

Application to Catalysis

1. Catalysis
2. Heterogeneous reactions
3. Measurement of surface kinetics/reaction mechanism
4. Harber-Bosch process
5. Fischer-Tropsch synthesis & related chemistry
6. Three-way automotive catalyst
7. Promoters & poisons
8. Bimetallic & bifunctional catalysts
9. Electrocatalysts
10. Optimal catalysis selection

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

Surface science & catalysis

- Catalysis: basis of chemical industry → billions of dollars of economic activity
- “**Catalysis**”, Greek “wholly loosening” (κατα + λυσις): it takes part in a reaction but is not consumed → changing activation barrier → speed up a reaction (but, not change equilibrated state) & perform selectively for the desired product

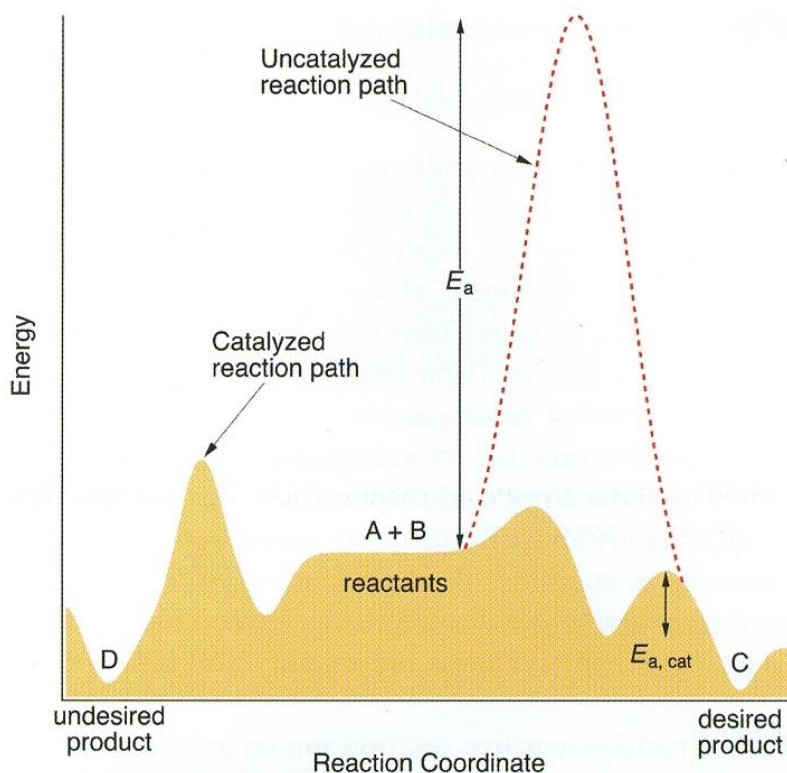


Fig.1.2.
Kolasinski

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

$$D = \left(\frac{48 M}{\pi \rho N_A} \right)^{1/3} \frac{1}{r}$$

$D = 0.55$ for $r = 1$ nm, $D = 0.11$ for $r = 5$ nm

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)

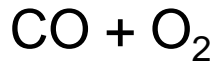
Material	Production/kMt	Process
1. H ₂ SO ₄	36 520 (Europe 19 024; World 165 000)	Contact process. Catalytic oxidation of SO ₂ over K ₂ SO ₄ promoted V ₂ O ₅ on a silica gel or zeolite carrier at 400–450 °C and 1–2 atm, followed by exposure to wet sulfuric acid.
2. Phosphate rock (P ₂ O ₅ , phosphoric 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)

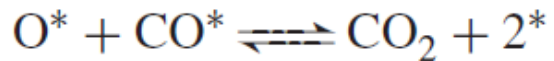
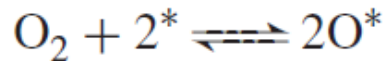
Gases	Production/Mm ³	
1. N ₂	26 448 (Europe 21 893)	Liquefaction of air
2. O ₂	16 735 (Europe 26 128)	Liquefaction of air
3. H ₂	13 989 (Europe 10 433)	Steam reforming of CH ₄ (natural gas) or naphtha over Ni catalyst supported on Al ₂ O ₃ , aluminosilicates, cement, and MgO, promoted with uranium or 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)



Langmuir-Hinshelwood reactions of $\text{CO(a)} + \text{O(a)}$



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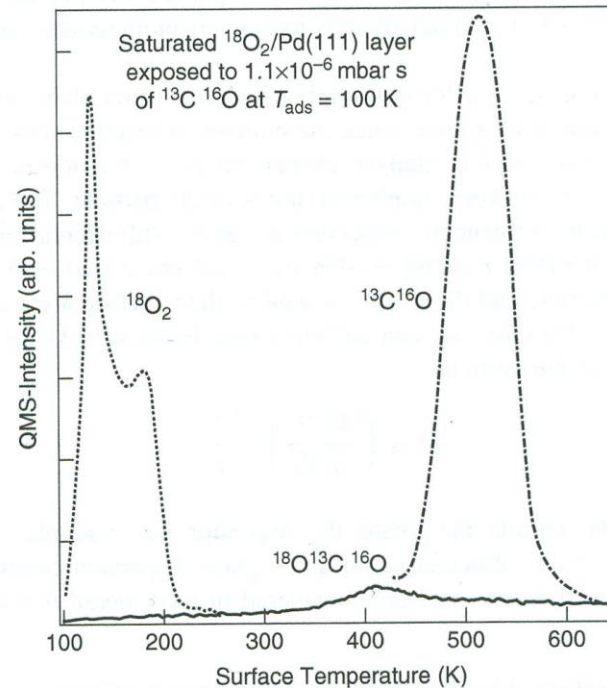


