CHEM53200: 表面化學

Lecture 5

Physisorption, Chemisorption & Catalysis

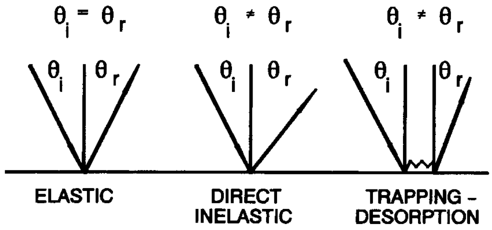


Figure 9.1 Possible outcomes of the collision of a gas atom with a surface. Elastic: low temperature; weak interaction; light molecule; energetically smooth, regular surface. Direct inelastic: higher temperature; weak interaction; heavier molecule; energetically rough, irregular surface. Trapping-desorption: low temperature, strong interaction, heavier molecule.

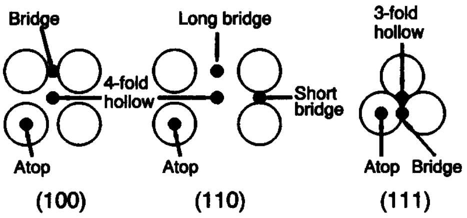


Figure 9.4 Possible impact sites for an atom approaching a solid surface, for various FCC surface geometries.

Table 9.1

Interaction	*Range*	*Strength*
Covalent	Very short, $1/r^6$	Very strong (E_o> 100 kcal/mol)
Coulomb (ionic)	Long, $1/r$	Strong
Polar		Weak
van der Waals	Long, $1/r^3$	Very weak (E_o < 5 kcal/mol)

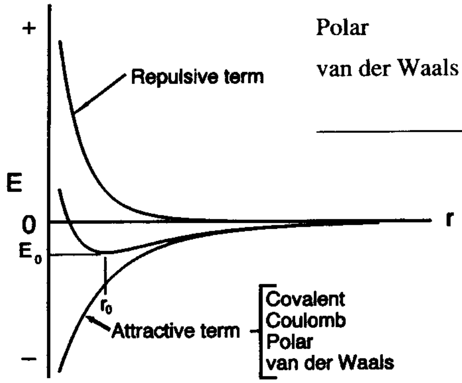


Figure 9.3 One-dimensional potential energy diagram for an atom approaching a solid surface along a path perpendicular to the surface.

Physical adsorption (physisorption)	Chemical adsorption (chemisorption)
no barrier (not activated)	may have barrier
fast	variable uptake kinetics
vdw/dipole interactions	covalent/metallic/ionic
weak (< 0.4 eV)	strong (> 0.4 eV)
always atomic/molecular	may be dissociative
reversible	often irreversible
surface symmetry insensitive	surface symmetry specific
may form multilayers	limited to monolayer
surface *T* < condensation *T*	wide range of surface *T*

Physisorption

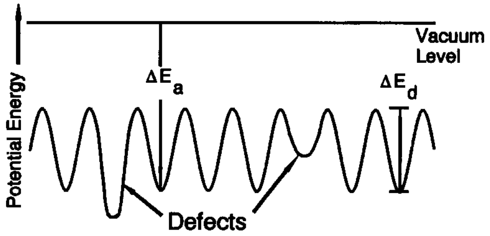


Figure 11.1 Potential energy of an adatom at a real surface as a function of position along a row of surface atoms.

ΔH_{ad} is of the order of $\Delta H_{condensation}$ for the adsorbate ($-\Delta H^{o}_{physisorption}$ < 35 kJ/mol)

一般 $|\Delta H^{o}_{ad}|$ 會稍大於 $|\Delta H^{o}_{condensation}|$ due to the surface potential at the solid-gas interfaces

Adsorbate 可極化性 ( ) 越大越顯著

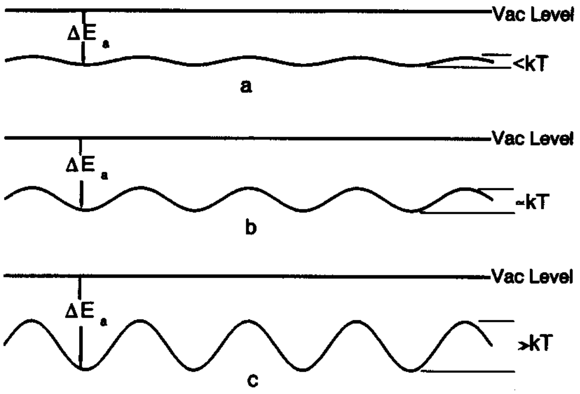


Figure 11.2 Potential energy of an adatom at a surface for three general classes of adsorption: Mobile adsorption (a), localized adsorption (b), and immobile adsorption (c).

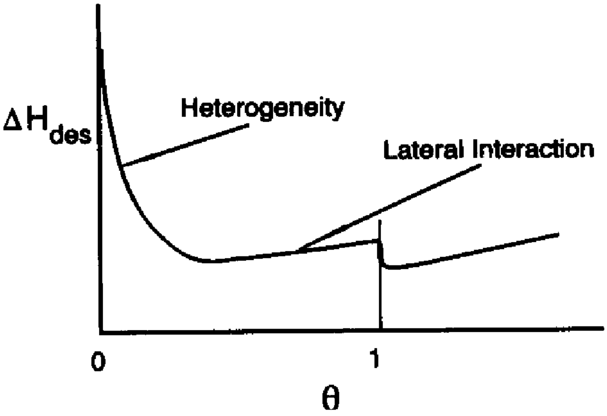
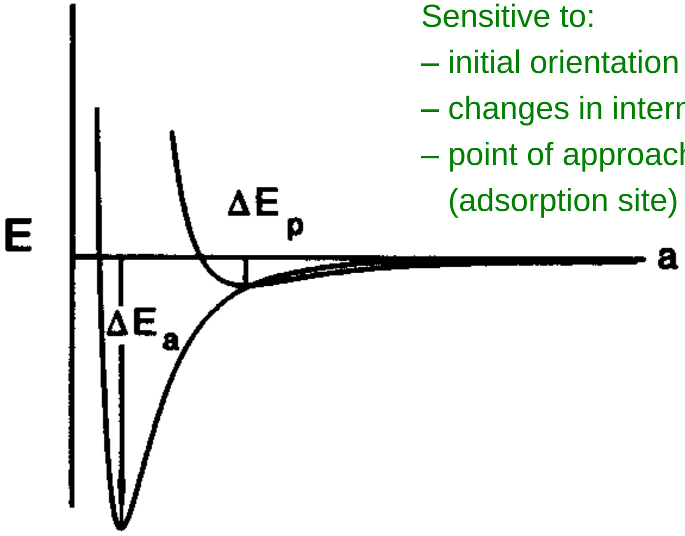


Figure 11.7 Heat of adsorption as a function of adlayer coverage for a slightly heterogeneous surface, showing effects due to high energy sites at low coverage, increasing heat of adsorption due to lateral interactions as the monolayer is approached, and a drop at the onset of second layer formation.

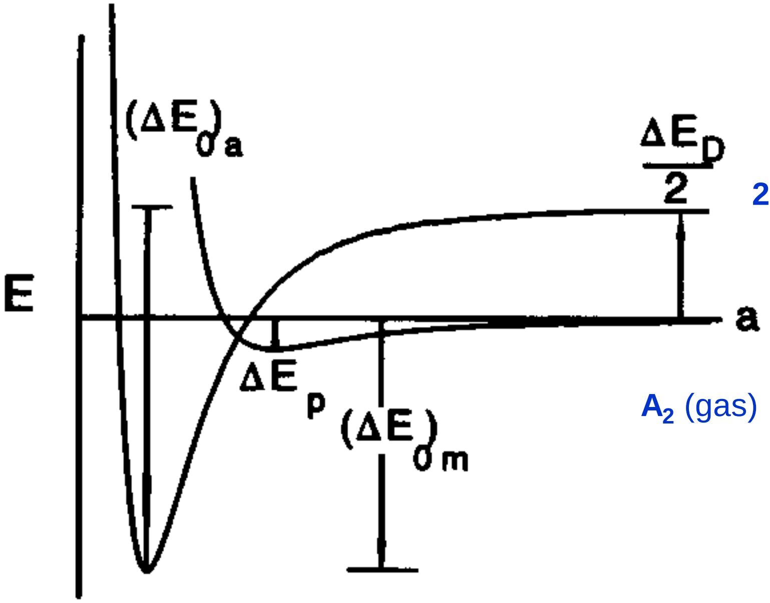
Chemisorption

Non-dissociative chemisorption

Sensitive to:
- initial orientation of molecules
- changes in internal bonding
- point of approach (adsorption site)



Dissociative chemisorption



2A (gas)

A_2 (gas)

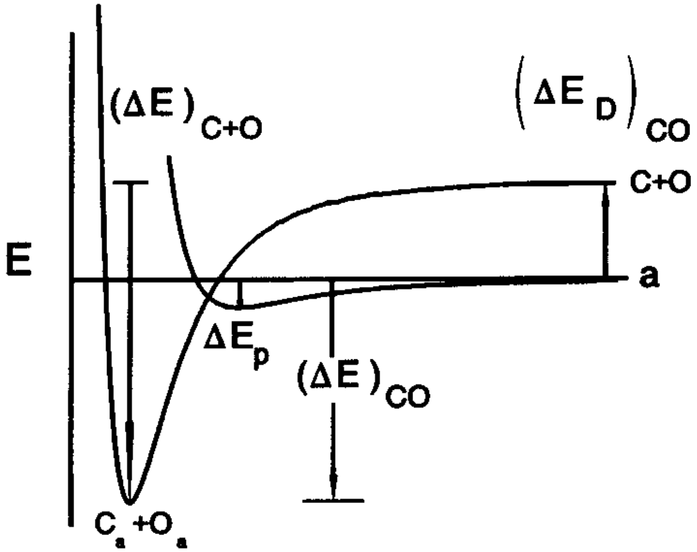
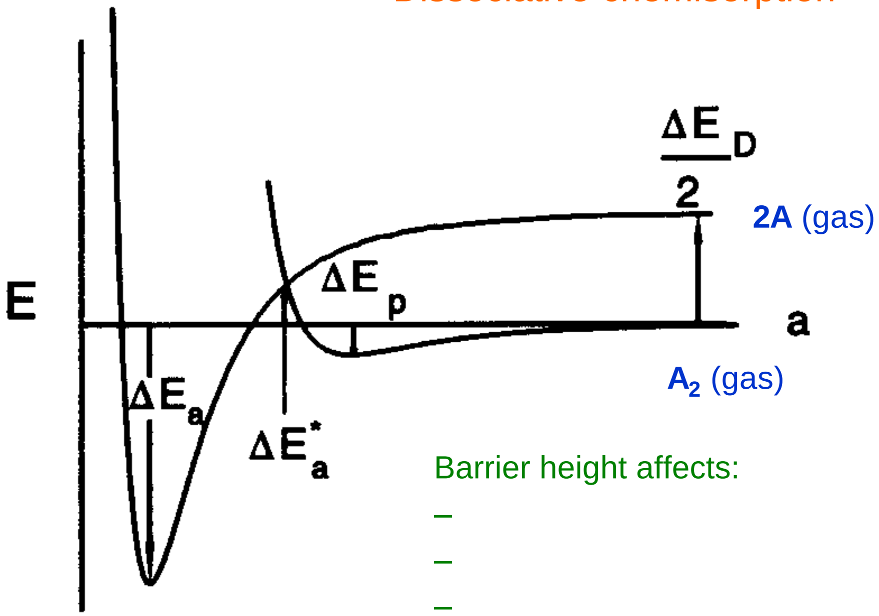


