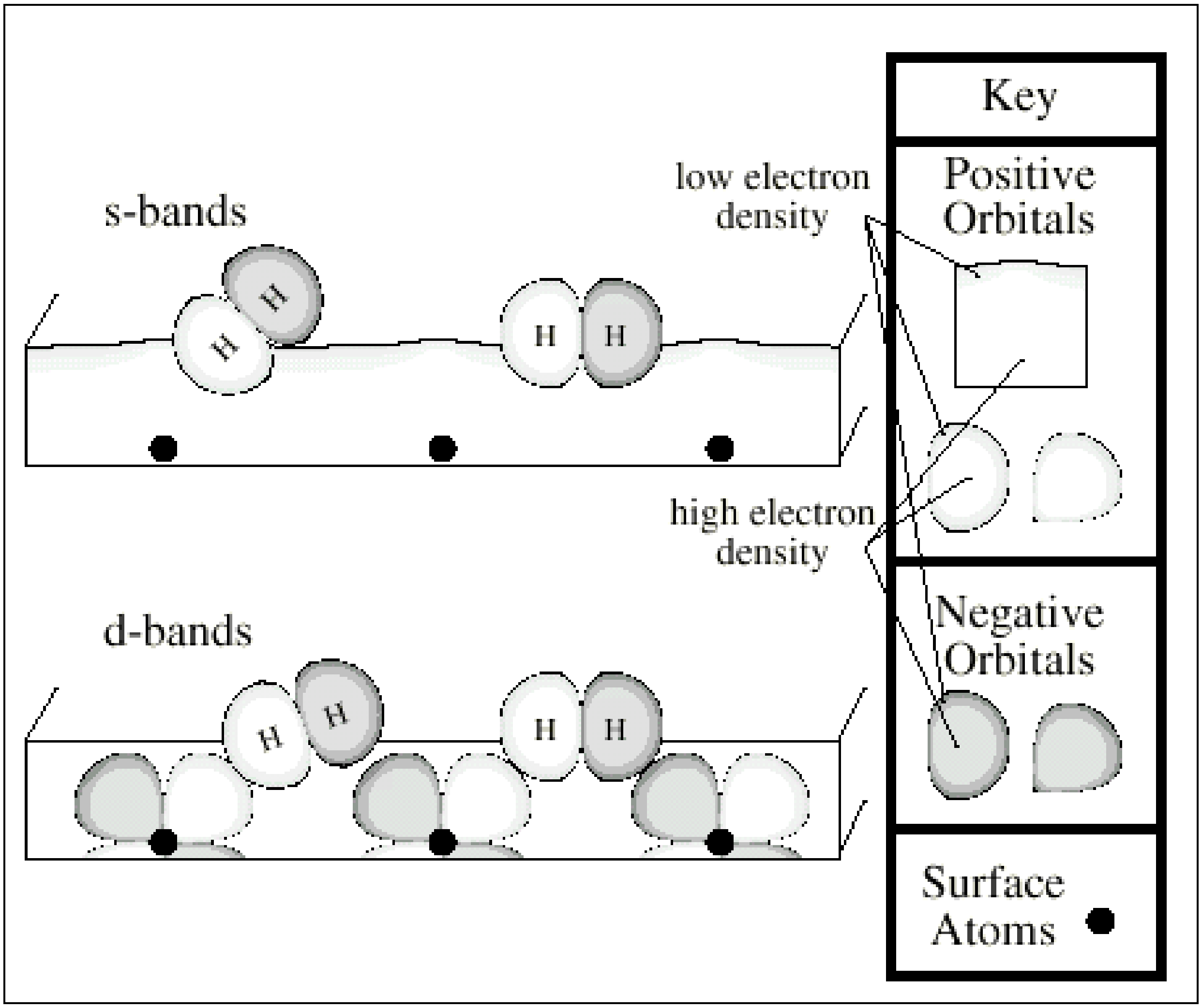


Figure 12.20 A diagram of the key interactions during the dissociation of hydrogen on platinum.