Figure 6.1 A co-adsorbed layer of $^{18}\text{O}_2 + ^{13}\text{C}^{16}\text{O}$ was prepared at $T_s = 100$ K on Pd(111). When heated, three products are observed in temperature programmed reaction spectrometry (TPRS): $^{18}\text{O}_2$, $^{13}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{16}\text{O}^{18}\text{O}$. 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

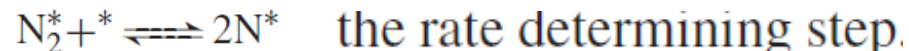
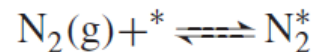
→ the production of ammonia consumes more than 3×10^{17} J which represents >1% of global energy consumption



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

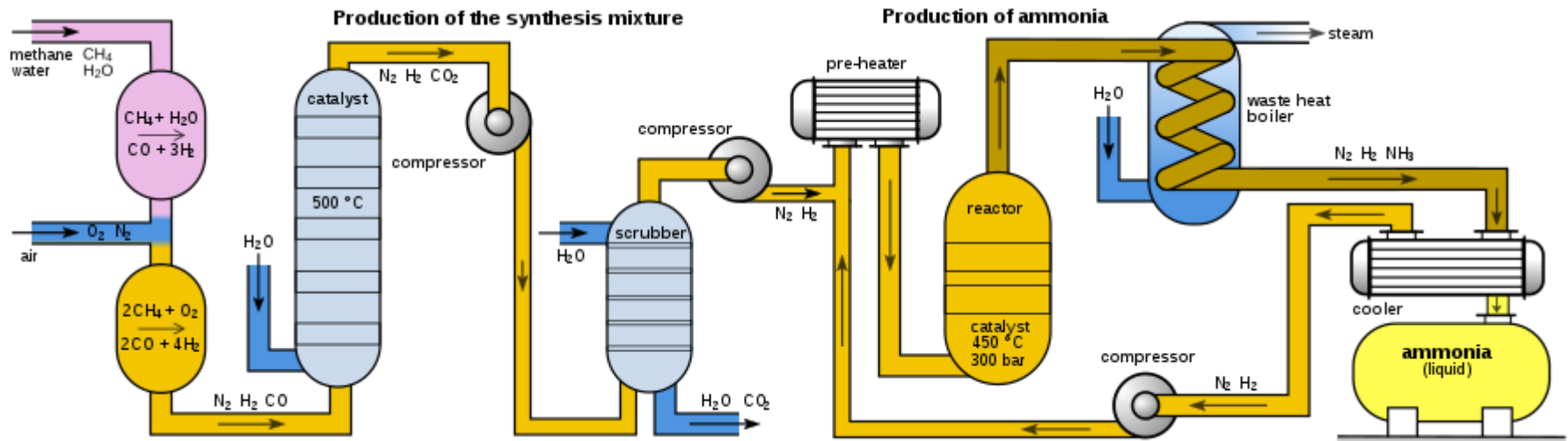
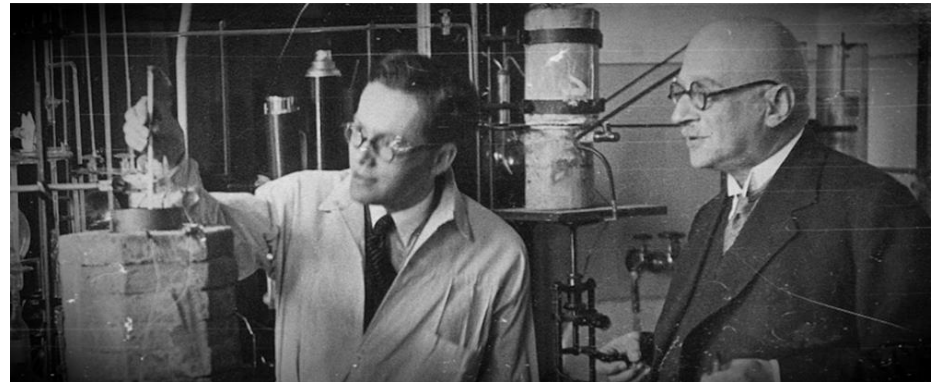
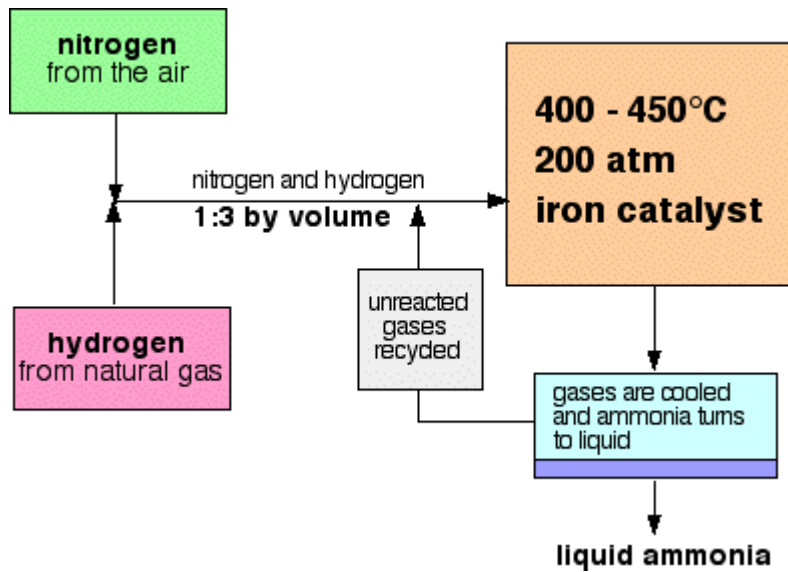
→ Haber-Bosch process: breaking $\text{N}\equiv\text{N}$ triple bond

N_2 dissociation is the rate-determining step in ammonia synthesis



Haber-Bosch Process

The Haber-Bosch process operates at 200–300 bar and 670–770 K over an Fe/K/CaO/Al₂O₃ catalyst.