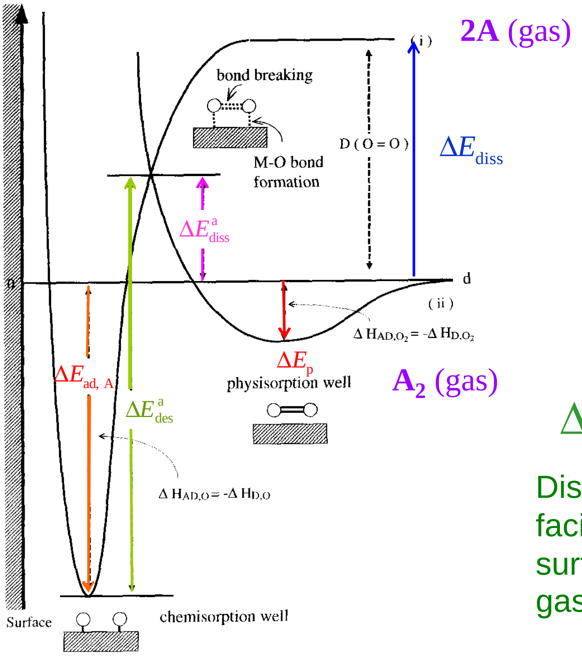
Figure 12.2 Potential energy curves for the dissociative adsorption of a heteronuclear diatomic molecule.

Dissociative chemisorption



Barrier height affects:

-
-
-



One-dimensional potential energy diagram for dissociative adsorption.

$$\Delta E^{a}_{diss} < \Delta E_{diss}$$

Dissociation may be facilitated by the surface respect to the gas phase.

- Direct chemisorption is usually not observed
  - – transient physisorption
  - – “precursor-mediated adsorption”

- The enthalpy of chemisorption (heat of chemisorption) depends strongly on the surface coverage of adsorbate, largely as a result of adsorbate-adsorbate lateral interactions.

  (declines with increasing coverage for most systems)

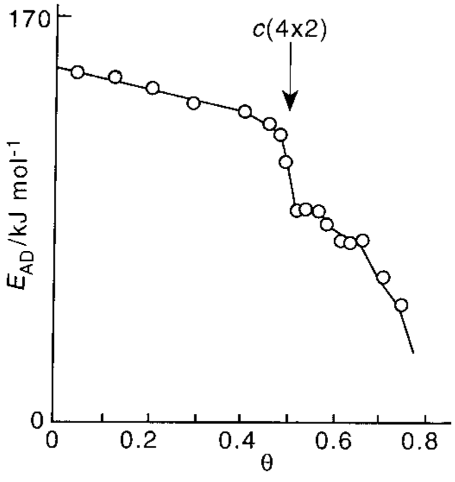


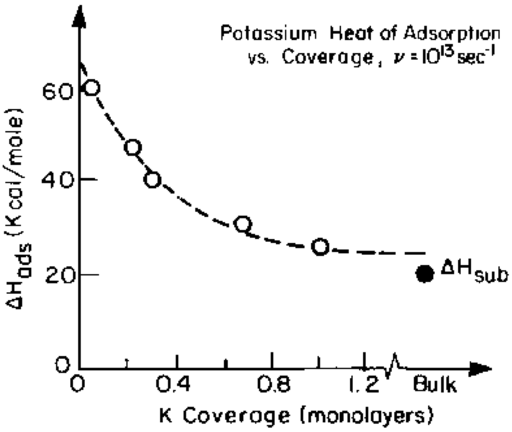
Fig. 1.6 Variation in the enthalpy of adsorption of CO on Pd(111). Adapted from ref. 4.

CO adsorption on Pd(111)

A precipitous fall in the value of ΔH_{ad} occurs at $q = 0.5$

原因: associated with the formation of an ordered of surface CO molecules

Further adsorption decreases separation of CO molecules and disrupts the ordered array ⇒ destabilize the adsorbed layer ($\therefore |\Delta H_{ad}| \downarrow$)



K adsorption on Rh(111)

At low q, K is strongly bound to the transition metal as it transfers e^- to become positively charged.

As q ↑, adsorbate-adsorbate interactions cause repulsion among charged species ⇒ weaken adsorption bonds until ΔH_{ad} becomes equal to $\Delta H_{sublimation}$ of K.

Kinetics/Dynamics of Surface Adsorption

sticking coefficient

$$S = \frac{\text{rate of adsorption}}{\text{rate of collision}}$$

Assuming Langmuir behavior, the probability of a molecule being associatively adsorbed (1st order) may be defined in terms of "sticking probability".

於下頁圖中 S can exceed the value predicted purely from Langmuir considerations.

⇒ precursor state (precursor mediated adsorption)

intrinsic precursor state: "physisorbed" to a

extrinsic precursor state: "physisorbed" to a

(through weak vdw-type bond)

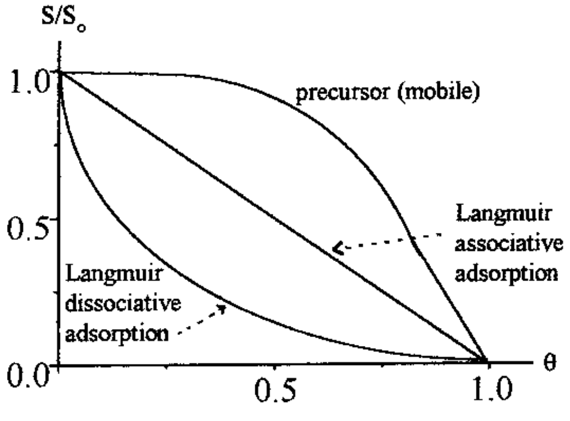


Fig. 1.7 The variation of sticking probability with surface coverage for precursor, Langmuir associative, and Langmuir dissociative adsorption.

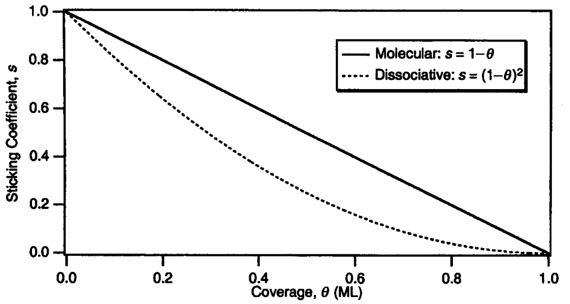


Figure 4.6 Langmuir models (molecular and dissociative) of sticking coefficient, *s*, as a function of coverage, *θ*

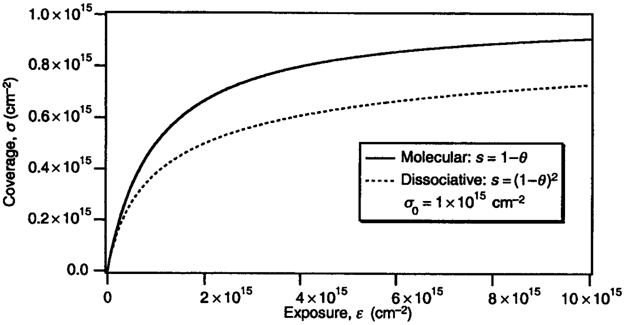


Figure 4.7 Langmuir models (molecular and dissociative) of coverage, *σ*, as a function of exposure, *ε*

