

Lecture Note #7 (Spring, 2019)

Application to Catalysis

Reading: Kolasinski, ch.6

Catalysis

-Catalysis

- (1) Homogeneous catalysis
- (2) Heterogeneous catalysis
- (3) Enzymatic reaction

-Definition: substances which alter the rate of a reaction, and are recoverable, essentially unchanged, after the reaction. They do not contribute energy to the reaction, nor initiate reactions, nor change the equilibrium point of reversible reactions

-Function: they do accelerate the reaction and may direct the course of the reaction by selectivity. Small amounts of catalysts are able to transform large amounts of reacting substances by virtue of their self-regeneration

Heterogeneous reactions

-Chemical industry: transformation of carbon containing molecules → all derived from petroleum. Benzene, toluene, xylene, ethylene, propylene, 1,3-butadiene, methanol

-Table 6.1: refinery of petroleum and the production of petrochemicals are not possible without the use of catalysis

-Heterogeneous reactions occur at the g/l, l/s interface → maximum surface area in order to maximize the number of reactive sites: dispersion↑ by decreasing size

e.g., spherical particles: radius r , mass m , density ρ , composed of N spherical atoms

Heterogeneous reactions

Table 6.1 US bulk chemical production in 2005 from C&ENews July 10, 2006. Aluminum, ammonia, phosphate rock and, pig iron data for 2010 from USGS Mineral Commodity Summaries 2011. Gasoline data from Energy Information Administration for 2009. Process information taken from Ullmann's Encyclopedia of Industrial Chemistry (Wiley-VCH, Weinheim, 2006)

Material	Production/kMt	Process
1. H ₂ SO ₄	36 520 (Europe 19 024; World 165 000)	Contact process. Catalytic oxidation of SO ₂ over K ₂ SO ₄ promoted V ₂ O ₅ on a silica gel or zeolite carrier at 400–450 °C and 1–2 atm, followed by exposure to wet sulfuric acid.
2. Phosphate rock (P ₂ O ₅ , phosphoric acid)	26 100 (China 65 000; World 176 000)	Digestion of phosphate rock with H ₂ SO ₄ , HNO ₃ or HCl
3. Ethylene (C ₂ H ₄)	23 974 (Europe 21 600; World 75 000)	Thermal steam cracking of naphtha or natural gas liquids at 750–950 °C, sometimes performed over zeolite catalysts to lower process temperature.
4. Propylene	15 333 (Europe 15 406)	By-product from ethylene and gasoline production (fluid catalytic cracking or FCC). Also produced intentionally from propane over Pt or Cr supported on Al ₂ O ₃ .
5. Ethylene dichloride	11 308 (Europe 6 646)	C ₂ H ₄ + HCl + O ₂ over copper chloride catalyst, T > 200 °C, with added alkali or alkaline earth metals or AlCl ₃
6. Cl ₂	10 175 (Europe 10 381)	Chlor-alkali process, anodic process in the electrolysis of NaCl. Originally at graphite anodes but new plants now exclusively use membrane process involving a Ti cathode (coated with Ru + oxide of Ti, Sn or Zr) or porous Ni coated steel (or Ni) cathode (with Ru activator).
7. NaOH	8 384 (Europe 10 588)	Chlor-alkali process, cathodic process in the electrolysis of NaCl.
8. NH ₃	8 300 (China: 42 000, World: 131 000)	Haber-Bosch process, 30 nm Fe crystallites on Al ₂ O ₃ promoted with K and Ca. SiO ₂ added as a structural stabilizer, 400–500 °C, 200–300 bar. Recently a more active but more expensive Ru catalyst has been developed.
9. Benzene	7 574 (Europe 7 908)	From catalytic cracking of petroleum. FCC process over solid acid catalysts (silica, alumina, zeolite) sometimes with added molybdena
10. Urea	5 801	Basaroff reactions of NH ₃ + CO ₂
11. Ethylbenzene	5 251 (Europe 4 276)	Ethylene + benzene over zeolite catalyst at T < 289 °C and pressures of ~ 4 MPa
12. Styrene	5 042 (Europe 4 963)	Dehydrogenation of ethylbenzene in the vapour phase with steam over Fe ₂ O ₃ catalyst promoted with Cr ₂ O ₃ /K ₂ CO ₃ at ~ 620 °C and as low pressure as practicable
Gasoline	379 800	FCC over solid acid catalysts (alumina, silica or zeolite) is performed to crack petroleum into smaller molecules. This is followed by naphtha reforming at 1–3 MPa, 300 ≤ T ≤ 450 °C, performed on Pt catalysts, with other metals, e.g. Re, as promoters.

