Catalysis

Chapter 17, Shriver and Atkins

Outline

- Importance
- General principles of catalysis
- Homogeneous catalysis
  - basic steps
  - example processes
- Heterogeneous catalysis
  - principles
  - examples

Importance of catalysis

- Many major industrial chemicals are prepared with the aid of catalysts
- Many fine chemicals are also made with the aid of catalysts
  - Reduce cost of production
  - Lead to better selectivity and less waste

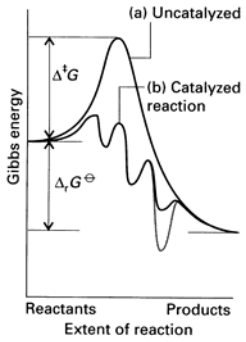
Table 17.1 The top 20 synthetic chemicals in the USA

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; heterogeneous
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 29 (1998) for production in 1997.

The basis for catalysis

- A catalyst lower the activation barrier for a transformation, by introducing a new reaction pathway
  - It does not change the thermodynamics!!



17.1 Schematic representation of the energetics in a catalytic cycle. The uncatalyzed reaction (a) has a higher Gibbs energy of activation $\Delta^{\ddagger}G$ than any step in the catalyzed reaction (b). The Gibbs energy of reaction, $\Delta_r G^{\ominus}$, for the overall reaction is unchanged from (a) to (b).

Heterogeneous versus homogeneous

- A heterogeneous catalyst is material that is in a different phase from the reactant and product
  - For example, Pt/Al_2O_3 for hydrogenation
    - » Often used industrially for large scale chemical manufacture. Can be cheap but catalytically active species hard to pin down
- A homogeneous catalyst is a substance that is in the same phase as the reactant and product
  - For example, Wilkinson's catalyst [$RhCl(PPh_3)$]for hydrogenation

Industrial use of homogeneous catalysis

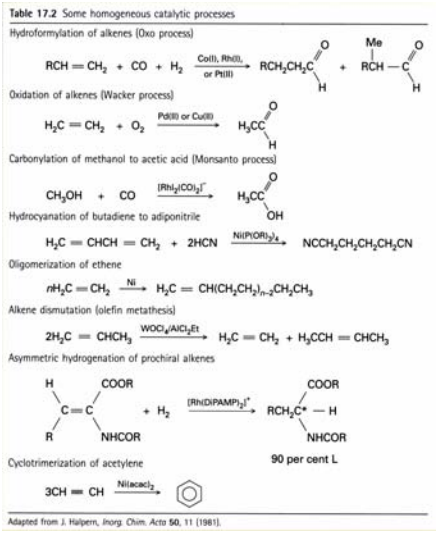


Table 17.2 Some homogeneous catalytic processes

Hydroformylation of alkenes (Oxo process)

$$RCH{=}CH_2 + CO + H_2 \xrightarrow[\text{or Pt(II)}]{\text{Co(I), Rh(I),}} RCH_2CH_2C(=O)H + RCH(Me)C(=O)H$$

Oxidation of alkenes (Wacker process)

$$H_2C{=}CH_2 + O_2 \xrightarrow{\text{Pd(II) or Cu(II)}} H_3CC(=O)H$$

Carbonylation of methanol to acetic acid (Monsanto process)

$$CH_3OH + CO \xrightarrow{[Rh_2(CO)_2I_4]^-} H_3CC(=O)OH$$

Hydrocyanation of butadiene to adiponitrile

$$H_2C{=}CHCH{=}CH_2 + 2HCN \xrightarrow{Ni[P(OR)_3]_4} NCCH_2CH_2CH_2CH_2CN$$

Oligomerization of ethene

$$nH_2C{=}CH_2 \xrightarrow{Ni} H_2C{=}CH(CH_2CH_2)_{n-2}CH_2CH_3$$

Alkene dismutation (olefin metathesis)

$$2H_2C{=}CHCH_3 \xrightarrow{WOCl_4/AlCl_2Et} H_2C{=}CH_2 + H_3CCH{=}CHCH_3$$

Asymmetric hydrogenation of prochiral alkenes

$$\begin{matrix} H & COOR \\ & C{=}C \\ R & NHCOR \end{matrix} + H_2 \xrightarrow{[Rh(DIPAMP)_2]^+} \begin{matrix} COOR \\ RCH_2C^*{-}H \\ NHCOR \end{matrix}$$