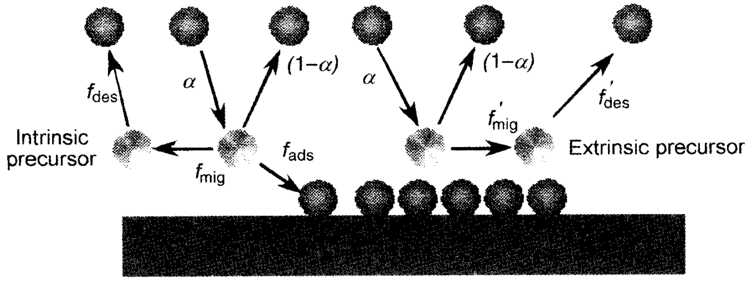


Figure 4.10 The Kisliuk model of precursor-mediated adsorption. Incident molecules trap into intrinsic or extrinsic precursors. Thereafter, sticking becomes a competitive process between desorption out of the precursor and transfer into the stable chemisorbed state. α, probability of entering the precursor state

$$s = \alpha\left(1+\frac{f_{des}}{f_{ads}}\right)^{-1}\left[1+K\left(\frac{1}{\theta_{req}}-1\right)\right]^{-1}$$

where

$$K = \frac{f'_{des}}{f_{ads}+f_{des}}$$

The initial sticking coefficient is

$$s_0 = \alpha\left(1+\frac{f_{des}}{f_{ads}}\right)^{-1}$$

q_{req} : the coverage dependence of the sites required for adsorption

$$\frac{s(\theta)}{s_0} = \left[1+K\left(\frac{1}{\theta_{req}}-1\right)\right]$$

e.g., for Langmuirian dissociative adsorption, $q_{req} = (1-q)^2$

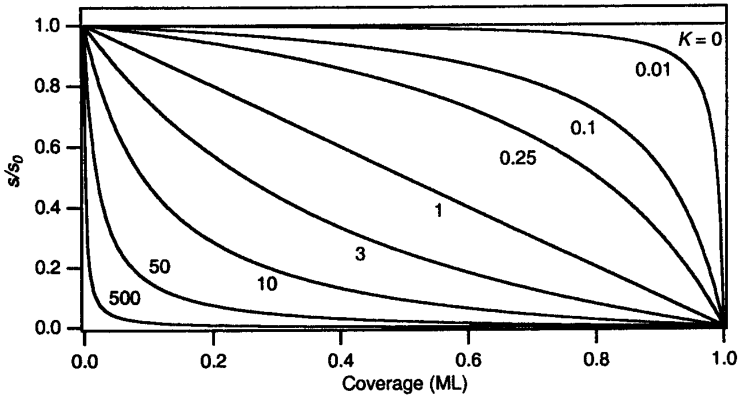


Figure 4.11 The change in sticking coefficient, s, with coverage for precursor-mediated adsorption. The change is characterized by the parameter K. For $K = 0$ the sticking coefficient is constant, whereas for $K = 1$ it drops linearly with coverage as in Langmuirian adsorption. Large values of K decrease s relative to Langmuirian adsorption

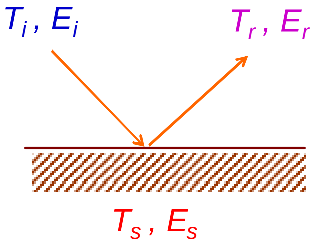
$$\frac{s(\theta)}{s_0} = \left[1+K\left(\frac{1}{\theta_{req}}-1\right)\right]^{-1}$$

Residence time

$$t = t_0 \cdot e^{-\Delta H_{ad}/RT} \qquad t_0 \approx 10^{-13}\,\mathrm{s}$$

The longer the molecule resides at the surface, the more probable is the process of energy exchange (thermalization) with the surface.

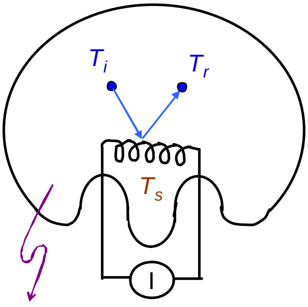
Thermal accommodation coefficient, α



T_i: initial T of molecule in gas phase

T_r: final T of molecule in gas phase after collision with surface

T_s: T of surface



l >> vessel's dimension

$T_s > T_r > T_i$

$a =$

initial kinetic energy $E_i = \frac{3}{2}kT_i$

- When $T_r = T_i \Rightarrow a =$
  least efficient energy transfer
  elastically scattered
- When $T_r = T_s \Rightarrow a =$
  most efficient energy transfer
  complete accommodation of adsorbate

- $E_i < \Delta E_p$ (depth of physisorption well):
  molecules will gradually lose energy and become accommodated
- $E_i \approx \Delta E_p$:
  energy exchange becomes less efficient & $a \downarrow$
  (a: minimum when $E_i = \Delta E_p$)
- $E_i \approx \Delta E_p$:
  a starts to increase again up to the “classical limit” [whereby at very high temperature $T \rightarrow \infty$, the energy transfer may be calculated in terms of a simple inelastic collision between on particle (adsorbate) and another (surface atom)

$$a(\infty) = \frac{2.4\mu}{(1+\mu)^2} \qquad \mu = \frac{\text{mass of adsorbate}}{\text{mass of surface atom}}$$

When $\mu =$ $\Rightarrow$ $a(\infty)$: most efficient

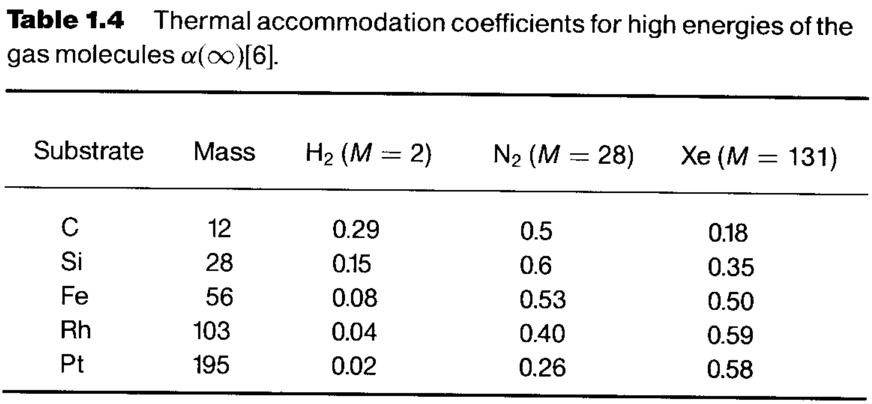


Table 1.4 Thermal accommodation coefficients for high energies of the gas molecules $\alpha(\infty)$[6].

Substrate	Mass	H_2 ($M = 2$)	N_2 ($M = 28$)	Xe ($M = 131$)
C	12	0.29	0.5	0.18
Si	28	0.15	0.6	0.35
Fe	56	0.08	0.53	0.50
Rh	103	0.04	0.40	0.59
Pt	195	0.02	0.26	0.58

In summary:

$$A_{(g)} \underset{k_d}{\overset{k_t}{\rightleftharpoons}} A_{(p)} \xrightarrow{k_a} A_{(ad)}$$

$$A_{2(g)} \underset{k_d}{\overset{k_t}{\rightleftharpoons}} A_{2(p)} \xrightarrow{k_a} 2A_{(ad)}$$

k_t: rate constant of trapping into precursor state

k_a: rate constant of adsorption from precursor state

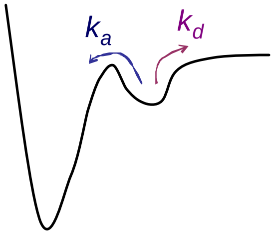
T_d: rate constant of desorption from precursor state

desorption :

$$k_d = n_d \exp\left(-\frac{\Delta E_d^*}{RT}\right)$$

adsorption :

$$k_a = n_a \exp\left(-\frac{\Delta E_a^*}{RT}\right)$$



$$\frac{k_d}{k_a} \approx \exp\left[\frac{-\Delta E_d^* + \Delta E_a^*}{RT}\right]$$

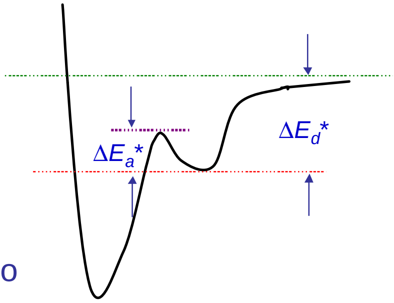
(A) $\Delta E_a^* < \Delta E_d^*$

non-activated adsorption

as T ↑ ⇒

chemisorption probability

the weakly held precursor tends to desorb instead of adsorb as T

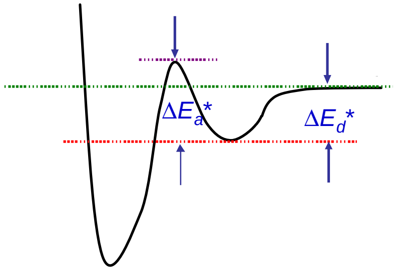


(B) $\Delta E_a^* > \Delta E_d^*$

activated adsorption

as T ↑ ⇒

chemisorption probability



除了以 Lennard-Jones potential energy diagram 定性探討吸附現象, many properties contribute to the variation in magnitude of the activation barrier in addition to those already mentioned

例如：dissociative adsorption of H_2 on Cu

activated process, S_o: low

To achieve adsorption:

- ↑ translational energy of H_2(g) [i.e. T ↑]
- excite H-H vibrationally (stretch H-H bond)
- ↑ rotational energy (as long as rotation is in the plane of surface)

To account fully for the real dynamics of surface adsorption, a multidimensional potential energy surface is required, inclusive of positional, translational, rotation, and vibrational degrees of freedom.

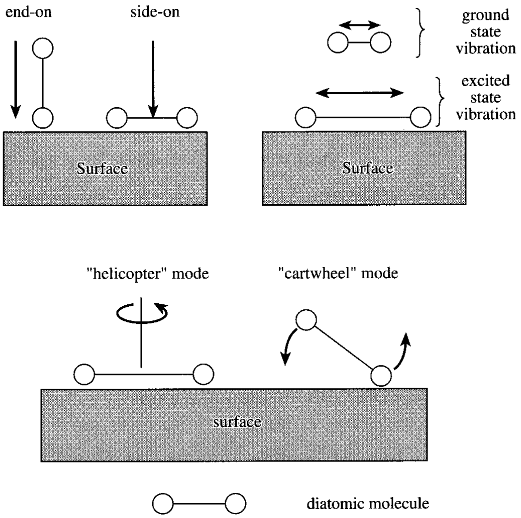


Fig. 1.9 **ORIENTATION** of molecule will affect rate of dissociation. May be interpreted as differences in extent of overlap between antibonding orbital on molecule and filled electronic states on solid. **VIBRATIONAL** state of molecule will affect rate of dissociation. Bond length in diatomic molecule is longer on average in excited vibrational state. **ROTATIONAL** excitation also leads to increase in molecular bond length. However, poor orbital overlap between molecule and surface is observed in the 'cartwheel' mode relative to the 'helicopter' mode. Therefore, a lower probability of sticking is encountered where the molecule adopts a 'cartwheel' configuration with respect to the surface.