Table 6.1 (Continued)

Gases	Production/Mm ³	
1. N ₂	26 448 (Europe 21 893)	Liquefaction of air
2. O ₂	16 735 (Europe 26 128)	Liquefaction of air
3. H ₂	13 989 (Europe 10 433)	Steam reforming of CH ₄ (natural gas) or naphtha over Ni catalyst supported on Al ₂ O ₃ , aluminosilicates, cement, and MgO, promoted with uranium or chromium oxides at <i>T</i> as high as 1 000 °C.
Metals		
1. Fe (pig iron)	29 000 (China: 600 000; World: 1 000 000)	Carbothermic reduction of iron oxides with coke/air mixture at <i>T</i> ≈ 2000 °C.
2. Al	1 720 (China: 16 800; World: 41 400)	Hall-Heroult process. Electrolysis of bauxite (Al ₂ O ₃) on carbon electrodes at 950–980 °C.

Measurement of surface kinetics & reaction mechanism

TPRS (temperature programmed reaction spectrometry)

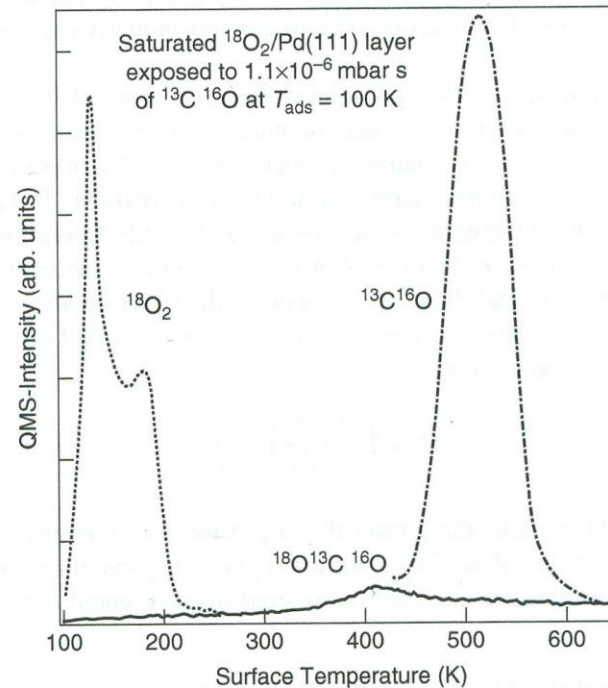


Figure 6.1 A co-adsorbed layer of $^{18}\text{O}_2 + ^{13}\text{C}^{16}\text{O}$ was prepared at $T_s = 100$ K on Pd(111). When heated, three products are observed in temperature programmed reaction spectrometry (TPRS): $^{18}\text{O}_2$, $^{13}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{16}\text{O}^{18}\text{O}$. The CO_2 arises from the Langmuir-Hinshelwood reaction of $\text{CO}(a) + \text{O}(a)$. Reproduced from K. W. Kolasinski, F. Cemič, A. de Meijere, E. Hasselbrink, Surf. Sci., 334, 19. © 1995 with permission from Elsevier Science.