90 per cent L

Cyclotrimerization of acetylene

$$3CH{\equiv}CH \xrightarrow{Ni(acac)_2} C_6H_6$$

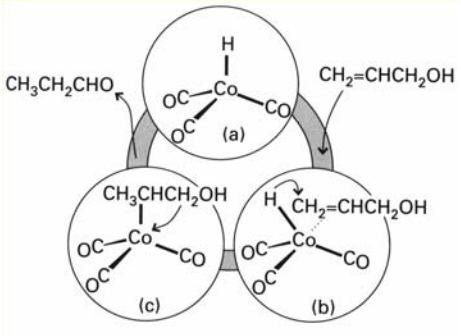
Adapted from J. Halpern, *Inorg. Chim. Acta* **50**, 11 (1981).

Catalytic cycles

- A catalyst is not consumed in a reaction
  - but may be changed from one species to another and back again
- The ‘catalyst’ may be a number of species
  - a lot of different species derived from the added catalyst may appear on the reaction pathway

The catalytic cycle

- The action of a catalyst can be represented with the aid of a cycle where all the steps leading from reactants to products are laid out
- See for example the conversion of allyl alcohol to an aldehyde using the catalyst $HCo(CO)_4$
  - Note that the actual catalytic species is thought to be the 16 e compound $HCo(CO)_3$ rather than the added 18 e compound $HCo(CO)_4$



Cycle 17.1

Determining catalytic cycles

- The establishment of a reaction mechanism is always a difficult task. It is even harder to definitively establish a catalytic cycle as all the reactions are going on in parallel!
  - Many different types of information are used to establish the most likely catalytic cycle, but reaction pathways are often not known with certainty

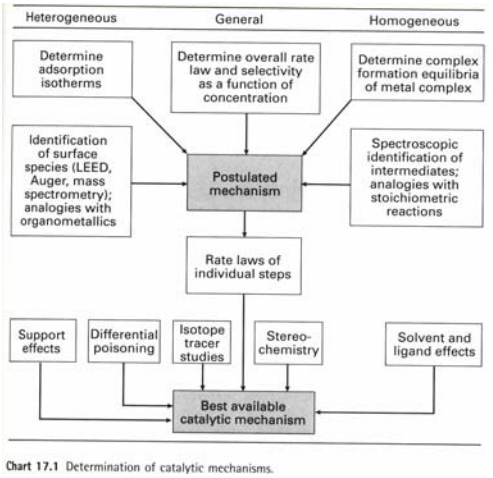


Chart 17.1 Determination of catalytic mechanisms.

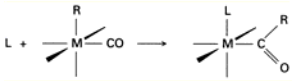
Important catalyst properties

- Activity
  - A reasonable rate of reaction is needed
- Selectivity
  - Byproducts should be minimized
- Lifetime
  - It is costly to replace the catalyst frequently
- Cost
  - The acceptable cost depends upon the catalyst lifetime and product value

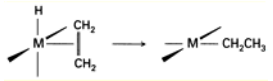
Catalytic steps in homogeneous reactions

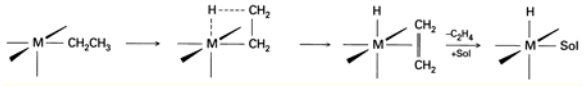
- Most catalytic process can be built up from a small number of different types of step
  - Association / dissociation of a ligand
    - » requires labile complexes
  - Insertion and elimination reactions
  - Nucleophilic attack on a coordinated ligand
  - Oxidation and reduction of a metal center
  - Oxidative addition / reductive elimination