View the adsorption process in terms of changes in filling of molecular orbitals on the molecules and electronic bands of the solid

H_2 on Cu, S_o: low
Because Cu atoms do not readily transfer charge to the σ* orbitals of H_2

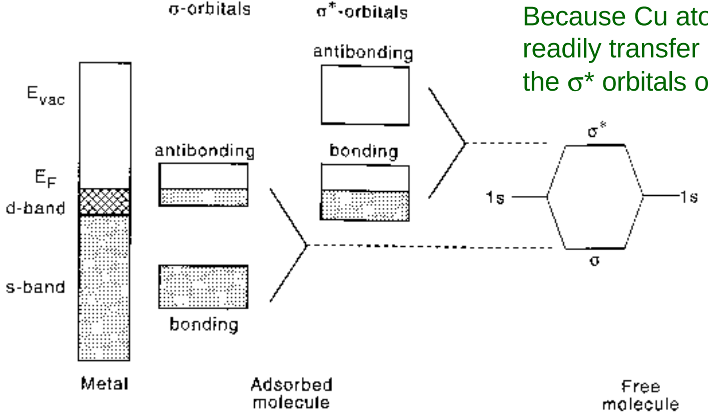


Fig. 1.10 Orbital scheme for chemisorption of a diatomic molecule on an open d-band transition metal. The metal–adsorbate bonds are formed from the original bonding and antibonding levels of the incident molecule interacting with the metal. Partial filling of the antibonding levels of the molecule weakens the intramolecular bond. Adapted from ref. 6.

以上圖來看， as diatomic gas molecules (e.g. H_2) interact with a metal surface, 2 effects should be noted:

(1) Broadening in the energy range of the individual molecular orbitals of H_2 relative to free molecules.

because of gradual mixing of electron wavefunctions on the metal and the molecule

(2) Two new sets of molecular orbitals between the adsorbed molecule and the metal (σ bonding & σ* antibonding) develop.

e^- transfer from the metal takes place into s* orbitals of the H_2 until the highest occupied electronic state of the molecule = Fermi energy E_f of the metal.

視 the extent of e^- transfer from metal to H_2 **而定**, H-H bond will weaken until the antibonding component of the bond energy exceeds the bonding component

⇒ dissociation into adsorbed atoms occurs.

Adsorbate–Adsorbate (Lateral) Interactions

There are 4 types of adsorbate–adsorbate interactions to be considered:

-
- van der Waals forces, permanent/induced dipoles, quadropoles, hydrogen bonding
-
- indirect substrate-mediated forces

♦ Direct Coulombic interactions

For adatoms that have undergone charge transfer with the substrate

For example: adsorption of alkali metals ⇒

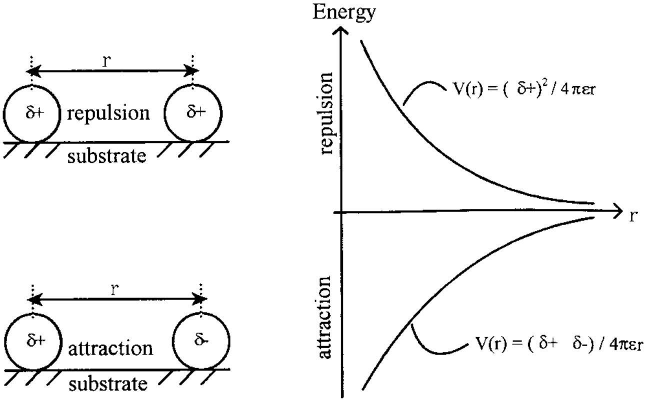


Fig. 1.31 Variation in electrostatic interactions as a function of adsorbate separation for adsorbates forming strongly polar bonds to the surface.

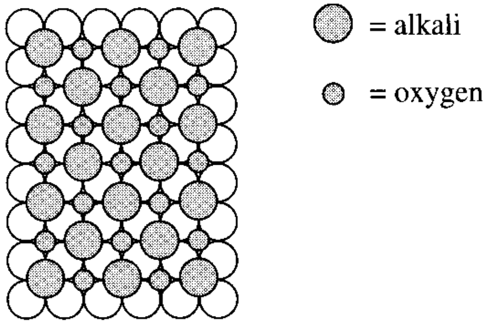


Fig. 1.32 Co-adsorption of electropositive and electronegative adsorbates to generate an intermixed phase. This phase is a surface analogue of a two-dimensional salt.

Co-adsorption of a strongly electropositive element with a strongly electronegative element

⇒ form intimately mixed structures that maximize ionic interactions between oppositely charged adsorbates

- **Covalent / metallic bonding**

  "metallic" – can occur between two adsorbates as long as each possesses a partially filled valence orbital

  典型例子：adsorption of transition metal onto metal surface

  ⇒ metal-metal bond

  Covalent bonding **則較** rare

- **van der Waals forces**
  - generally attractive in origin
  - occur in the so-called self-organization or self-assembled monolayers
  - M.W. ↑, vdw force ⇒ dominant in adlayers of large non-polar adsorbates

- **Indirect interactions**

  complex in nature (beyond the scope of this course)

Effect of lateral interactions on the distribution of adsorbates

- **Net attractive lateral interactions**

Attractive lateral interactions lead to a distribution of adsorbates in the form of “2D islands”, exhibiting “local” coverages considerably higher than the overall coverage averaged over the entire surface.

“edge” atoms **位能較高：**

to maximize stability ⇒ growth of islands

For a perfect, defect-free surface at 0 K, the lowest energy state is for adsorbates to condense into one large circular 2D island.

“ ”：Formation of large islands from small ones

當 $T > 0\text{K}$ **時,** $G = H - TS$, $\Delta S = S_{\text{random}} - S_{\text{island}}$, $T\Delta S$ favors break-up of islands

As T↑ ⇒ driving forces for adatoms to detach themselves from the island & form a “2D gas”

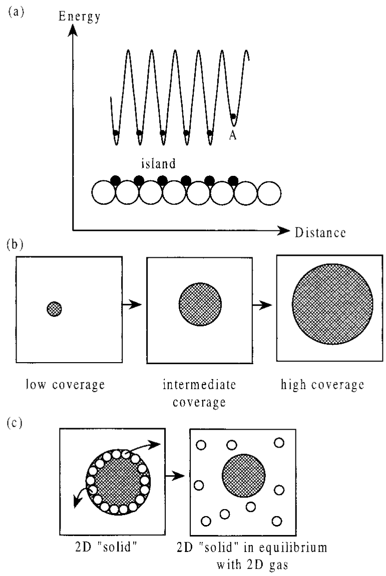


Fig. 1.33 (a) Potential energy diagram for atoms exhibiting attractive lateral interactions and forming a two-dimensional island. Note that edge atoms possess a higher potential energy than those within the island. (b) At 0 K, the island size increases with coverage (Ostwald ripening). (c) At finite temperatures, edge atoms may detach themselves from the island forming a two-dimensional gas in equilibrium with a two-dimensional solid (the island size decreases).

The arrangement of adsorbed atoms & molecules within the island relative to the underlying substrate (   ) may be termed:

“**commensurate**” overlayer forms when substrate-adsorbate interactions tend to dominate over lateral adsorbate-adsorbate interactions

⇒ All of the elements of the matrix notation are integers

⇒ Interadsorbate separation is either equal or a simple multiple of the substrate spacing “**incommensurate**” overlayer forms when adsorbate-adsorbate interactions are of similar magnitude to adsorbate-substrate interactions

⇒ The elements of the matrix notation are rational numbers (coincidence lattice)

⇒ Spacing adopted is a compromise between maximizing both adsorbate-substrate and adsorbate-adsorbate interactions

“incoherent”: if the elements of the matrix are irrational, no common periodicity exists between the overlayer and substrate lattice (also incommensurate)

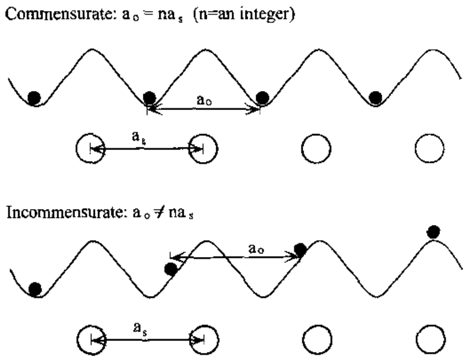


Fig. 1.34 Commensurate and incommensurate surface phases. Open circles represent substrate atoms. Filled circles correspond to adsorbate molecules. a_s = interatomic spacing of substrate surface atoms. a_o = interatomic spacing of overlayer atoms.

§ Net repulsive lateral interactions

Adsorbates exhibiting net repulsive interactions tend to form dispersed phases for a given surface coverage. The system’s free energy must be minimized by maximizing the average distance between adsorbates.

Such systems often form ordered “super structures” at least for low & medium coverages, usually commensurate.

[as θ , incommensurate phases may form.]

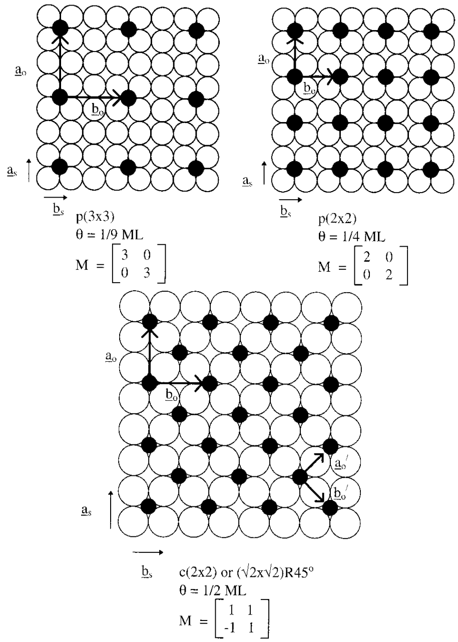


Fig. 1.35 Changes in the surface geometry as a function of coverage for an adsorbate exhibiting repulsive lateral interactions.