Haber-Bosch process

Ammonia: nitrogen fertilizers, nitrogen-containing chemicals,
hydrogen storage

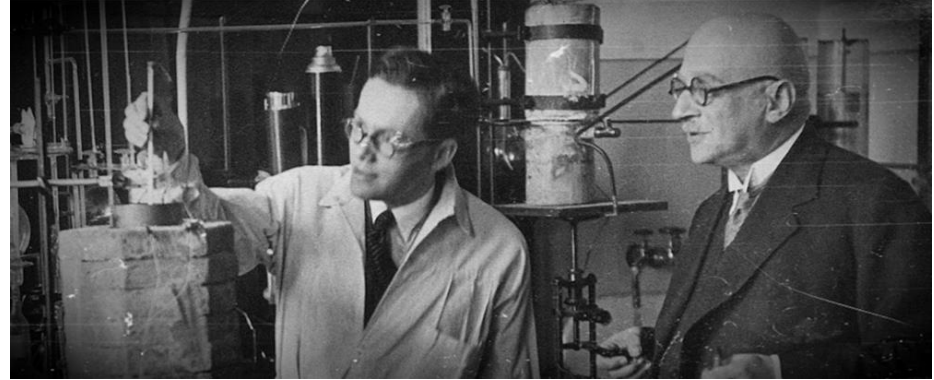
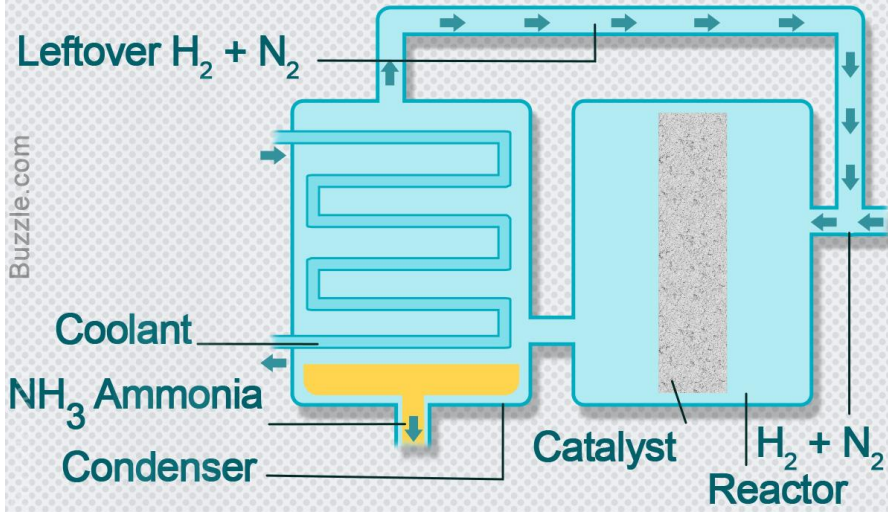
→ the production of ammonia consumes more than 3×10^{17} J which represents >1% of global energy consumption

$\text{N}\equiv\text{N}$ bond is so strong → N_2 is practically inert → catalyst needed

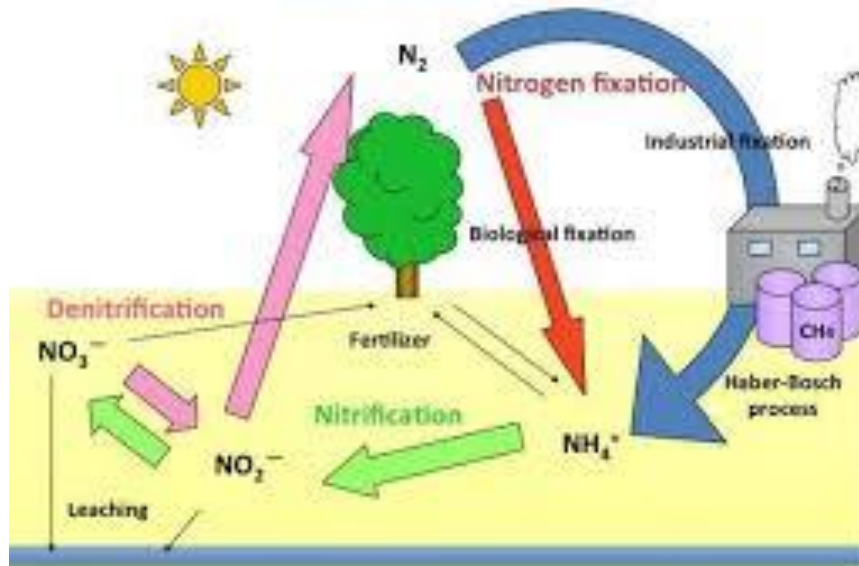
→ Haber-Bosch process: breaking $\text{N}\equiv\text{N}$ triple bond