Insertion and elimination



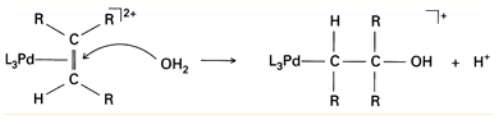
Migratory insertion



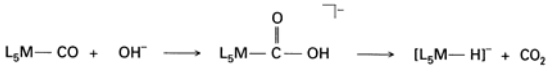


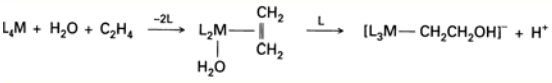
β elimination

Attack on coordinated ligands



Ligand attacked by external nucleophile





Ligand attacked by internal species

Oxidation and reduction

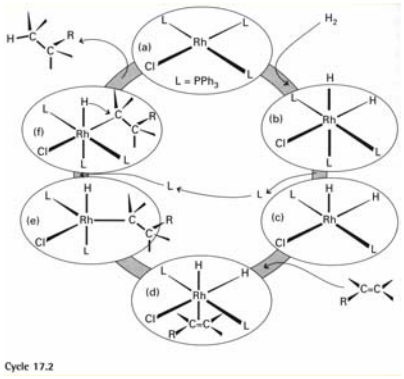
- Redox process at metal centers can be important for initiating radical reactions
  - oxidation of para xylene to terephthalic acid

Oxidative addition / reductive elimination

- $IrCl(CO)(PPh_3)_2 + RI \rightarrow Ir(R)Cl(CO)I(PPh_3)_2$
  - oxidative addition involving an increase in coordination number and an increase in oxidation state
- $Rh(RCO)Me(PPh_3)_2(CO)Cl \rightarrow RCOMe + Rh(PPh_3)_2(CO)Cl$
  - reductive elimination involves a decrease in coordination number and oxidation state of the metal atom

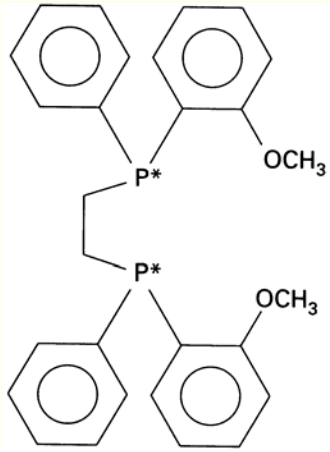
Alkene hydrogenation using Wilkinson's catalyst

- Wilkinson's catalyst is widely for hydrogenation



Chiral hydrogenation catalysts

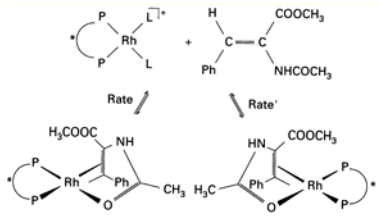
- Catalysts similar to Wilkinson's but using chiral phosphine ligands have been used for the asymmetric hydrogenation of small molecules
  - Important in the fine chemicals/pharmaceutical industry
- Noles and Nyori received the 2001 chemistry Nobel prize (along with Sharpless) for the development of asymmetric hydrogenation catalysis
  - http://www.nobel.se/chemistry/laureates/2001/index.html



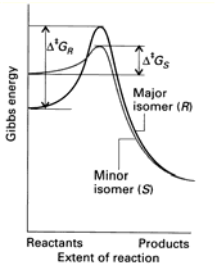
2 DiPAMP

Chiral hydrogenation

- The chiral catalyst works because the two different ways of binding a prochiral alkene lead to diastereomeric precursors and transition states and hence different activation energies for the pathways to the two different enantiomeric products



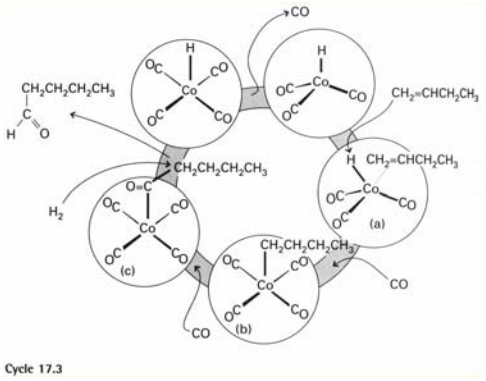
17.2 The diastereomeric complexes that may form from a complex with chiral phosphine ligands (*) and a prochiral alkene.



17.3 Kinetically controlled stereoselectivity. Note that $\Delta^{\ddagger}G_S < \Delta^{\ddagger}G_R$, so the minor isomer reacts faster than the major isomer.