Mechanism vs. experimental

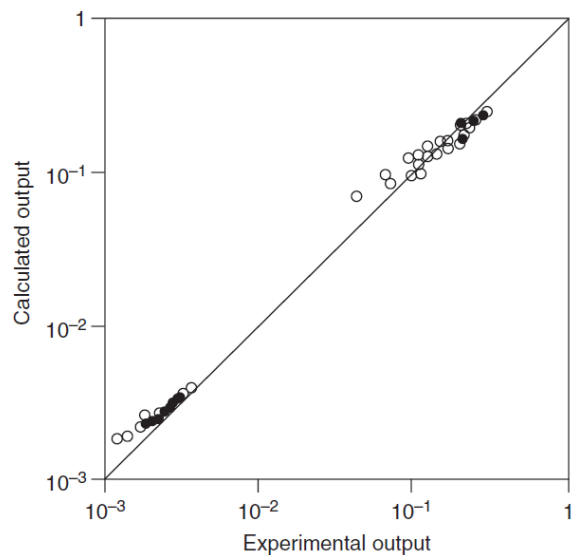


Figure 6.4 The measured NH_3 mole fraction at the reactor outlet (data points) is compared to the calculation of Stoltze and Nørskov (solid line). The Topsøe KM1R catalyst was operated at 1–300 atm and 375–500°C. Reproduced from P. Stoltze, J. K. Nørskov, *J. Catal.*, 110, 1. © 1988 with permission from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

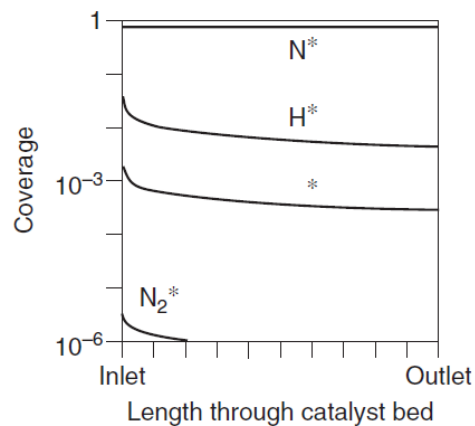
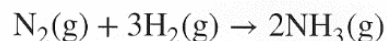


Figure 6.5 Coverages calculated by Stoltze and Nørskov for a K-promoted Fe catalyst operating at 400°C with an initial mixture (at inlet) of 25% N_2 , 75% H_2 and 0% NH_3 . Percentage of NH_3 at outlet: 20.6%. The curves are for adsorbed nitrogen (N^*), hydrogen (H^*), free sites ($*$) and molecular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

- Ammonia synthesis



Nitrogen fertilizers underpin modern agriculture [6]. The inexpensive production of fertilizers would not be possible without the Haber-Bosch process. Ammonia synthesis is almost exclusively performed over an alkali metal promoted Fe catalyst invented by Haber, optimized by Mittasch and commercialized by Bosch. The establishment of the Haber-Bosch process is a fascinating story [6]. Ostwald (who misinterpreted his results), Nernst (who thought yields were intolerably low and abandoned further work), and Le Châtelier (who abandoned his work after an explosion in his lab), all could have discovered the secret of heterogeneously catalysed ammonia synthesis but did not. Technical innovations such as lower pressure reforming and synthesis, better catalysts and integrated process designs have reduced the energy consumption per ton of fixed nitrogen from 120 GJ to roughly 30 GJ, which is only slightly above the thermodynamic limit. This factor of four improvement in energy efficiency represents an enormous decrease in energy usage since over 140 million metric tons (MMt) of NH_3 are produced each year. Therefore, the improvement also represents a tremendous decrease in cost (revenues from NH_3 synthesis are roughly \$60 billion annually) as well as CO_2 release.

Ammonia synthesis is a structure-sensitive reaction run on an alkali metal promoted Fe catalyst. Already a number of questions arise. Why an Fe catalyst? Why is the reaction run at high pressure and temperature? What do we mean by promoted, and why does an alkali metal act as a promoter? What is a structure sensitive reaction? What is the reforming reaction used to produce hydrogen, and how is it catalysed? By the end of this book all of these answers should be clear.

However, consideration of NH_3 as merely a precursor to fertilizer may be too limited a conception. NH_3 could also constitute an energy carrier that does not emit CO_2 upon combustion. To realize this potential of NH_3 we would need to master an electrochemical route to NH_3 that generates the required H atoms from a non-hydrocarbon based source. The ideal electrochemical cell would encompass the reactions



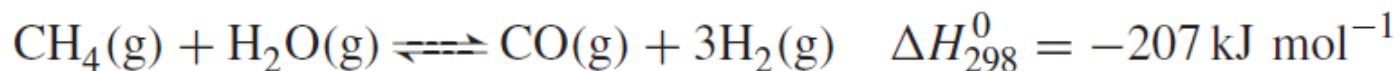
If the electrical current required to drive this electrolytic reaction can be generated renewably through, e.g. wind turbines or photovoltaic cells, then the NH_3 constitutes a carbon neutral energy carrier. This section should convince you that applications of surface science lie at the heart of the Energy-Water-Food Nexus [9].