N_2 dissociation is the rate-determining step in ammonia synthesis

Haber-Bosch Process



Nitrogen Cycle



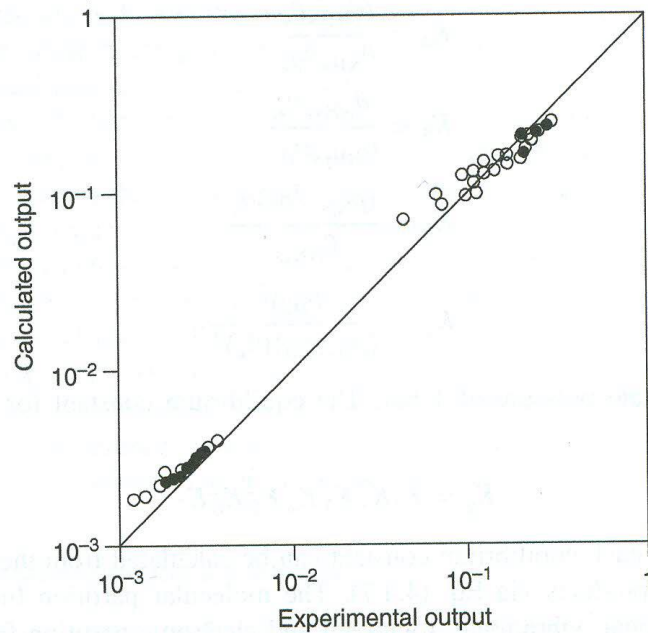


Figure 6.4 The measured NH_3 mole fraction at the reactor outlet (data points) is compared to the calculation of Stoltze and Nørskov (solid line). The Topsøe KM1R catalyst was operated at 1–300 atm and 375–500°C. Reproduced from P. Stoltze, J. K. Nørskov, *J. Catal.*, 110, 1. © 1988 with permission from Academic Press.

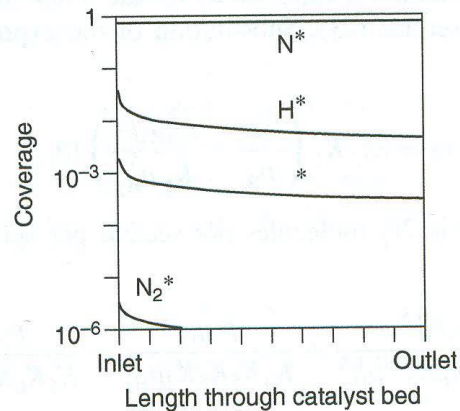


Figure 6.5 Coverages calculated by Stoltze and Nørskov for a K-promoted Fe catalyst operating at 400°C with an initial mixture (at inlet) of 25% N_2 , 75% H_2 and 0% NH_3 . Percentage of NH_3 at outlet: 20.6%. The curves are for adsorbed nitrogen (N^*), hydrogen (H^*), free sites ($*$) and molecular nitrogen (N_2^*). Reproduced from P. Stoltze, J. K. Nørskov, *J. Catal.*, 110, 1. © 1988 with permission from Academic Press.

Fischer-Tropsch synthesis and related chemistry

- Fischer-Tropsch(FT) synthesis: the production of hydrocarbons and oxygenated hydrocarbon from synthesis gas(or syngas, a mixture of CO + H₂)
- Closely related reaction with FT: methanation reaction (CH₄), methanol synthesis, Mobil process (convert methanol into transportation fuels)
- Syngas is produced from oil, natural gas, shale gas, coal or other carbonaceous mineralogical deposits by steam reforming. Carbon can also be supplied in a renewable form by the use of biomass

-steam reforming: the reaction of hydrocarbons with water to form CO and H₂

-Water gas shift reaction: the reaction of water gas(CO + H₂O) to form CO₂ and H₂