Acid catalysts: charges simplify reactions

Consider

$$R\mathrm{HC}=\mathrm{C}R\mathrm{H}\Rightarrow RR\mathrm{C}=\mathrm{CHH}$$

(12.96

Possible mechanism: ion

$$R\mathrm{HC}=\mathrm{C}R\mathrm{H}+\mathrm{H}^{+}\rightarrow\left[R\mathrm{HC}=\mathrm{C}R\mathrm{HH}\right]^{+}$$

(12.97)

$$\left[R\mathrm{HC}=\mathrm{C}R\mathrm{HH}\right]^{+}\rightarrow\left[RR\mathrm{HC}=\mathrm{CHH}\right]^{+}$$

(12.98)

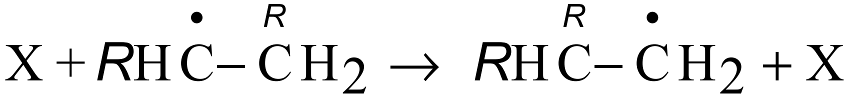
$$\left[RR\mathrm{HC}=\mathrm{CHH}\right]^{+}\rightarrow RR\mathrm{C}=\mathrm{CHH}+\mathrm{H}^{+}$$

(12.99)

Possible mechanism radical

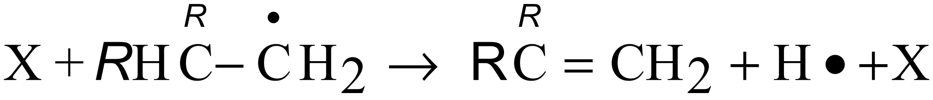
$$\mathrm{X}+R\mathrm{HC}=\mathrm{CRH}+\mathrm{H}\bullet\rightarrow R\mathrm{H}\overset{\bullet}{\mathrm{C}}-\overset{R}{\mathrm{C}}\mathrm{H}_2+\mathrm{X}$$

(12.100)



$$X + RH\overset{\bullet}{C} - \overset{R}{C}H_2 \rightarrow RH\overset{R}{C} - \overset{\bullet}{C}H_2 + X$$

(12.101)



$$X + RH\overset{R}{C} - \overset{\bullet}{C}H_2 \rightarrow R\overset{R}{C} = CH_2 + H\bullet + X$$

(12.102)