NH_3 : a carbon neutral energy carrier

Fischer-Tropsch synthesis and related chemistry

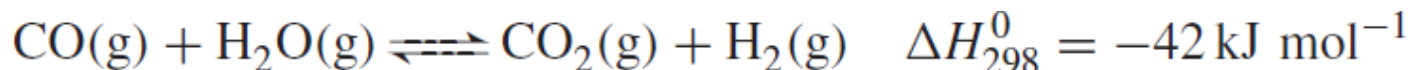
- Fischer-Tropsch(FT) synthesis: the production of hydrocarbons and oxygenated hydrocarbon from synthesis gas(or syngas, a mixture of CO + H₂)
- Closely related reaction with FT: methanation reaction (CH₄), methanol synthesis, Mobil process (convert methanol into transportation fuels)
- Syngas is produced 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: reaction of hydrocarbons with water to form CO and H₂



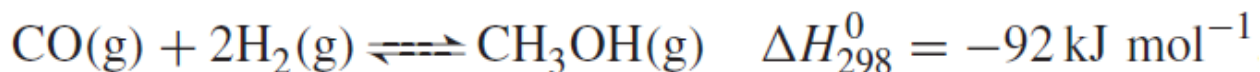
The first challenge of steam reforming is activity and, thus, a K₂O promoted Ni catalyst is used at 700–830 °C, 20–40 bar pressure, on an alumina or calcium aluminate substrate [61]. The reverse reaction

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



This reaction is used to increase the H₂ content of synthesis gas, and is important in automotive catalysis. An Fe₃O₄ catalyst supported on Cr₂O₃ is used as a high-temperature shift catalyst (400–500 °C). This

-Methanol synthesis

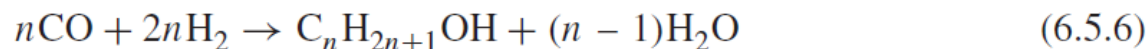
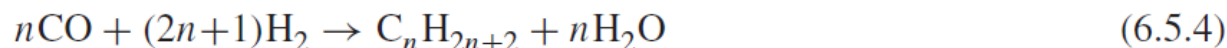


does not rapidly desorb from the catalyst. The use of CuO+ZnO+Al₂O₃ or CuO+ZnO catalyst allows the process to be run at the relatively mild temperature of 230–270 °C. Again, the Cu-based catalyst is highly



Fischer-Tropsch chemistry

Fischer-Tropsch chemistry proceeds via a complex set of reactions, which consume CO and H₂, and produce alkanes (C_nH_{2n+2}), alkenes (C_nH_{2n}), alcohols (C_nH_{2n+1}OH) and other oxygenated compounds, aromatics as well as CO₂ and H₂O. Some examples of these reactions are



All of these reactions are accompanied by negative free energy changes and are exothermic [64]. It is

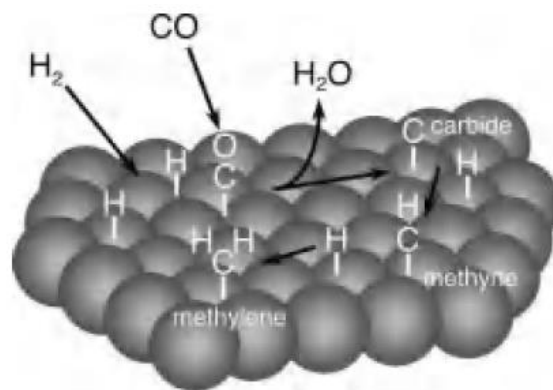


Figure 6.6 The dissociation of CO followed by hydrogenation to form an adsorbed methylene (CH₂) species. The formation of CH₂ is an essential step in Fischer-Tropsch synthesis. CH₂ is the product of sequential H addition steps that follow the dissociative adsorption of H₂ and CO. Oxygen is removed from the surface via H₂O formation.