-Methanol process



Fischer-Tropsch chemistry

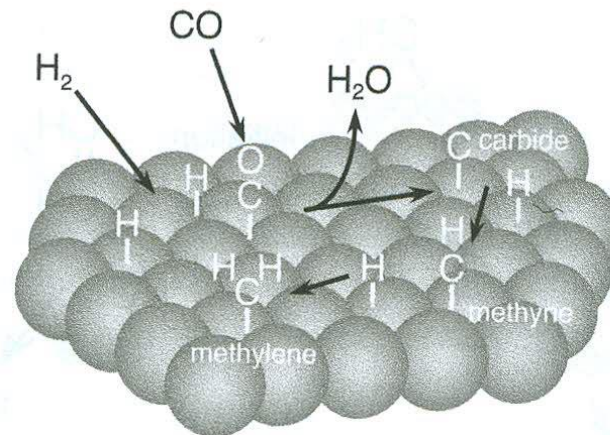


Figure 6.6 The dissociation of CO followed by hydrogenation to form an adsorbed methylene (CH_2) species. The formation of CH_2 is an essential step in Fischer-Tropsch synthesis. CH_2 is the product of sequential H addition steps that follow the dissociative adsorption of H_2 and CO . Oxygen is removed from the surface via H_2O formation.

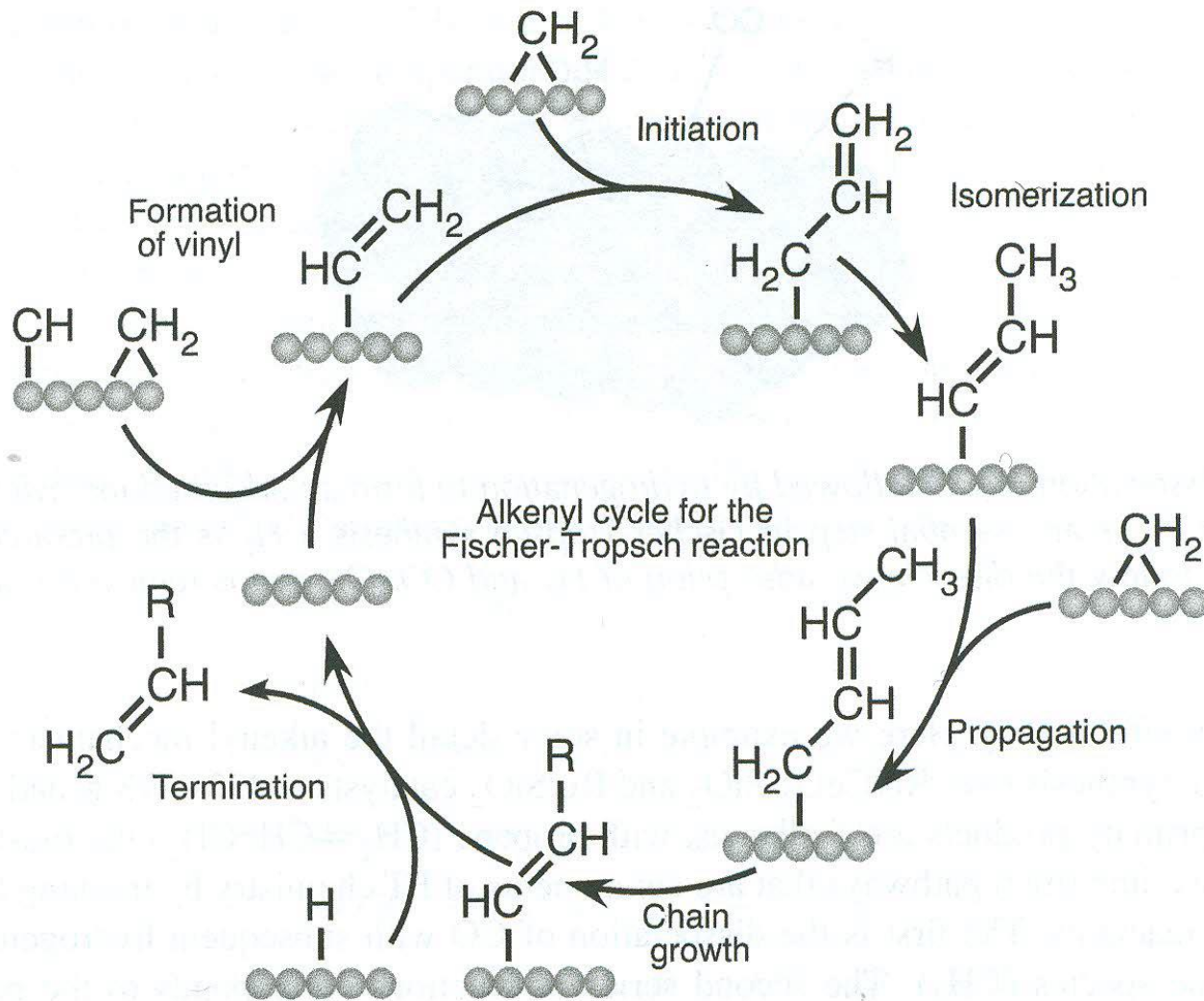
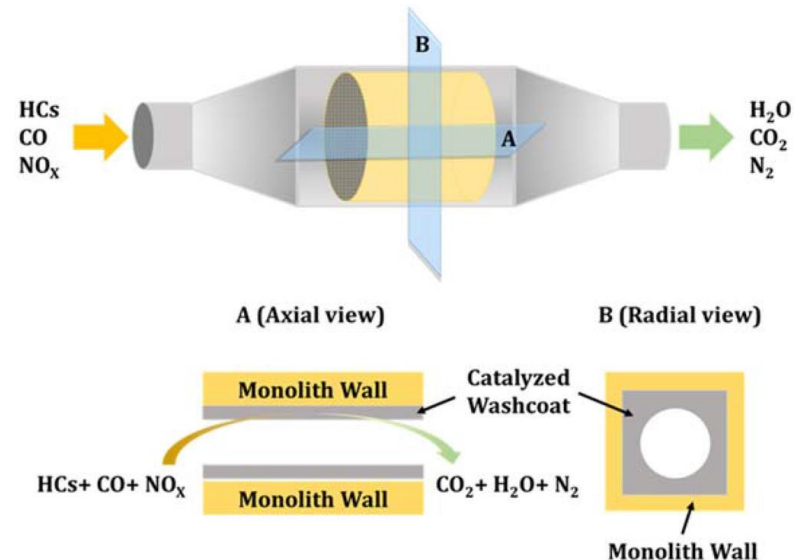
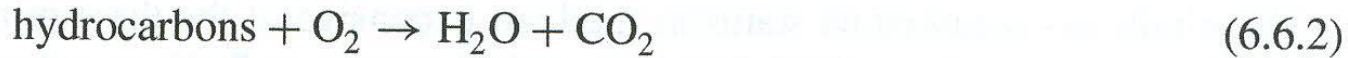