In both cases isomerization is rate determining step

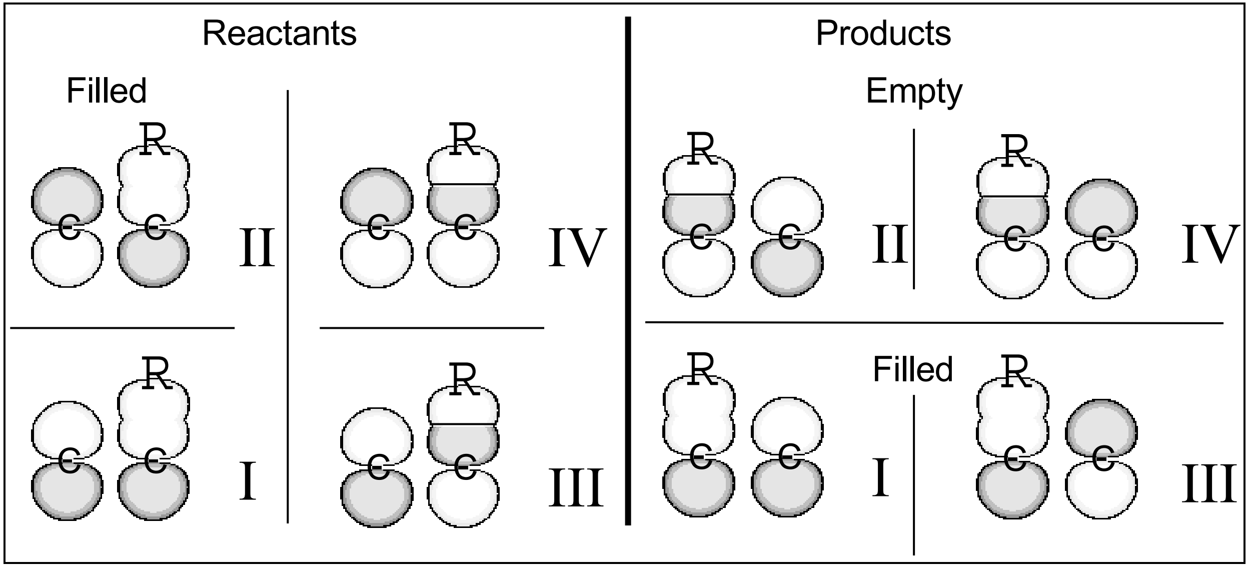
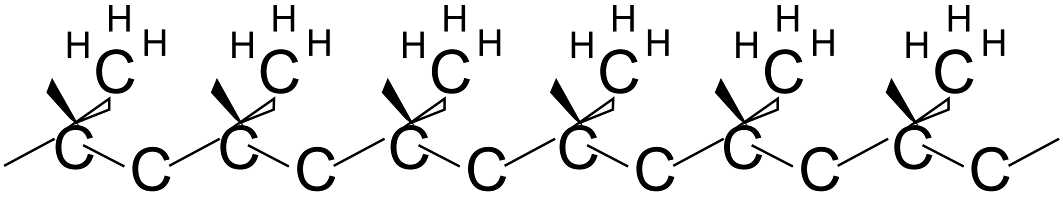
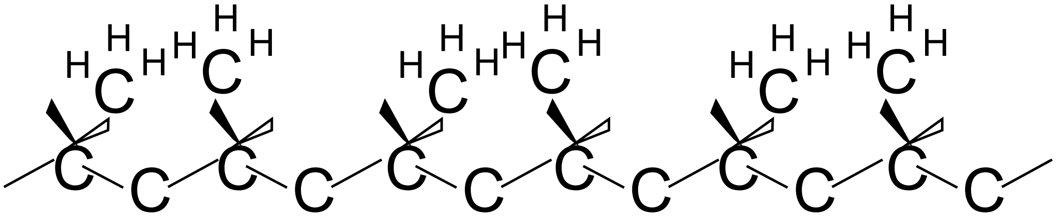


Figure 12.22 A rough diagram of the key MO's during reactions (12.101).

Catalysts can block side reactions:



(12.104)



(12.105)

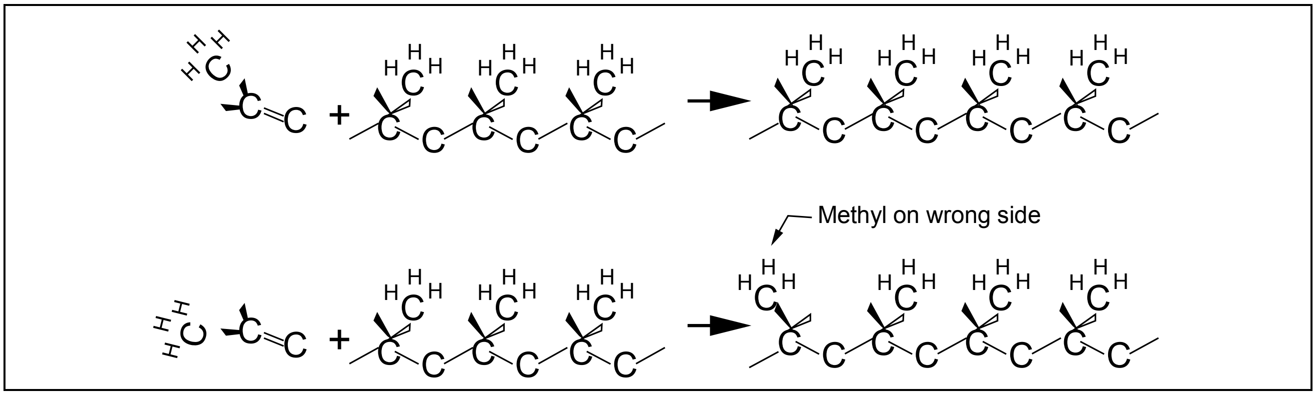


Figure 12.23 A rough diagram of one step during the production of isotatic polypropylene.