Mobility in Two Dimensions

Surface diffusion: the process of migration of atoms/molecules across a surface

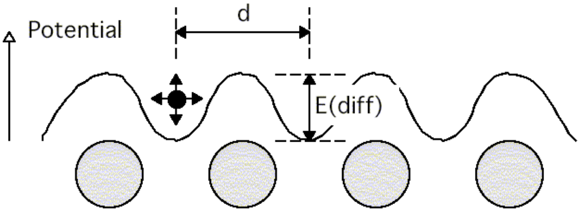
For a given substrate-adsorbate combination, the rate of diffusion is critically dependent on:

(a)

(b)

(c)

Surface diffusion



$$D(q,T) = D_0 \exp(-\frac{E_{\text{diff}}(q)}{RT})$$

$D(q, T)$: diffusion coefficient (cm^2·s^{-1})

E_{diff}: activation energy barrier (KJ·mol^{-1})

D_0: pre-exponential factor called diffusivity (cm^2·s^{-1})

T: absolute temperature

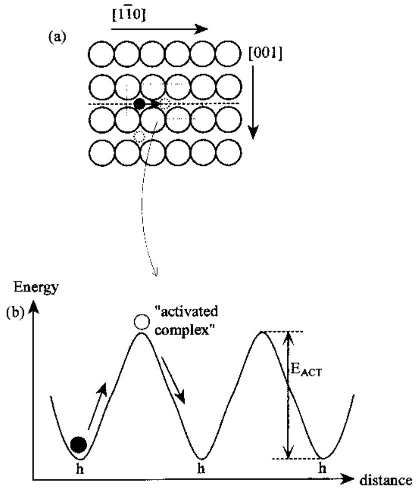


Fig. 1.27 (a) Diffusion of an adatom between adjacent fourfold hollow sites along the [0$\bar{1}$1] direction. (b) The corresponding potential energy diagram for diffusion in this direction. h = fourfold hollow site.

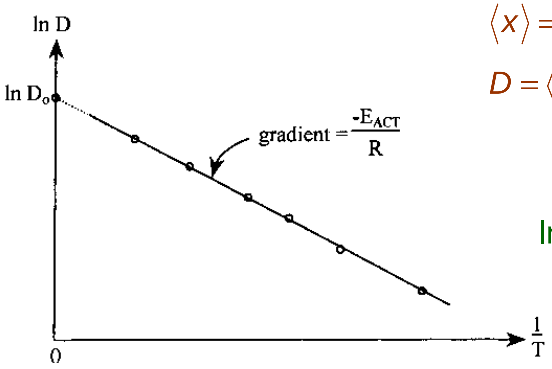
$$D(q,T) = D_0 \exp(-\frac{E_{\text{diff}}(q)}{RT})$$

The diffusivity is related to the entropy change between the equilibrium hollow site and the “activated complex”. An approximation often assumed is that the entropies of the two are the same. In such cases, D_0 may be assumed to be ≅ 10^{-2} $\text{cm}^2 \cdot \text{s}^{-1}$.

The activation barrier and hence the diffusion coefficient will be different in the two crystallographic direction.

⇒ Surface diffusion is an anisotropic process.

Assume that diffusion occurs via a “**random walk**” process:



average distance travelled

$$\langle x \rangle = (Dt)^{1/2}$$

$$D = \langle x \rangle^2 / t$$

$$\ln\left(\frac{\langle x \rangle^2}{t}\right) = \ln D_0 - \frac{E_{\text{diff}}}{R}\frac{1}{T}$$

Fig. 1.28 Determination of E_{ACT} and D_0 from measurements of the diffusion coefficient as a function of temperature.

Activation energies for surface self-diffusion E_{diff} and diffusion constant D_0 for several metals

Material	E(diff) ($\text{kJ}\cdot\text{mol}^{-1}$)	D_0 ($\text{cm}^2\cdot\text{s}^{-1}$)
Ni	158.8	300
Pt	110-125	$4\text{x}10^{-3}$
Rh	173.5	$4\text{x}10^{-2}$
Re	217.4	1.0
W	284-326	0.85
Cu	171-192	650
Au	146-176	0.37
Mo	217-234	0.8

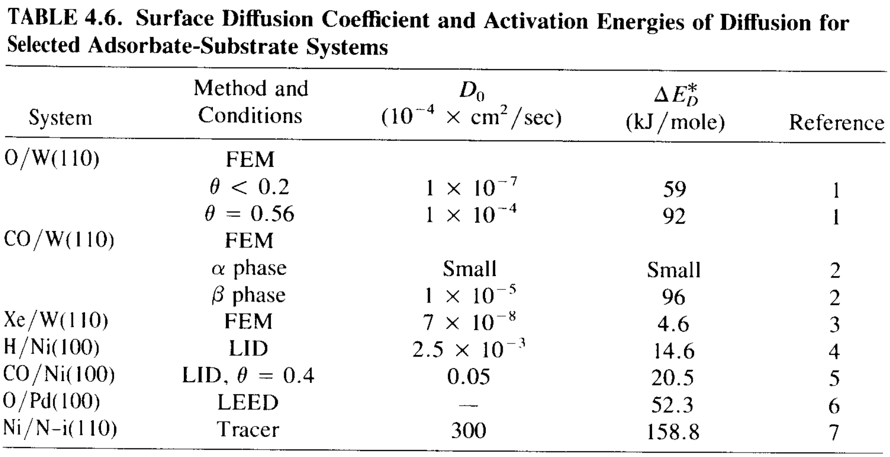


TABLE 4.6. Surface Diffusion Coefficient and Activation Energies of Diffusion for Selected Adsorbate-Substrate Systems

System	Method and Conditions	D_0 ($10^{-4} \times \text{cm}^2/\text{sec}$)	ΔE_D^* (kJ/mole)	Reference
O/W(110)	FEM			
	$\theta < 0.2$	1×10^{-7}	59	1
	$\theta = 0.56$	1×10^{-4}	92	1
CO/W(110)	FEM			
	α phase	Small	Small	2
	β phase	1×10^{-5}	96	2
Xe/W(110)	FEM	7×10^{-8}	4.6	3
H/Ni(100)	LID	2.5×10^{-3}	14.6	4
CO/Ni(100)	LID, $\theta = 0.4$	0.05	20.5	5
O/Pd(100)	LEED	—	52.3	6
Ni/N-i(110)	Tracer	300	158.8	7

For strongly interacting atoms, particularly for metal atoms deposited on metal substrate, exchange mechanism can occur.

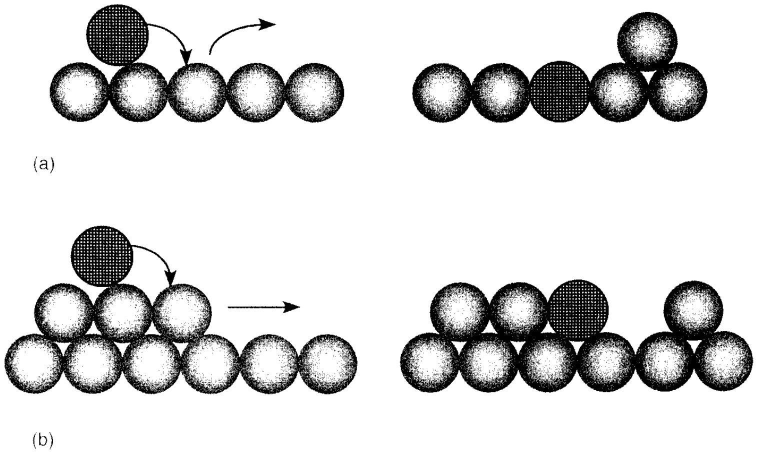


Figure 3.4 The exchange mechanism of diffusion. Mass transport occurs via the replacement of one atom with another. This can happen either (a) on a terrace or (b) at a step

This mechanism is particularly important for metal-on-metal growth system.

Some general observations:

- In general, high ΔH_{ads} produces high E_{diff}.

  physisorbed molecules: lower diffusion activation energies

  $\Rightarrow$ mobile at ambient temperatures

  chemisorbed molecules: higher diffusion activation energies

  $\Rightarrow$ remain virtually immobile at similar temperatures

$$\Omega = \frac{E_{diff}}{\Delta H_{ads}} \qquad \text{corrugation ratio}$$

For metal/metal $\Omega \sim 0.13$

for nonmetal/metal $\Omega \sim 0.23$

- D and E_{diff} can be strongly dependent upon surface coverage (due to lateral interactions).

Diffusion of atomic oxygen on body-centered cubic W(100) surface

As $q < 0.5$ ML, no O atoms need to occupy nearest-neighbor sites.

As $q \geq 0.5$ ML, O atoms are forced into nearest-neighbor sites. The strong mutual repulsion leads to an increase in the potential of these adsorbate, hence the rapid lowering of E_{diff}.

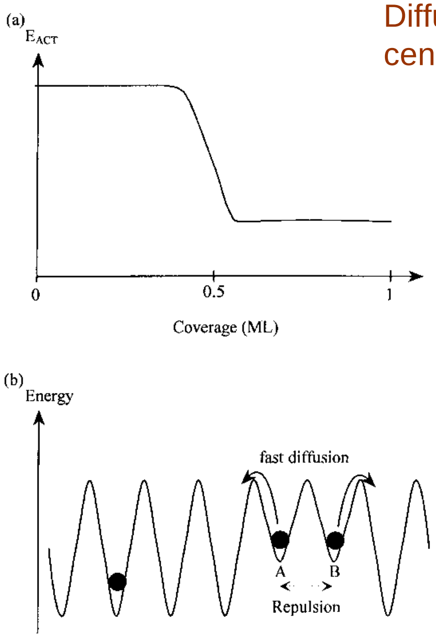
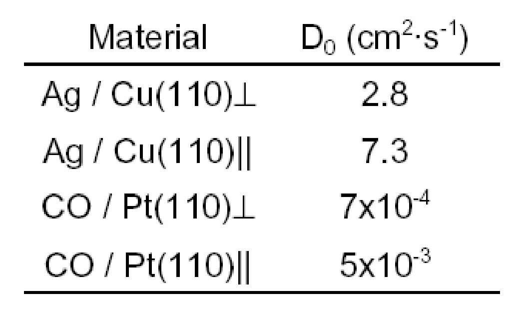


Fig. 1.30 (a) Variation of E_{ACT} as a function of coverage. (b) The corresponding potential energy diagram. Note that at coverages greater than 0.5 ML, nearest–neighbour sites become occupied leading to a decrease in E_{ACT} owing to repulsive lateral interactions.