Figure 6.7 The alkenyl carrier cycle. The cycle begins in the top left with the formation of adsorbed vinyl ($\text{HC}=\text{CH}_2$) from CH and CH_2 . Chain growth ensues, initiated by the addition of CH_2 . Isomerization forms an adsorbed allyl ($\text{H}_2\text{C}-\text{CH}=\text{CH}_2$). Subsequently, further addition of CH_2 (propagation and chain growth) competes with addition of H (termination). Reproduced from P. M. Maitlis, H. C. Long, R. Quayum, M. L. Turner, Z. Q. Wang, *Chem. Commun.*, 1. © 1996 with permission from the Royal Society of Chemistry.

Three-way automotive catalyst

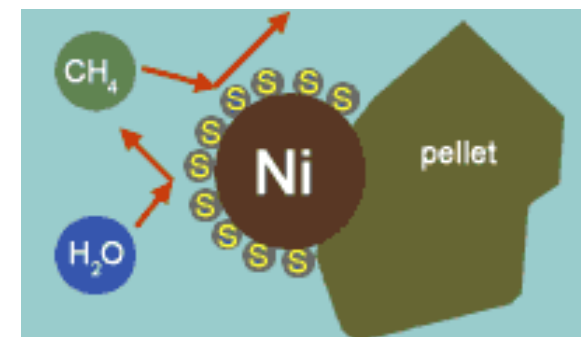
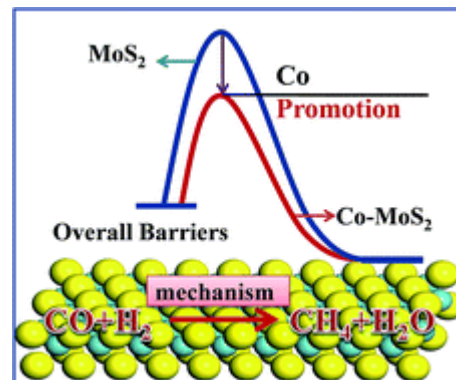
- To achieve clean burning internal combustion engines
→ hydrocarbon(HC)↓ nitrogen oxides(NO_x)↓ CO↓ (sulfur comp'ds ↓) in automotive emissions → automotive catalyst
- Automotive catalyst must efficiently oxidize CO, HC, and reduce NO_x
→ three-way automotive catalyst (it removes the three unwanted products of CO, HC, and NO_x)
- General composition of Rh, Pt, Pd dispersed on Al_2O_3 with CeO_2 added as a type of promoter
Rh: NO_x reduction to N_2
Pt, Pd: CO, HC oxidation