Hydroformylation

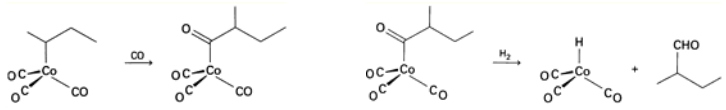
- Hydroformylation is used industrially in the manufacture of plasticizers, surfactants etc.
  - $R\text{-}CH = CH_2 + CO + H_2$ → $R\text{-}CH_2\text{-}CH_2\text{-}CO\text{-}H$
    - » Note there are isomeric product possibilities as the CO could go to either carbon of the double bond



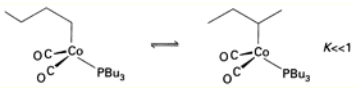
Added catalyst is $HCo(CO)_4$

Using bulky ligands to control byproduct formation

- The Co carbonyl catalyst produces some branched aldehydes



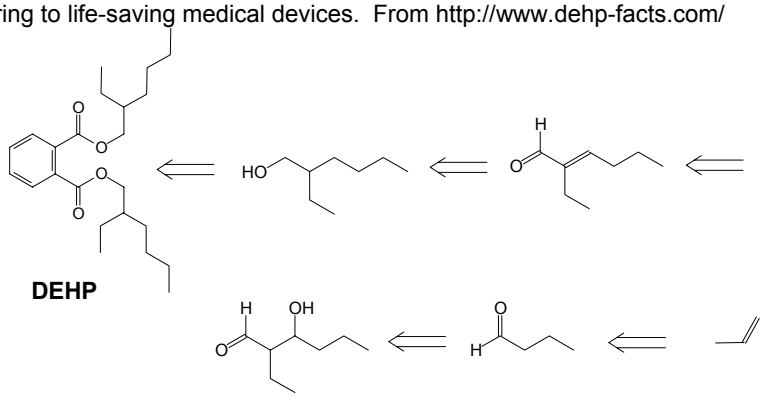
- Alkylphosphanes in the reaction mix suppresses the formation of these products
  - Phosphanes inhibit the formation of bulky intermediates



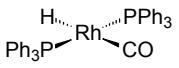
Hydroformylation

$$RCH{=}CH_2 + CO + H_2 \rightarrow RCH_2CH_2CHO$$

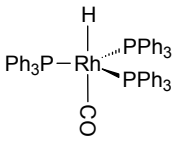
DEHP (di(2-ethylhexyl) phthalate, also known as di-octyl phthalate, DOP) is the most widely used plasticizer in the world. Approximately 2.7 million tons are used each year, mostly in the manufacture of soft PVC articles ranging from flooring to life-saving medical devices. From http://www.dehp-facts.com/



Hydroformylation



$$RCH{=}CH_2 + CO + H_2 \rightarrow RCH_2CH_2CHO \;+\; RCH(CHO)CH_3$$

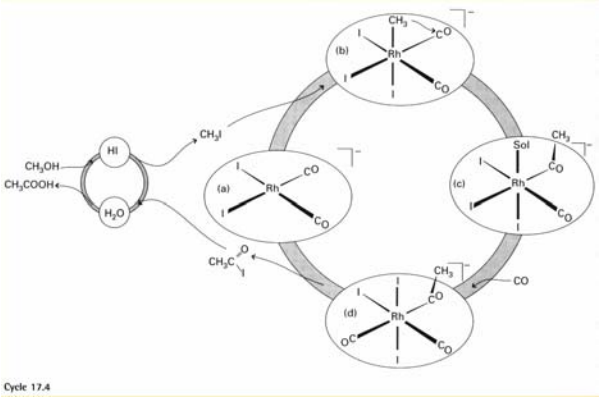


(active for hydroformylation; lower overall linear to branched product ratio)

Addition of PPh_3 has large effects
- decreases rate of conversion
- increases linear to branched product ratio

Monsanto acetic acid process

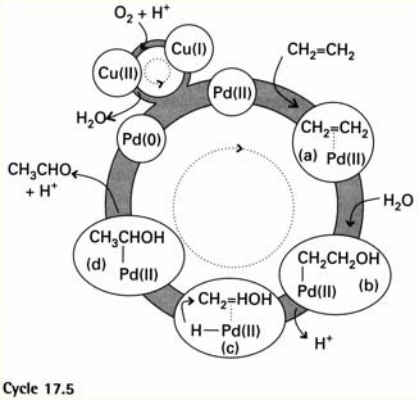
- MeOH + CO -([$RhI_2(CO)_2]^-$)→ MeCOOH