- Adatoms may self-diffuse by exchange with surface.
- Vacancies diffuse by successive atom filling.
- Adatoms may hop multiple *d* spacing in single event.
- *D* is higher along natural troughs in surface. – FCC(110)



Material	D_0 ($cm^2 \cdot s^{-1}$)
Ag / Cu(110)⊥	2.8
Ag / Cu(110)‖	7.3
CO / Pt(110)⊥	7×10^{-4}
CO / Pt(110)‖	5×10^{-3}

- *D* often higher for close-packed surfaces

  For FCC surfaces

stepped < (100) < (110) < (111)

$\longrightarrow$

increasing diffusion coefficient

$\longleftarrow$

increasing surface ‘roughness’

- Vacancies diffuse by successive atom filling.

Material	D_0 ($cm^2 \cdot s^{-1}$)
W / W(211)⊥	4.2×10^{-9}
W / W(211)||	7.7×10^{-3}
H / W(211)⊥	1×10^{-5}
H / W(211)||	2×10^{-4}

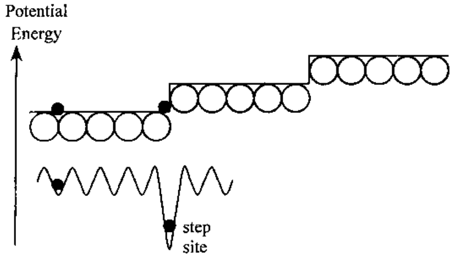


Fig. 1.29 One-dimensional energy profile in the direction of a surface step. Note, the larger activation energy barrier for diffusion from step to terrace sites as compared to diffusion on terraces.

於 step sites ⇒ offers more coordination

∴ adatom is bound more strongly at a step site

(i.e. higher diffusion activation energy across a surface step)

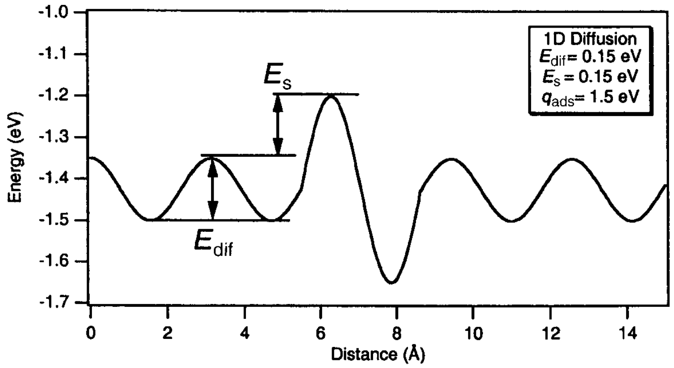


Figure 3.3 The effect of a step on diffusion energy, E_{dif} [one-dimensional (1D) diffusion]. Note that step-up diffusion is often negligible because of the increased barrier; note also the increased binding strength at the bottom of the step—a feature that is often observed. E_s, Ehrlich–Schwoebel barrier; q_{abs}, depth of the attractive well

---

Surface Chemical Reactions

Surface reactions may be divided into three categories:

1. reactions: materials from the gas phase interacts with the surface to produce new chemical species that include atoms from the surface.

- *volatilization reactions:* product species returns to the gas phase and the surface is progressively consumed.

e.g. $H_2O + C \rightarrow CO + H_2$

$Cl_2 + Ni \rightarrow NiCl_2$

$3O_2 + 2Mo \rightarrow 2MoO_3$

- *corrosion layer formation:* nonvolatile surface compounds is formed.

$O_2 + Fe \rightarrow FeO_x$

$S + Ni \rightarrow NiS$

2. reactions: material is deposited on the surface, with or without a decomposition reaction, to extend the surface or to form the solid phase of new material.

- *physical vapor deposition (PVD):*

  $(Ag)_v \rightarrow (Ag)_s$

- *molecular beam epitaxy (MBE):*

  $2(Ga)_v + (As_2)_v \rightarrow 2GaAs$

- *chemical vapor deposition (CVD):*

  $(NiCl_2)_g \rightarrow (Ni)_s + (Cl_2)_g$

---

3. reactions: material from the surface is not directly involved in the species synthesized or decomposed. The surface serves as a site at which the reaction is enhanced relative to its rate in the gas phase.

- *exchange reactions:*

  $(H_2)_g + (D_2)_g \rightarrow 2(HD)_g$

- *recombination reactions:*

  $H_a + H_a \rightarrow (H_2)_g$

- *unimolecular decomposition reactions:*

  $(N_2O)_g \rightarrow (N_2)_g + O_a$

  $(CHOOH)_g \rightarrow CO + CO_2 + H_2 + H_2O$

- *bimolecular decomposition reactions:*

  $2(CO)_g + (O_2)_g \rightarrow 2(CO_2)_g$

  $CO + 2H_2 \rightarrow CH_4 + H_2O$

Heterogeneous Catalysis

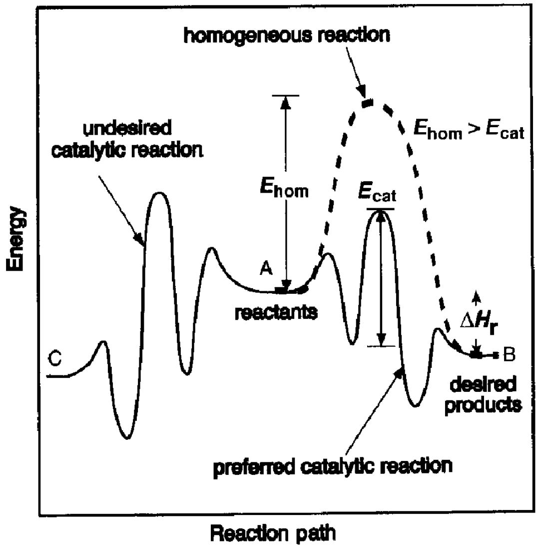


Figure 2 Activation energies and their relationship to an active and selective catalyst. (a) Reactants; (b) desired product; (c) undesired product; E_{hom}, activation barrier for the homogeneous reaction; E_{cat}, activation barrier with use of catalyst; ΔH_r, change in enthalpy of reactants compared with product.

Catalytic action

Kinetic expressions

- catalytic reaction turnover frequency *J*:

  the # of molecules formed per second
- turnover time 1/*J*:

  the time necessary to form a product molecule
- specific turnover rate *R* = *J*/*A*:

  (molecules/cm^2/s), *A*: catalyst surface area

  Since the total # of catalytically active sites could be much smaller than the total # of available surface sites, *R* defined this way gives a conservative lower limit of the catalytic turnover rate.
- turnover number: $R \cdot \delta t$, δt is the total reaction time

  The turnover number must be on the order of 10^2 or larger for the reaction to qualify as catalytic.

While the turnover number provides a figure of merit for the activity of the catalyst sites, the reaction probability RP reveals the overall efficiency of the catalytic process under the reaction conditions.

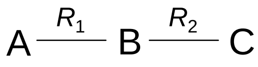
$$\mathrm{RP} = \frac{\text{rate of formation of product molecules}}{\text{rate of incident of reactant molecules}}$$

RP can be readily obtained by dividing *R* by the rate of molecular incidence *I*.

Selective catalysis

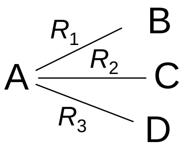
In general, catalyzed reactions involve either

(a) successive kinetic steps to the final product or



Example: stepwise dehydrogenation of cyclohexane to cyclohexene to benzene.

(b) simultaneous reaction paths yielding two or more products.



Example: reaction of *n*-hexane in the presence of excess H_2 can produce benzene, cyclic molecules, branched isomers, or shorter-chain species.

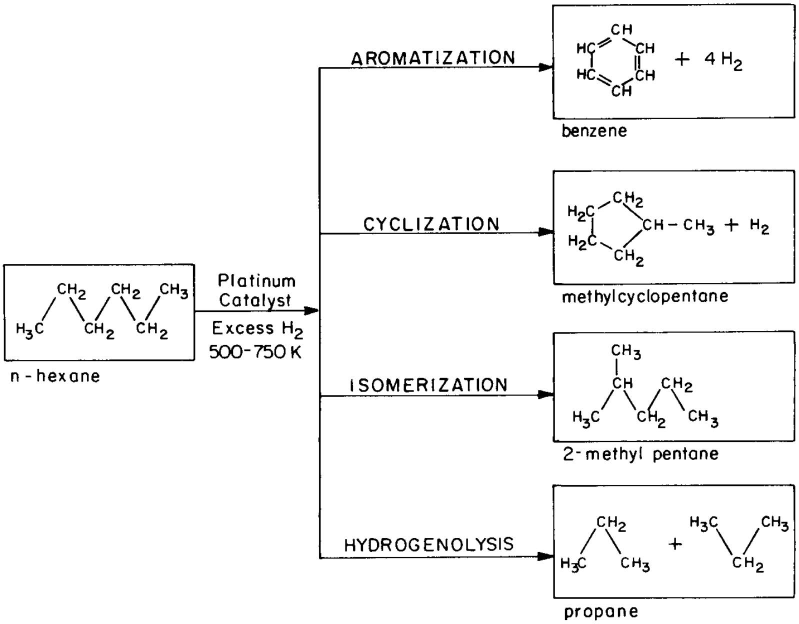


Figure 7.2. Various organic molecules that can all be produced by the catalyzed reactions of *n*-hexane [188].

Source: "Introduction to Surface Chemistry and Catalysis" by G. A. Somorjai (1994).