Promoters & poisons

- Promoter: to promote catalysis → increasing the activity of the catalyst → it lowers the barrier to reaction: it facilitates charge transfer (electronic promoter)
- Promoter stabilize the transition state → it lowers the activation barrier
- Ammonia synthesis: Al_2O_3 and CaO as structural promoters → enhance surface area of dispersed Fe particle
- Fischer-Tropsch synthesis: K promoter → increase selectivity
- Poisons: to poison catalysis → adsorbed species that lower the activity of a catalyst
CO, S...



Bifunctional catalysts

-Each metal contributes a function to the overall chemical mechanism, which is the sum of at least two parallel steps that occur at different sites

CO oxidation on PtRu catalyst

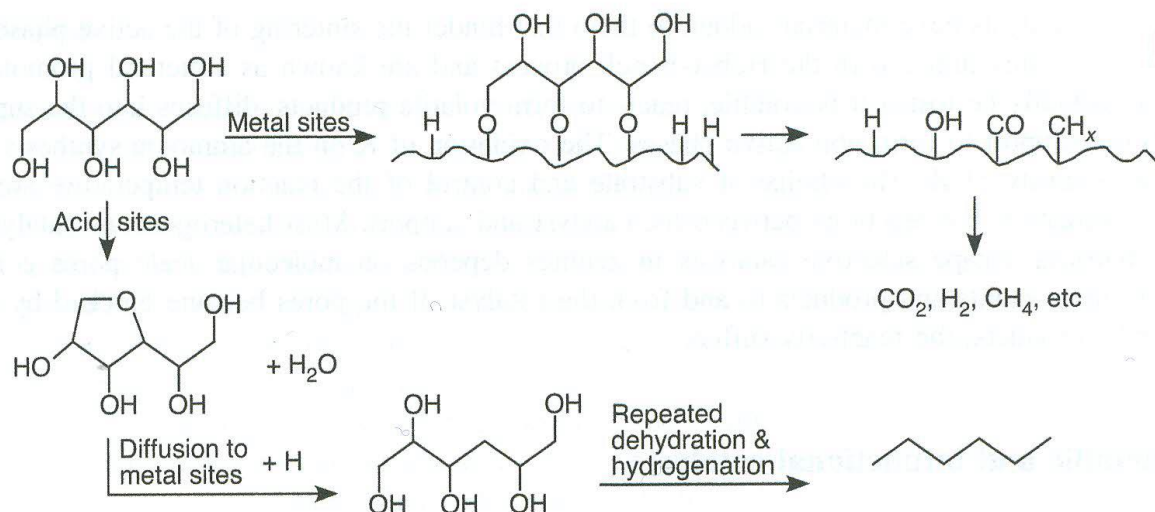


Figure 6.8 A schematic representation of the function of a bifunctional catalyst containing supported metal particles and acid sites on the support.

Optimal catalyst selection

-Correlation between activation energy for a reaction (E_a) and the energy released during reaction (ΔE)

(6.11.1)

for dissociation N_2 , CO , NO , O_2

-A volcano plot

-A good catalyst \rightarrow low E_a , not so tightly binding to the surface \rightarrow intermediately strong interactions with the species involved in the reaction

-Sabatier principle

If we can identify reactions for which the dissociation of a molecule such as N_2 , CO , NO , O_2 is rate determining, eq. 6.11.1 allows to identify the optimal catalyst because eq. 6.11.1 help us determine which material has the most favorable rate for the reaction