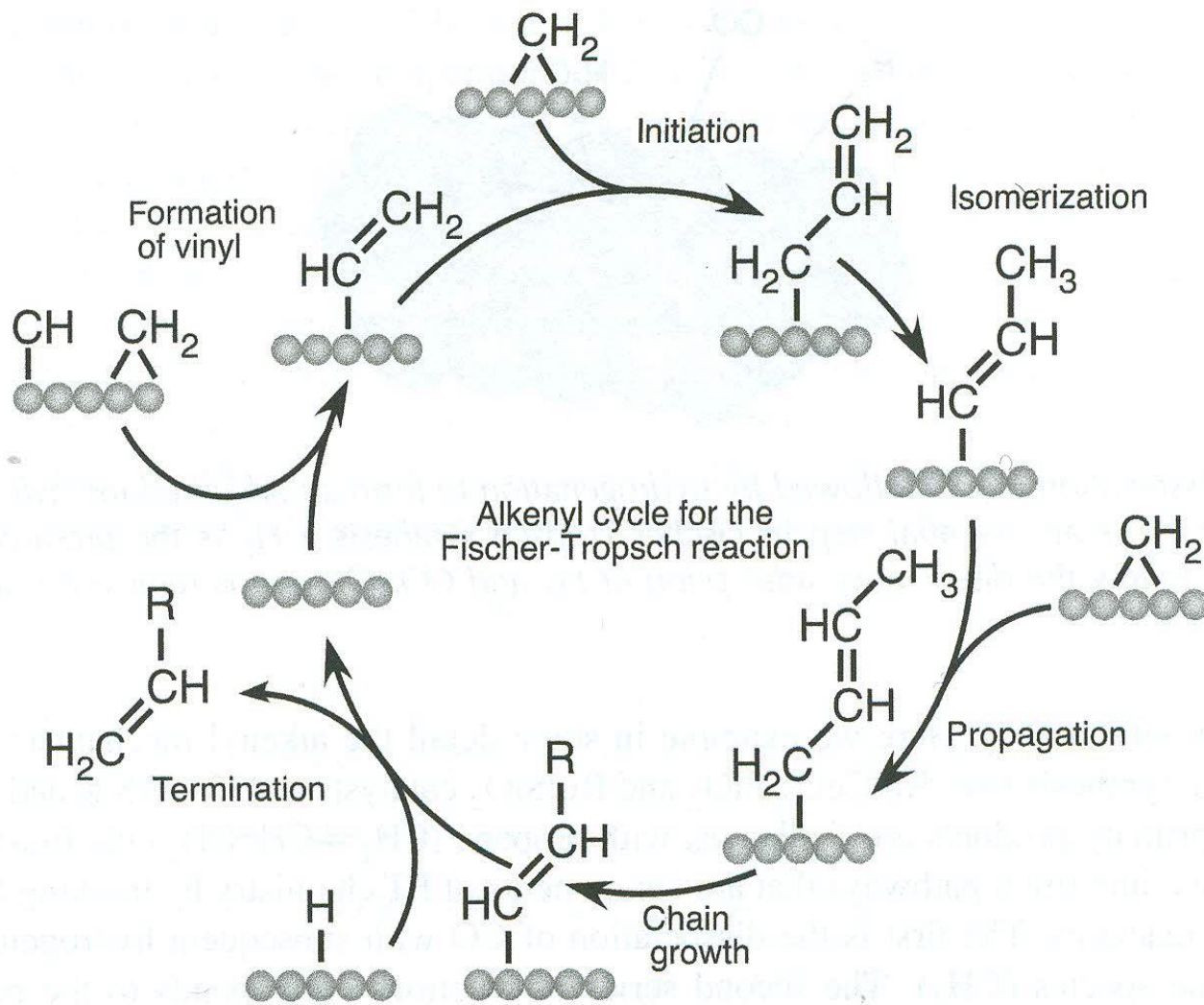


Figure 6.7 The alkenyl carrier cycle. The cycle begins in the top left with the formation of adsorbed vinyl ($\text{HC}=\text{CH}_2$) from CH and CH_2 . Chain growth ensues, initiated by the addition of CH_2 . Isomerization forms an adsorbed allyl ($\text{H}_2\text{C}-\text{CH}=\text{CH}_2$). Subsequently, 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.

- Gas-to-liquids: Fischer-Tropsch synthesis, C1 chemistry, artificial photosynthesis

$H_2 + CO \rightarrow$ liquid hydrocarbons (HC) and oxygenates (Fischer – Tropsch)

$CO, CO_2, CH_4, CH_3OH + \dots \rightarrow$ liquid hydrocarbons (C1 chemistry)

$H_2O + CO_2 \rightarrow$ liquid hydrocarbons (artificial photosynthesis)

-Transforming natural gas & coal

-Biomass

-Artificial photosynthesis: a branch of photocatalysis, H_2 production, CO_2 conversion, solar fuels

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

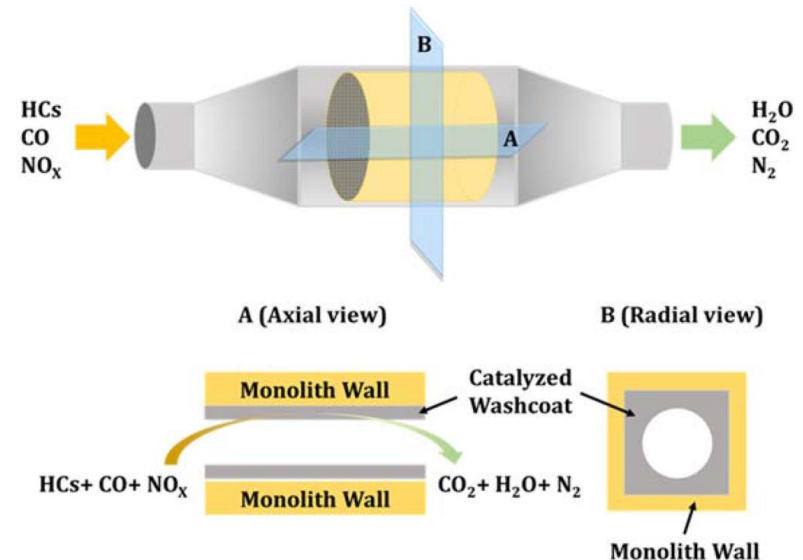
-Automotive catalyst must efficiently oxidize CO, HC, and reduce NO_x

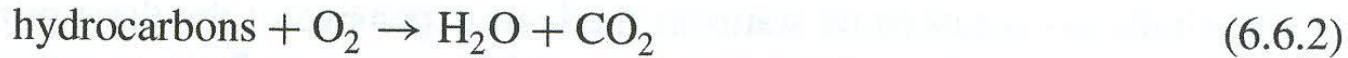
→ three-way automotive catalyst (it removes the three unwanted products of CO, HC, and NO_x)

-General composition of Rh, Pt, Pd dispersed on Al_2O_3 with CeO_2 added as a type of promoter