Fractional catalytic selectivity:

For competitive parallel reactions

$$A \xrightarrow{R_1} B$$

$$X \xrightarrow{R_2} Y$$

Kinetic selectivity:

Qualitative aspects of heterogeneous catalysis

A sequence of events of a surface-catalyzed process might be:

(1) gas diffusion to surface (usually fast)

(2) adsorption of reactants onto surface (slow if activated)

(3) surface diffusion of reactants to active sites

(4) reaction of adsorbed species (often rate-determining)

(5) desorption of products (often slow)

(6) gas diffusion away from surface

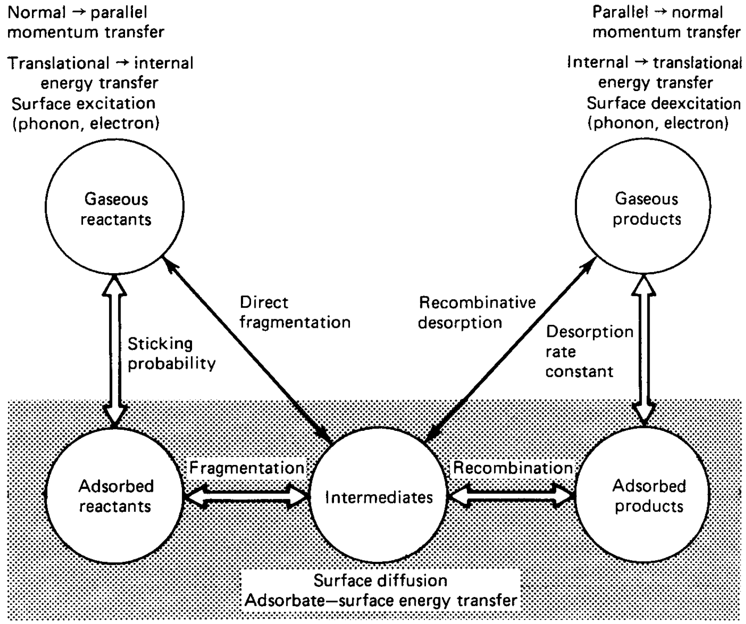


Fig. XVII-18. Schematic illustration of the steps that may be involved in a surface-mediated reaction: initial adsorption, subsequent thermalization, diffusion and surface reaction, and desorption. (From Ref. 180; copyright 1984 by the AAAS.)

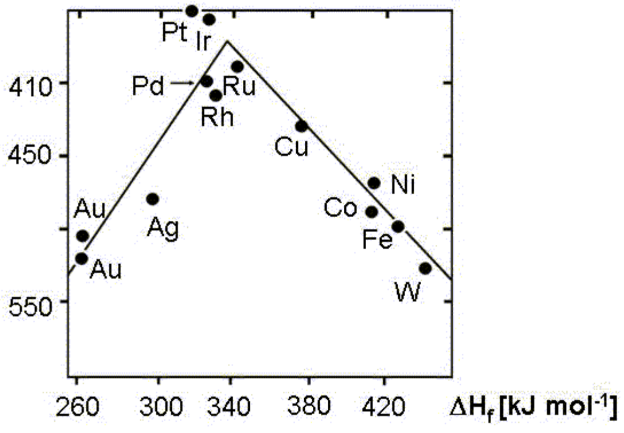
Source: "Physical Chemistry of Surfaces" by A. W. Adamson, 5th Ed.

- Diffusion-limited behavior (1 & 6) can result from porous catalyst surfaces, when molecules have to travel in & out of these pores to reach their adsorption sites.
- Adsorption- or desorption-limited behavior (2 & 5) can result when reactants or products are strongly adsorbed (i.e. $|\Delta H_{ad}|$ is large).

⇒ An effective catalyst thus requires the appropriate relationship between reactant and product binding energies

Bad case 1: the reactants are so weakly bound as to not allow sufficient residence time on the surface.

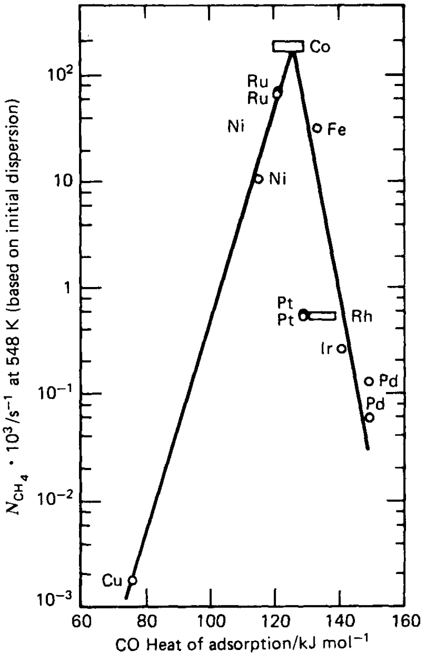
Bad case 2: the products are so strongly bound as to not allow their desorption at reasonable temperature, thus self-poisoning the reaction. New reactants cannot adsorb on filled sites.



Activity ~ temperature [K] for a specified conversion of formic acid on a metal catalyst

„... an intermediate compound is formed at the surface of the catalyst. Too high an enthalpy of formation would not facilitate catalysis, and neither would too low a value as, in this case, there would be little propensity for the intermediate compound to form. An optimum value of the enthalpy would balance out these two conflicting tendencies, and this is why the peak of the "volcano" corresponds to the highest catalytic activity."

Source: http://www.techem.ruhr-uni-bochum.de/techem/de/katalyse/Valcano.html



Source: "Physical Chemistry of Surfaces" by A. W. Adamson, 5th edition (1990).

Fig. XVII-21. Turnover frequencies for methanation using silica-supported metals.

Examples of important heterogeneous catalysis

- Habor-Bosch process

  $N_2 + 3H_2 \rightarrow 2NH_3$

  (200-300 bar, 670-770 K, catalyst: $Fe/K/CaO/Al_2O_3$)

- Fischer-Tropsch synthesis & related chemistry

  Fischer-Tropsch chemistry proceeds via a complex set of reactions that consume CO and H_2 (synthesis gas or "syn" gas) and produce alkanes, alkenes, alcohols, and other oxygenated compounds, aromatics as well as CO_2 and H_2O.

$$nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$$

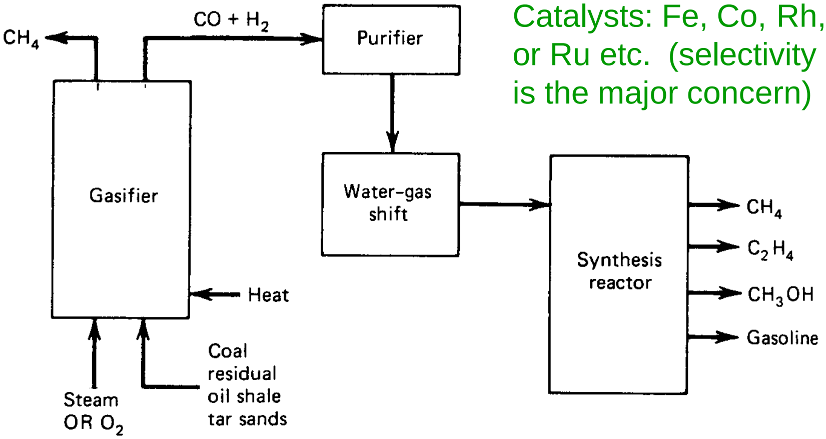
$$nCO + 2nH_2 \rightarrow C_nH_{2n} + H_2O$$

$$nCO + 2nH_2 \rightarrow C_nH_{2n+1}OH + (n-1)H_2O$$

$$2nCO + (n+1)H_2 \rightarrow C_nH_{2n+2} + nCO_2$$

$$2nCO + nH_2 \rightarrow C_nH_{2n} + nCO_2$$

$$(2n-1)CO + (n-1)H_2 \rightarrow C_nH_{2n+1}OH + (n-1)CO_2$$



Catalysts: Fe, Co, Rh, or Ru etc. (selectivity is the major concern)

Fig. XVII-20. Gasification of hydrogen-deficient materials as a route to the production of clean fuels and chemicals. Reprinted with permission from M. A. Vannice, *Adv. in Chemistry*, No. 163, J. B. Goodenough and M. S. Whittingham, eds., American Chemical Society, Washington, D.C., 1977 (Ref. 237). Copyright 1977, American Chemical Society.

Fischer-Tropsch chemistry is the basis of the synthetic fuels industry.

Source: "Physical Chemistry of Surfaces" by A. W. Adamson, 5th edition (1990).

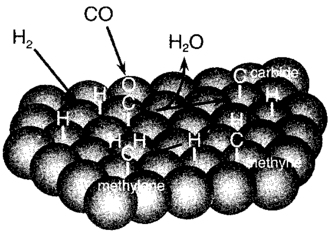


Figure 5.5 The dissociation of CO followed by hydrogenation to form an adsorbed methylene (CH_2) species. The formation of methylene is an essential step in Fischer–Tropsch synthesis. CH_2 is the product of sequential hydrogen addition steps that follow the dissociative adsorption of H_2 and CO. Oxygen is removed from the surface via H_2O formation

Source: "Surface Science" by K. W. Kolasinski (2002).

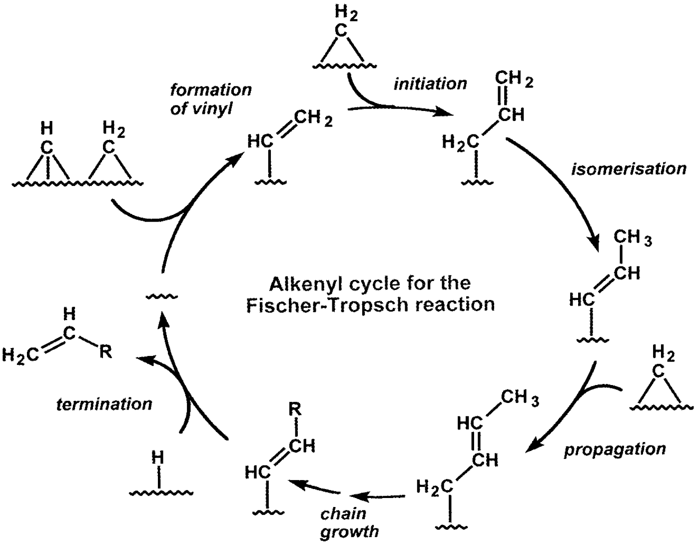


Figure 5.6 The alkenyl carrier cycle. The cycle begins in the top left-hand side of the figure with the formation of adsorbed vinyl ($HC{=}CH_2$) from CH and CH_2. Chain growth ensues, initiated by the addition of CH_2. Isomerization forms an adsorbed allyl ($H_2C{-}CH{=}CH_2$). Subsequently, further addition of CH_2 (propagation and chain growth) competes with addition of H (termination). Reproduced with permission from P. M. Maitlis, H. C. Long, R. Quyoum, M. L. Turner and Z.-Q. Wang, *Chem. Commun.* (1996) 1, by permission of the Royal Society of Chemistry

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- Three-way automotive catalyst

The threeway automotive catalyst is so named because it removes the three unwanted products CO, HC, and NO_x.