Note CH_3I goes into the catalytic cycle. It is generated by reaction of HI with MeOH

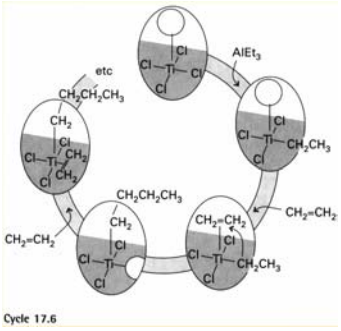
Wacker process

- $C_2H_4 + 1/2O_2$ → CH_3CHO
  - No longer used industrially but illustrates the use of metals for redox catalysis.
  - Cu(II) and Pd(II) chloride catalyst



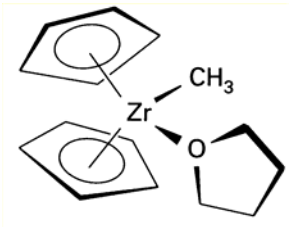
Ziegler-Natta Catalysis

- Ziegler-Natta catalysts are used for the production of polyenes (polypropene, polyethene). Not really a homogeneous catalyst as modified solid $TiCl_3$ actually acts as the catalyst, but there are homogeneous analogues.
  - Mixed $TiCl_4$ and $AlEt_3$ used to prepare the catalyst

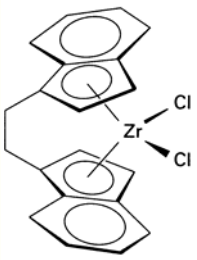


Homogeneous olefin polymerization catalysts

- Compounds such as those shown below are thought to polymerize olefins by a similar mechanism to that shown for the Ziegler-Natta catalysts
  - Compound 6 is chiral and can be used to prepare optically pure polypropylene



5 $[Zr(Cp)_2(CH_3)(thf)]^+$



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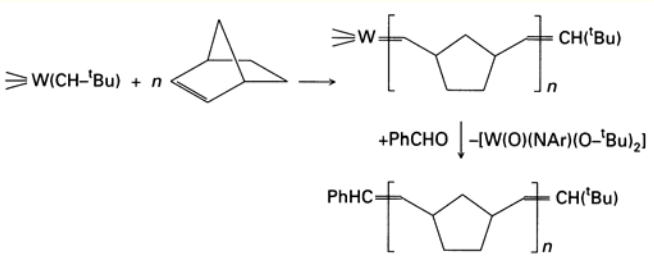
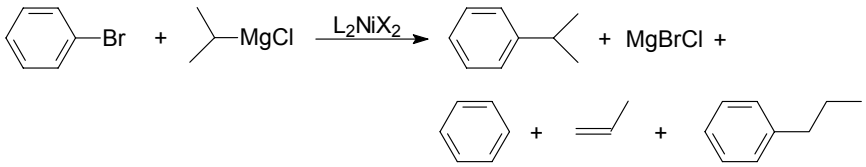
ROMP catalysts

- ROMP, Ring Opening Metathesis, can be used to polymerize strained cyclic olefins such as norbornene
  - Catalyzed by carbenes
  - Reaction is driven by strain relief
  - Reaction is a living polymerization. Adding more monomer allows the process to continue
  - Products usually have a low polydispersity (MW weight distribution is narrow)



Cross-coupling of isopropyl Grignard with bromobenzene (Kumada reaction)