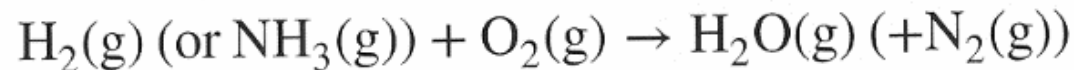
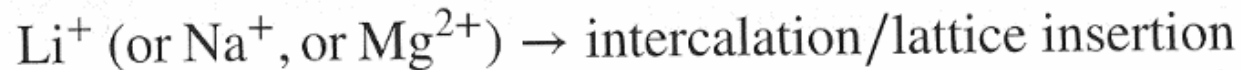
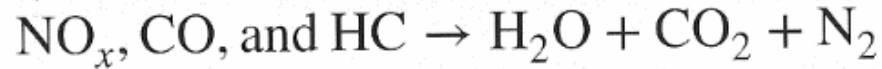
Rh: NO_x reduction to N_2

Pt, Pd: CO, HC oxidation





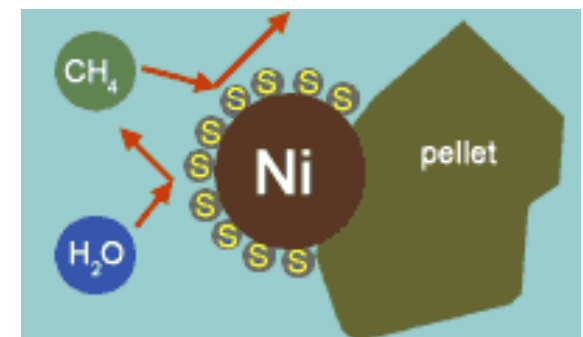
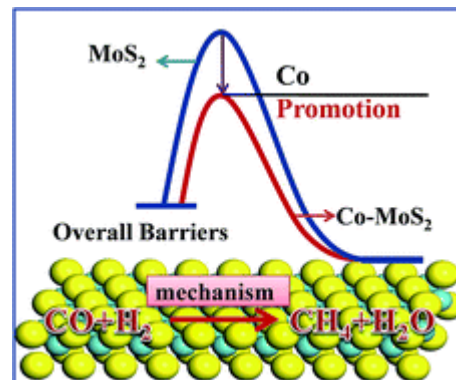
- Clean propulsion: three-way catalyst, batteries, fuel cells



- reduce pollution, (ultra)fine particle (PM 2.5, particulate matter)
- batteries, photovoltaics, fuel cells, thermoelectrics: surface, interface, pores

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...



Bimetallic & 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

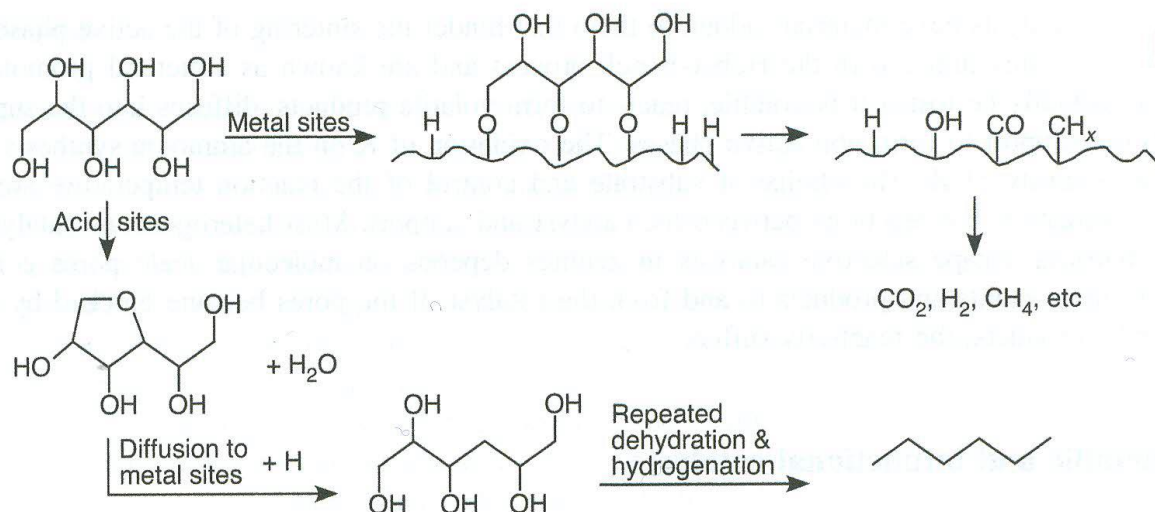
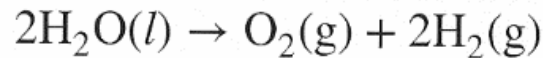


Figure 6.8 A schematic representation of the function of a bifunctional catalyst containing supported metal particles and acid sites on the support.

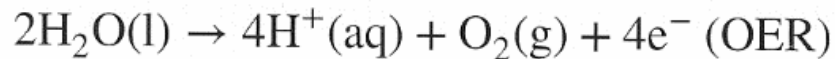
Electrocatalysis

- Water splitting

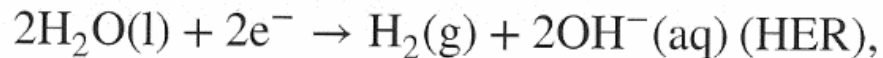
a fundamental understanding of interfacial electron transfer. The splitting of water



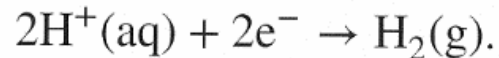
is related to two related half-reactions; namely, the oxygen evolution reaction (OER)



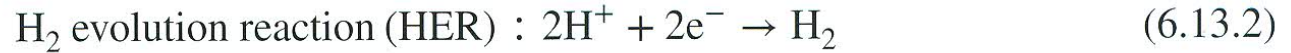
and the hydrogen evolution reaction (HER)