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

$$\text{hydrocarbons} + O_2 \rightarrow H_2O + CO_2$$

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O$$

$$NO + CO \rightarrow \tfrac{1}{2}N_2 + CO_2$$

$$NO + H_2 \rightarrow \tfrac{1}{2}N_2 + H_2O$$

$$\text{hydrocarbons} + NO \rightarrow N_2 + H_2O + CO_2$$

$$NO + \tfrac{5}{2}H_2 \rightarrow NH_3 + H_2O$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

$$\text{hydrocarbons} + H_2O \rightarrow CO + CO_2 + H_2$$

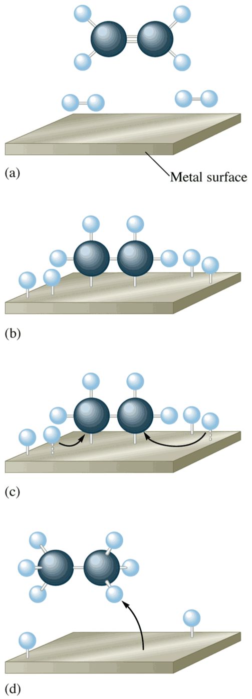
$$3NO + 2NH_3 \rightarrow \tfrac{5}{2}N_2 + 3H_2O$$

$$2NO + H_2 \rightarrow N_2O + H_2O$$

$$2N_2O \rightarrow 2N_2 + O_2$$

$$2NH_3 \rightarrow N_2 + 3H_2$$

The general composition consists of Rh, Pt, and Pd dispersed on Al_2O_3 with CeO_2 added as a type of promoter.



Heterogeneous catalysis of the hydrogenation of ethylene

$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$

Catalyst: Pt, Pd, or Ni

Another example:

$2\ SO_2(g) + O_2(g) \rightarrow 2\ SO_3(g)$

Catalyst: Pt/V_2O_5

$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$

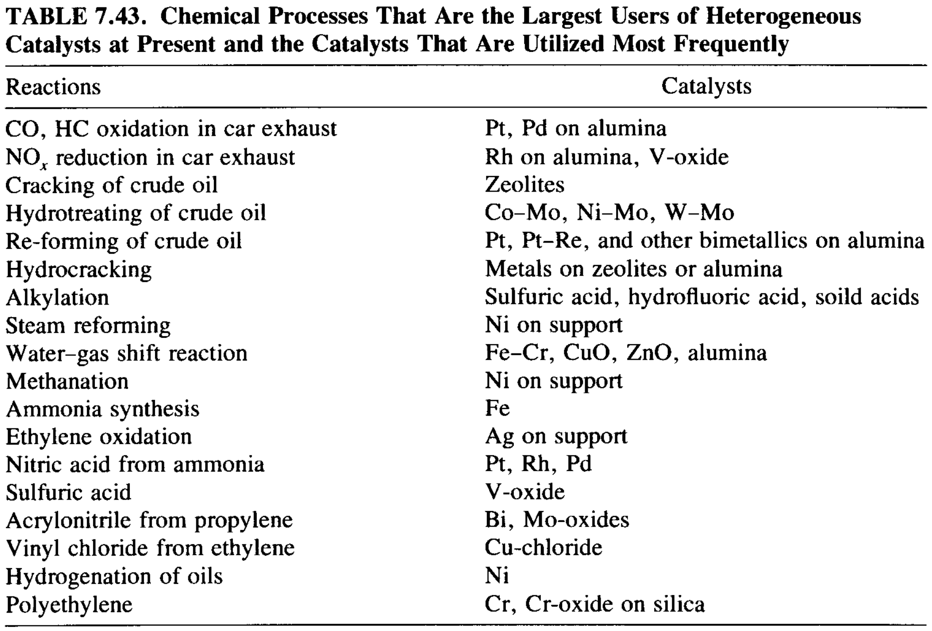


TABLE 7.43. Chemical Processes That Are the Largest Users of Heterogeneous Catalysts at Present and the Catalysts That Are Utilized Most Frequently

Reactions	Catalysts
CO, HC oxidation in car exhaust	Pt, Pd on alumina
NO_x reduction in car exhaust	Rh on alumina, V-oxide
Cracking of crude oil	Zeolites
Hydrotreating of crude oil	Co–Mo, Ni–Mo, W–Mo
Re-forming of crude oil	Pt, Pt–Re, and other bimetallics on alumina
Hydrocracking	Metals on zeolites or alumina
Alkylation	Sulfuric acid, hydrofluoric acid, soild acids
Steam reforming	Ni on support
Water–gas shift reaction	Fe–Cr, CuO, ZnO, alumina
Methanation	Ni on support
Ammonia synthesis	Fe
Ethylene oxidation	Ag on support
Nitric acid from ammonia	Pt, Rh, Pd
Sulfuric acid	V-oxide
Acrylonitrile from propylene	Bi, Mo-oxides
Vinyl chloride from ethylene	Cu-chloride
Hydrogenation of oils	Ni
Polyethylene	Cr, Cr-oxide on silica

Source: “Introduction to Surface Chemistry and Catalysis” by G. A. Somorjai (1994).

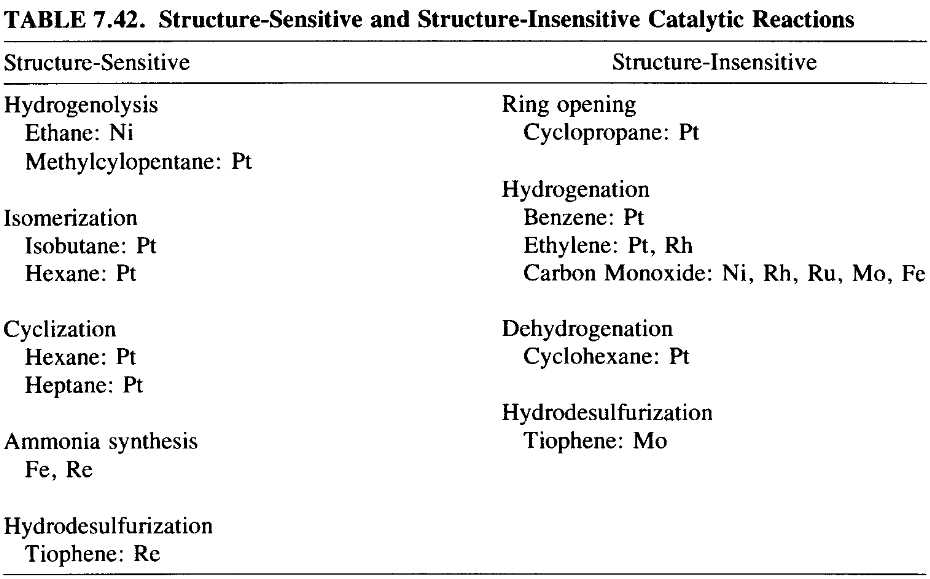


TABLE 7.42. Structure-Sensitive and Structure-Insensitive Catalytic Reactions

Structure-Sensitive	Structure-Insensitive
Hydrogenolysis	Ring opening
Ethane: Ni	Cyclopropane: Pt
Methylcylopentane: Pt	
	Hydrogenation
Isomerization	Benzene: Pt
Isobutane: Pt	Ethylene: Pt, Rh
Hexane: Pt	Carbon Monoxide: Ni, Rh, Ru, Mo, Fe
Cyclization	Dehydrogenation
Hexane: Pt	Cyclohexane: Pt
Heptane: Pt	
	Hydrodesulfurization
Ammonia synthesis	Tiophene: Mo
Fe, Re	
Hydrodesulfurization	
Tiophene: Re	

Source: "Introduction to Surface Chemistry and Catalysis" by G. A. Somorjai (1994).

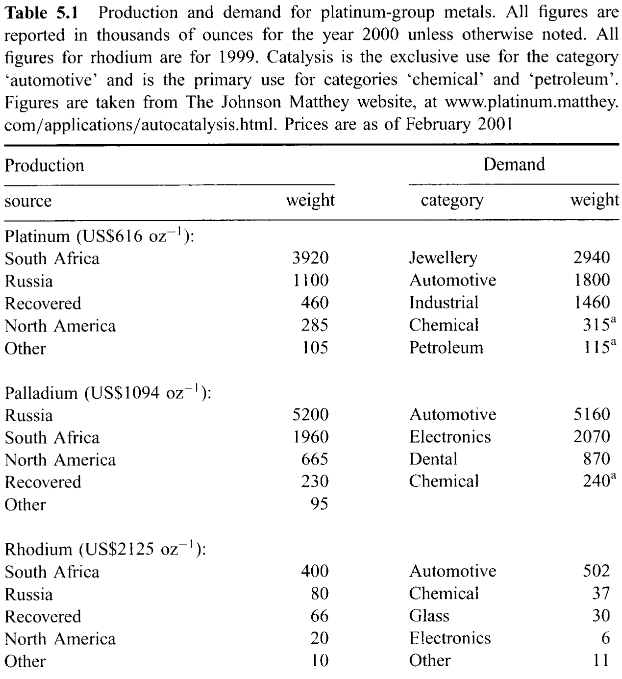


Table 5.1 Production and demand for platinum-group metals. All figures are reported in thousands of ounces for the year 2000 unless otherwise noted. All figures for rhodium are for 1999. Catalysis is the exclusive use for the category 'automotive' and is the primary use for categories 'chemical' and 'petroleum'. Figures are taken from The Johnson Matthey website, at www.platinum.matthey.com/applications/autocatalysis.html. Prices are as of February 2001

Production		Demand	
source	weight	category	weight
Platinum (US\$616 oz^{-1}):			
South Africa	3920	Jewellery	2940
Russia	1100	Automotive	1800
Recovered	460	Industrial	1460
North America	285	Chemical	315[a]
Other	105	Petroleum	115[a]
Palladium (US\$1094 oz^{-1}):			
Russia	5200	Automotive	5160
South Africa	1960	Electronics	2070
North America	665	Dental	870
Recovered	230	Chemical	240[a]
Other	95		
Rhodium (US\$2125 oz^{-1}):			
South Africa	400	Automotive	502
Russia	80	Chemical	37
Recovered	66	Glass	30
North America	20	Electronics	6
Other	10	Other	11

[a] 1999.

Source: "Surface Science" by K. W. Kolasinski (2002).