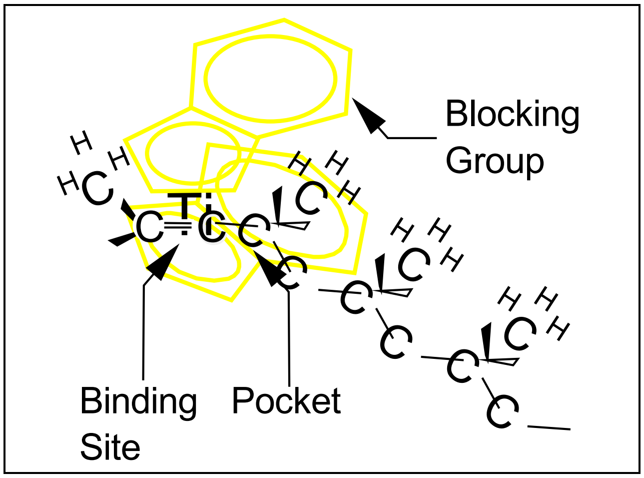


Figure 12.24 A diagram of propylene polymerization in a Ziegler-Natta catalyst.

Catalysts can be designed to donate and accept electrons

$$Cu_2O + 1/2O_2 \rightarrow 2CuO$$

(12.106)

$$2CuO + CO \rightarrow Cu_2O + CO_2$$

(12.107)

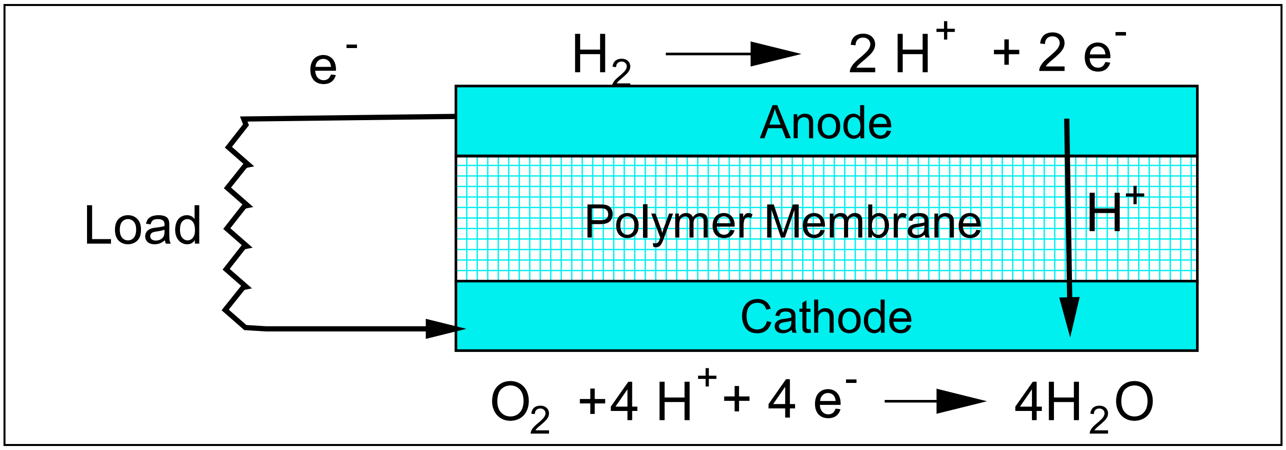


Figure 12.25 A diagram of a polymer fuel cell

Summary:

- Catalysts can be designed to help initiate reactions.
- Catalysts can be designed to stabilize the intermediates of a reaction.
- Catalysts can be designed to hold the reactants in close proximity.
- Catalysts can be designed to hold the reactants in the right configuration to react.
- Catalysts can be designed to block side reactions.
- Catalysts can be designed to sequentially stretch bonds and otherwise make bonds easier to break.
- Catalysts can be designed to donate and accept electrons.
- Catalysts can be designed to act as efficient means for energy transfer.

It is also important to realize that:

- One needs a catalytic cycle to get reactions to happen.
- Mass transfer limitations are more important when a catalyst is present.