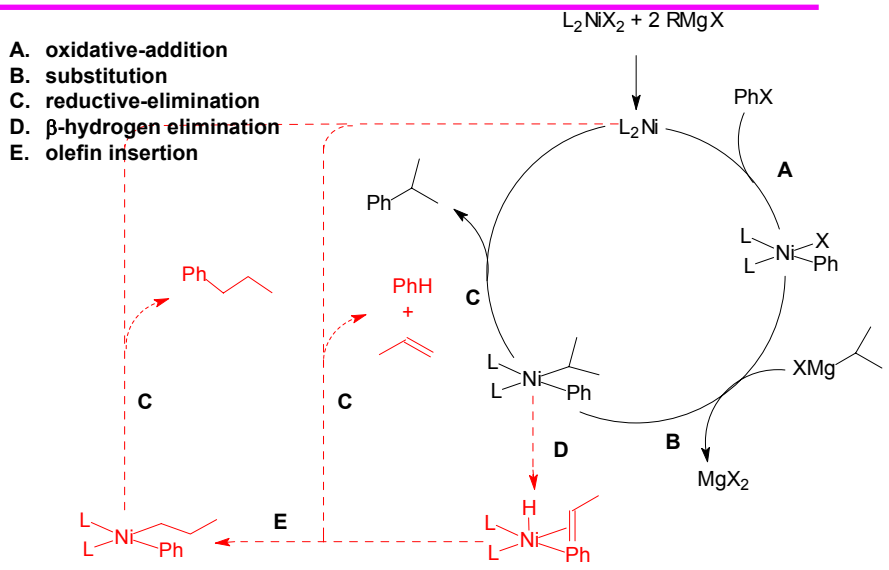


L_2NiX_2

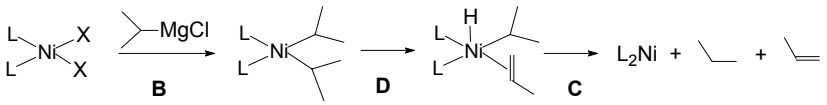
$Ni(PPh_3)_2Br_2$

$Ni(diphos)Cl_2$ diphos = $Ph_2PCH_2CH_2PPh_2$

Catalytic cycle for coupling of Grignard with aryl halide (Kumada reaction)



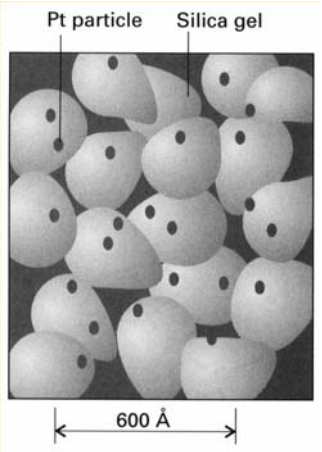
Formation of catalytically active species



A. oxidative-addition
B. substitution
C. reductive-elimination
D. β-hydrogen elimination
E. olefin insertion

Heterogeneous catalysis

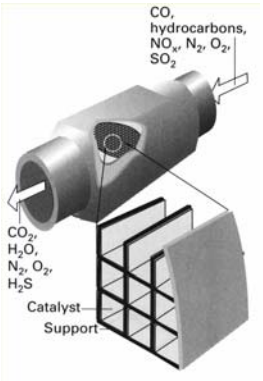
- Many heterogeneous catalysts are multiphasic
  - dispersed metals on a support
    - » automobile catalytic converters
- Some are uniform catalysts
  - the acid catalysts ZSM5 is porous and active throughout the bulk of the solid material
- In all cases, good activity requires a very high accessible surface area as the reaction take place on the surface



17.5 Schematic diagram of metal particles supported on silica gel.

Automobile catalytic converters

- Automobile catalytic converters need to catalyze several reactions
  - $CH_x + O_2 \rightarrow CO_2 + H_2O$
  - $CO + O_2 \rightarrow CO_2$
  - $NO_x + CH_x \rightarrow N_2 + H_2O + CO_2$
  - This is achieved by the use of a supported precious metal catalyst
    - » mixture of metals is used, platinum, palladium etc
  - Note catalyst does not work at low temps (when engine first starts)
  - Catalyst needs O_2 to operate, so there can be problems when the engine is running fuel rich
    - » CeO_2 and other oxygen buffers are being examined
      - Acts as a temporary regenerable source of O_2. $CeO_2 = Ce_2O_3 + 1/2O_2$



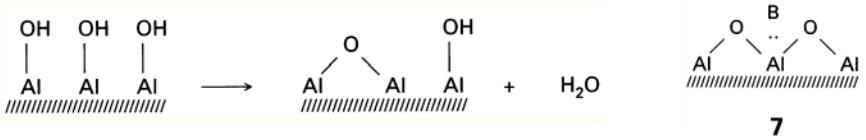
17.4 A reactor for heterogeneous catalysis. This automobile catalytic converter oxidizes CO and hydrocarbons and reduces nitrogen and sulfur oxides. The metal catalyst is supported on a ceramic honeycomb, which is more robust in this application than a bed of loose particles.