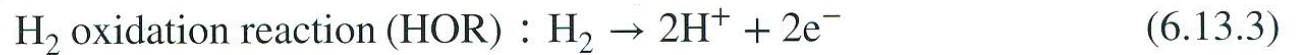
which in acid solutions reduces to



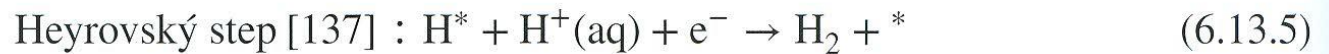
Hydrogen evolution reaction(HER) & H₂ oxidation reaction (HOR)



or its reverse, the hydrogen oxidation reaction



has been elucidated by the work of Skúlason et al. [134, 135] and plays out in terms of two different combinations of three elementary reactions:



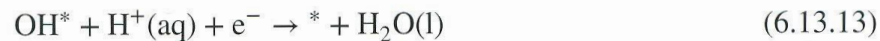
Oxygen evolution reaction(OER) & O₂ reduction reaction (ORR)



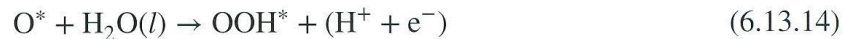
or its reverse



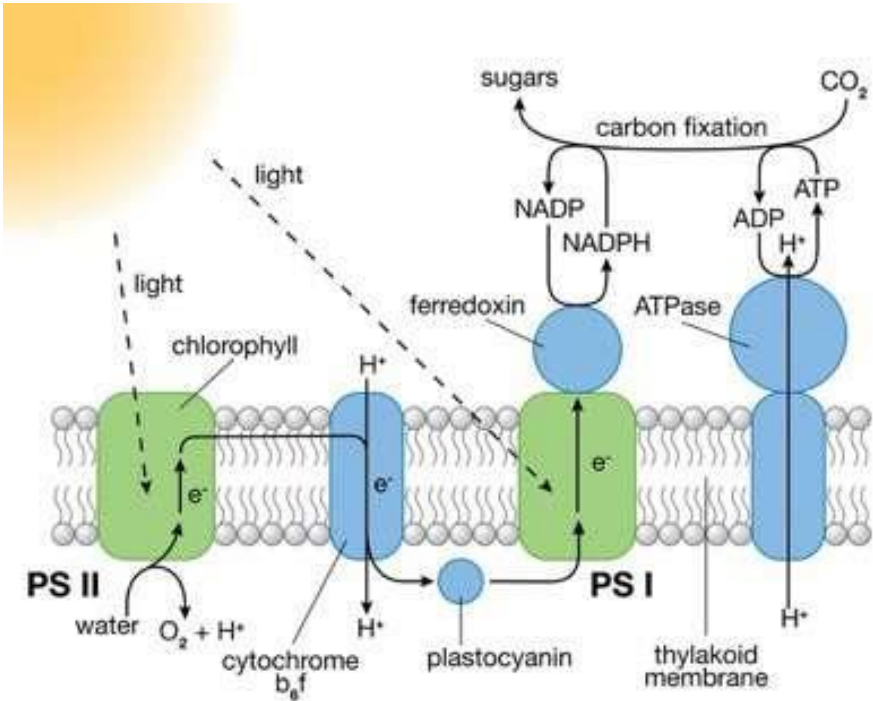
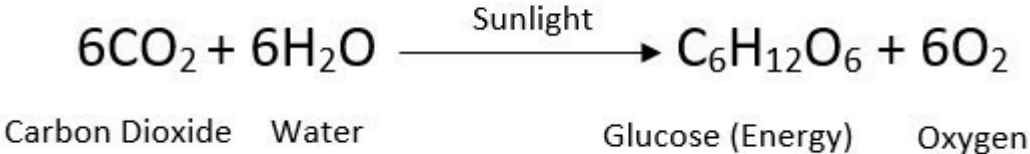
Two different mechanisms have been proposed to describe the ORR. The dissociative mechanism begins with dissociative adsorption of O₂ onto the electrode surface. In the associative mechanism, the oxygen adsorbs molecularly. Both mechanisms share the final two steps in common. We focus on the associative mechanism, which is a series of five steps, sometimes written as four as the first step is fast. The final four steps comprise sequential addition of a proton followed by electron transfer [140]:



The associative OER mechanism is composed of six steps, four of which again involve proton-coupled electron transfer denoted (H⁺ + e⁻) and two that are purely chemical.



Water splitting in photosystem



<https://phys.org/news/2017-06-scientists-molecular-artificial-photosynthesis.html>

Optimal catalyst selection

-Correlation between activation energy for a reaction (E_a) and the energy released during reaction (ΔE) either an adsorption enthalpy or the enthalpy of a surface reaction

$$E_a = \alpha_1 \Delta E_1 + \beta_1 \quad (6.11.1)$$

with $\alpha_1 = 0.87$ and $\beta_1 = 1.34 \text{ eV}$

for C-H bond breaking
& dissociation of
 N_2 , CO, NO, O_2 on transition metals

Relation between
barrier height vs. enthalpy \rightarrow
Brønsted-Evans-Polanyi (BEP) relationship

Linear relationship is directly
responsible for a volcano plot
 \rightarrow low E_a : strong binding..