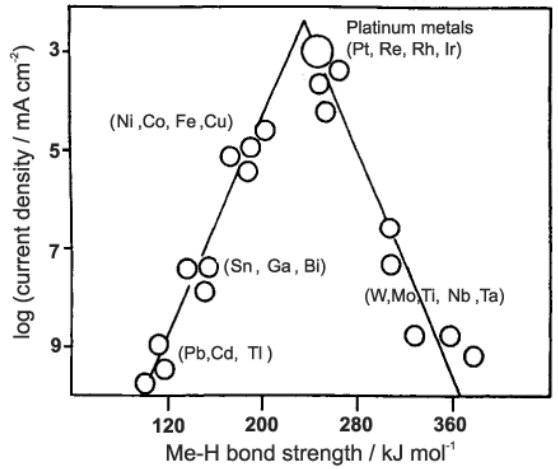
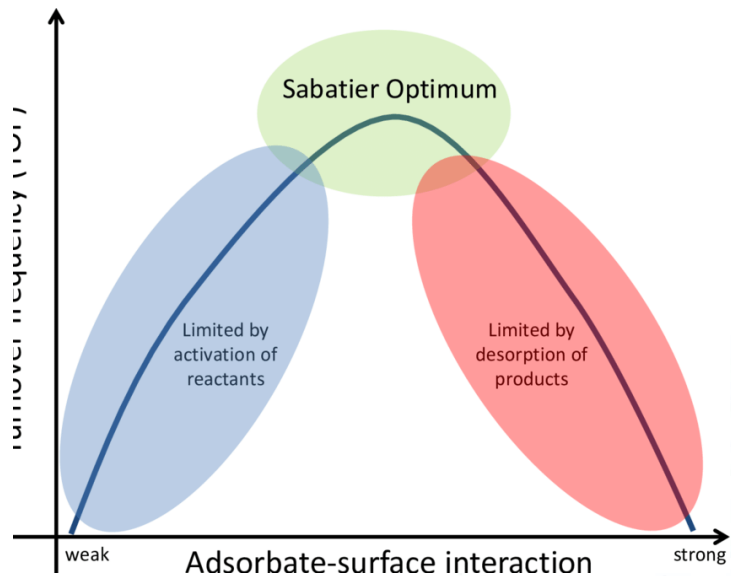


Figure 5. Volcano-type correlation of catalytic activity of different metals and the Me-H binding energy

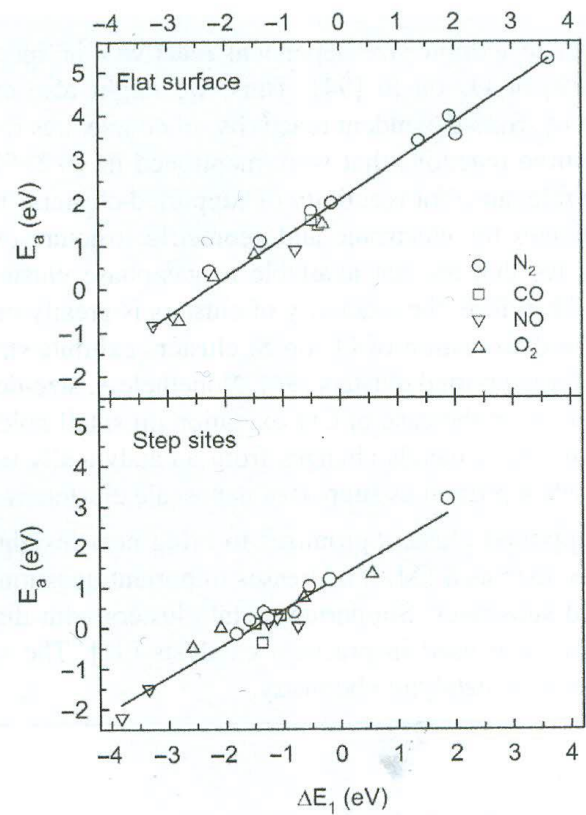


Figure 6.10 Calculated transition state energies (E_a) and dissociative chemisorption energies (ΔE_1) for N_2 , CO , NO , and O_2 on a number of transition metal surfaces. Results for close packed as well as stepped surfaces are shown. Reproduced from T. Bligaard, J. K. Nørskov, S. Dahl, J. Matthiesen, C. H. Christensen, J. Sehested, *J. Catal.*, 224, 206. © 2004 with permission from Elsevier.