Catalyst surface area

- Heterogeneous catalysts have their active sites on the surface
  - high surface area materials produce better catalysts
    - » This implies the use of very small catalyst particles or solids that are porous on a molecular lengths scale
  - Typically, very high surface area supports (silica gel, gamma alumina etc.) are used to support very small particles of active material
  - zeolites are porous and have a lot of accessible internal surface

Acid and base sites

- A lot of industrial processes that are carried out with heterogeneous catalysts make use of acid or base sites
  - Alkylation, alkene isomerization etc.
- Dehydration of γ alumina and various zeolites produces materials with acidic and in some cases basic sites
  - low temperatures produce acid OH on γ alumina
  - high T produces Lewis acid sites as well

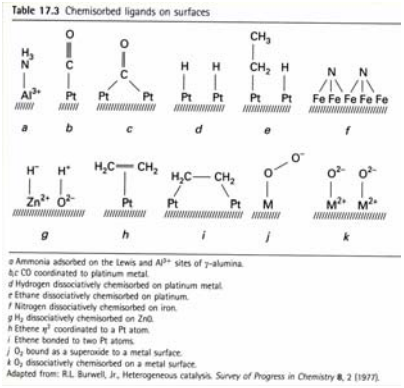


Characterizing surface acid sites

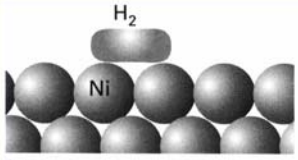
- It is difficult to directly examine the nature of surface acid sites
- Typically, probe molecules are used to evaluate the nature of surface sites
  - The IR spectrum of pyridine (a base) shows frequency shifts depending on wether it is interacting with a Bronsted site or Lewis acid site
    - » This can be used to distinguish a quantify the sites that are present on a catalyst surface

Reactions on metal surfaces

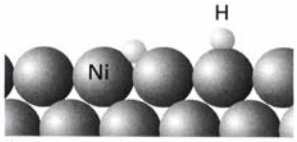
- Many molecules react or coordinate to metal surfaces
  - Formation of a chemical bond with the surface is referred to as chemisorption
  - If there are no chemical bonds to the surface the species is physisorbed
- The surface bonded species are similar to organometallics / coordination complexes
- These species are involved in catalyst action



Physisorption and chemisorption



(a)



(b)

17.7 Schematic representation of (a) physisorption and (b) chemisorption of hydrogen on a nickel metal surface.

Chemisorption ability

- Early and mid transition metals have good chemisorption abilities. Thermodynamically they are capable of forming bonds that make it worthwhile for the molecule to break up

Table 17.4 The ability of metals to chemisorb simple molecules

	Gases						
	O_2	C_2H_2	C_2H_4	CO	H_2	CO_2	N_2
Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Fe, Ru, Os	+	+	+	+	+	+	+
Ni, Co	+	+	+	+	+	+	+
Rh, Pd, Pt, Ir	+	+	+	+	+	+	+
Mn, Cu	+	+	+	+	±	+	+
Al, Au	+	+	+	+	−	−	−
Na, K	+	+	−	−	−	−	−
Ag, Zn, Cd, In, Si, Ge, Sn, Pb, As, Sb, Bi	+	−	−	−	−	−	−

+ Strong chemisorption, ± weak, − unobservable.
Adapted from G.C. Bond, *Heterogeneous catalysis*, p. 29. Oxford University Press (1987).

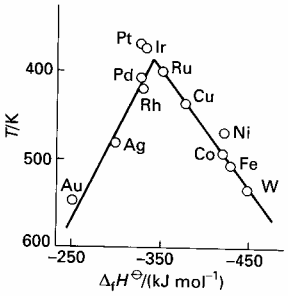
Catalytic steps

- Catalysis on surfaces goes via steps that are related to those observed for homogeneous reactions
  - good catalysts have to be efficient for each step for every step in a cycle

Consider, HCOOH → CO + H_2O

Late TMs do not do a good job of chemisorbing the starting material.