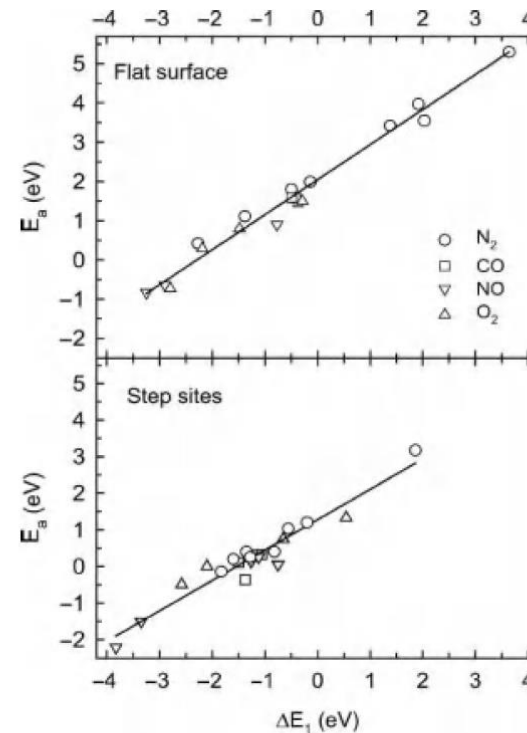


Figure 6.10 Calculated transition state energies (E_a) and dissociative chemisorption energies (ΔE_1) for N_2 , CO, NO, and O_2 on a number of transition metal surfaces. Results for close packed as well as stepped surfaces are shown. Reproduced from T. Bligaard, J. K. Nørskov, S. Dahl, J. Matthiesen,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

-A volcano plot: reactivity

(reaction rate) vs. group number of transition metal

-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

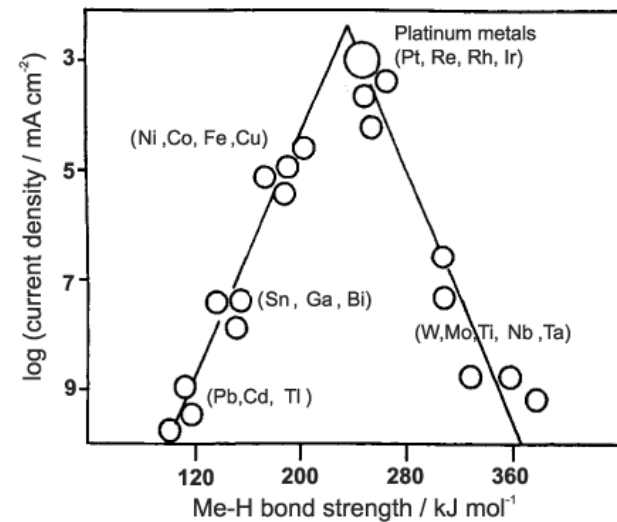
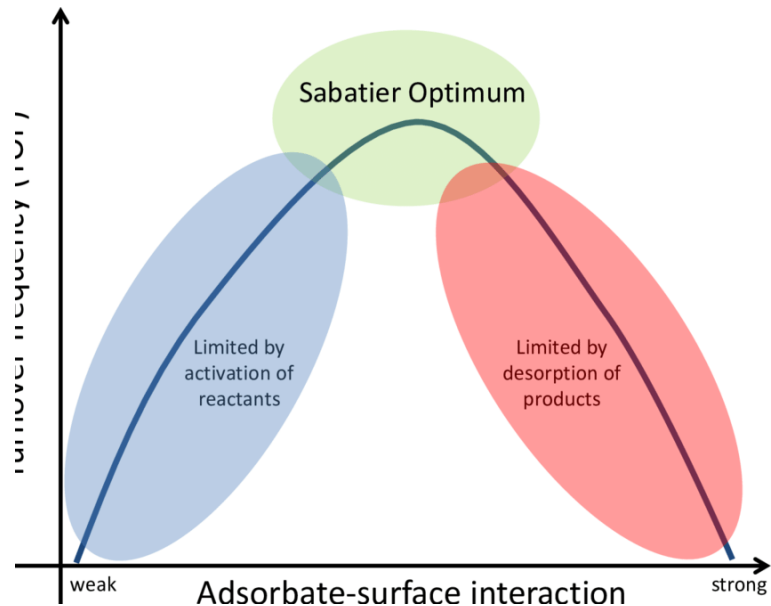


Figure 5. Volcano-type correlation of catalytic activity of different metals and the Me-H binding energy

reactivity \uparrow up to a plateau, then decrease

Summary

- The pressure gap and materials gap are not intrinsic barriers to understanding catalysis on the basis of UHV surface studies.
- Some catalytic reactions exhibit kinetics that depends strongly on the presence of certain types of sites or crystallographic planes. These are structure-sensitive reactions. Particularly reactive sites are known as active sites.
- Structure-insensitive reactions have kinetic parameters that are similar across a range of sites.
- The kinetics of a series of reactions is often controlled by a single reaction – the rate determining step – which has the largest degree of rate control.
- Both activity and selectivity are important characteristics of industrial catalysts.
- A practical catalyst is usually composed of an active phase and a support that helps to maintain the catalytic material in the active phase.
- A promoter enhances the reactivity and/or selectivity of the active phase by either electronic effects or direct interactions with the reactants.
- Poisons reduce activity either through site blocking or electronic effects.
- Poisons are sometimes strategically added to practical catalysts.
- Bifunctional catalysts incorporate different activities as different sites, for example, by combining two different metal sites or a metal site with an acid or base site on the support.
- Non-linearities in surface kinetics can lead to rate oscillations and spatiotemporal pattern formation.
- An optimal catalyst exhibits balanced binding interactions so that the appropriate bonds are weakened or broken to lower activation energies, while not binding reactants and products too tightly so that site blocking occurs.