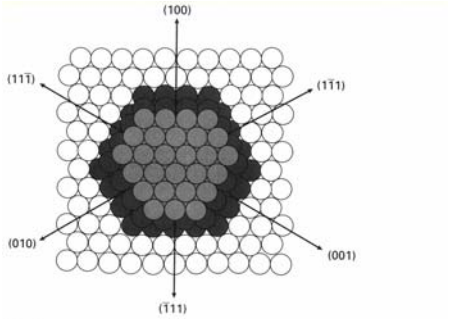
Early TMs bind fragments too well and efficient catalysis is prevented by difficulty in getting products off the catalyst surface



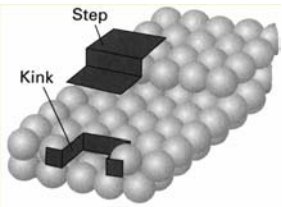
17.8 A volcano diagram. In this case the reaction temperature for a set rate of formic acid decomposition is plotted against the stability of the corresponding metal formate as judged by enthalpy of formation. (W.J.M. Rootsaert and W.M.H. Sachtler, *Z. Physik. Chem.* **26**, 16 (1960).)

Reactive sites on metal surfaces

- Metal surfaces are not atomically smooth and different faces of a crystal have different atomic arrangements
  - This means that there are often many different types of site available on the surface of a catalysts where a reaction could occur
    - » These different sites will have different catalytic capabilities



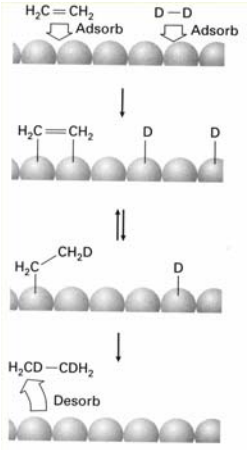
17.9 A collection of metal crystal planes that might be exposed to reactive gases. ($\bar{1}$11), (1$\bar{1}$1), etc. are close-packed hexagonal planes. The planes represented by (100), (010), etc. have square arrays of atoms.



17.10 Schematic representation of surface irregularities, steps and kinks.

Alkene hydrogenation

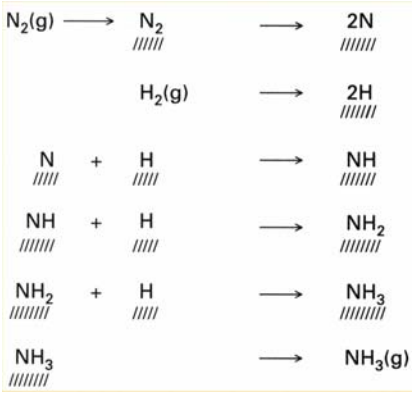
- Alkene hydrogenation with supported metals such as nickel or platinum black is commonplace



17.11 Schematic diagram of the hydrogenation of ethene by deuterium on a metal surface.

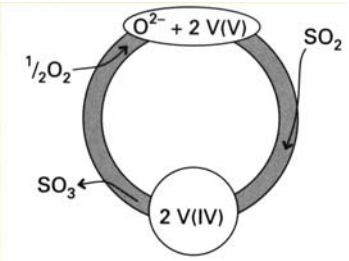
Ammonia synthesis

- $N_2 + 3H_2 \rightarrow 2NH_3$
- Performed over a promoted iron catalyst
  - Promoted means that a witch's brew of additives has been used to enhance the catalyst
    - » Mechanism of action is often not clear!
    - » Reaction performed at high T for kinetic reasons even though thermodynamically this is a bad thing (reduces the equilibrium constant). NN bond is difficult to breaks



SO_2 oxidation

- Concentrated sulfuric acid is made by the reaction of dilute sulfuric acid with SO_3
- SO_3 does not form in significant amounts when sulfur is burnt.
  - Produced by catalytic oxidation of SO_2 using a supported molten vanadate salt



Cycle 17.7

Acid sites in zeolites

- Zeolites are crystalline microporous solids. The walls of the pore system can be functionalized and used for catalysis. Particularly acid catalysis


17.12 The structure of ZSM-5 has intersecting channels defined by the crystal structure. The tubes in this diagram represent the channels with the three-dimensional structure.