Chapter 14 Summary
Catalysis by Metals

Metals are very common catalysts

Table 12.7 A selection of the reactions catalyzed by supported metals

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

Metals work by same mechanisms as other catalysts:

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

Generally metal catalyzed reactions follow catalytic cycle with adsorbtion, reaction, desorption

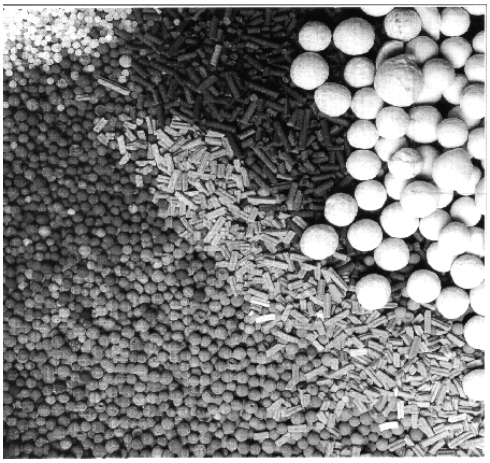


Figure 12.3 Pictures of some heterogenous catalysts. From Wijngaarden et al. Industrial Catalysis, Wiley 1998.

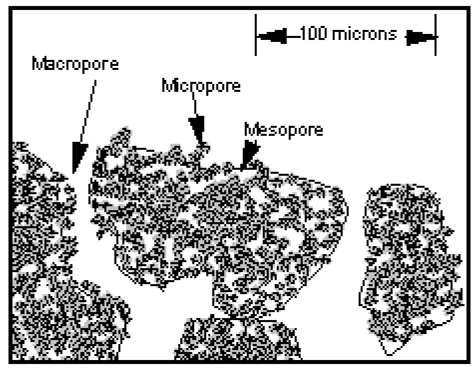


Figure 14.3 A cross sectional diagram of a typical catalyst support.

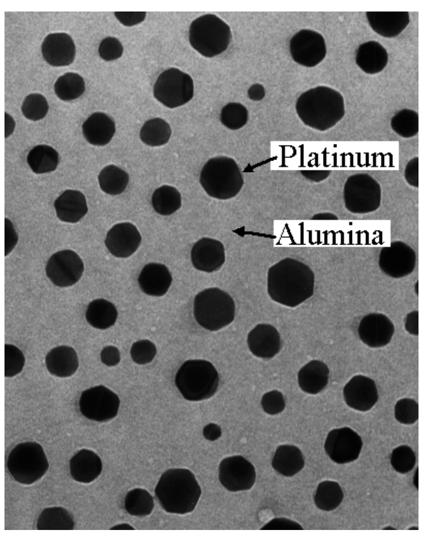


Figure 12.4 A picture of a supported metal catalyst.

Types of surface reactions:

- Simple molecular adsorption reactions
- Dissociative adsorption reactions
- Bond scission reactions
- Addition reactions
- Recombination reactions
- Desorption reactions

Molecular Adsorption

$$CO + S \rightarrow CO_{(ad)}$$

(14.1)

$$HCo(CO)_3 + H_2C{=}CHR \rightarrow HCo(CO)_3(H_2C{=}CHR)$$

(14.2)

Dissociative adsorption (oxidative addition)

$$H_2 + 2S \rightarrow 2H_{ad}$$

$$HCo(CO)_3 + H_2 \rightarrow H_3Co(CO)_3$$

(14.3)

Bond fragmentation reactions

$$CH_3CH_2OH_{(ad)} + S \rightarrow CH_3CH_2O_{(ad)} + H_{(ad)}$$
$$CH_3CH_3O_{(ad)} + S \rightarrow CH_3CHO_{(ad)} + H_{(ad)}$$
$$CH_3CHO_{(ad)} + S \rightarrow CH_3CO_{(ad)} + H_{(ad)}$$
$$CH_3CO_{(ad)} + S \rightarrow CO_{(ad)} + CH_{3(ad)} \quad (14.4)$$

$$CH_3CH_2CO_{(ad)} + S \rightarrow CH_3CH_{2(ad)} + CO_{(ad)} \quad (14.5)$$

Association reactions

$$CH_3CH_{2(ad)} + CO_{(ad)} \rightarrow CH_3CH_2CO_{(ad)} + S \quad (14.6)$$

Combined displacement-association reactions

$$CO + CH_3CH_{2(ad)} + CO_{(ad)} \rightarrow CO_{(ad)} + CH_3CH_2CO_{(ad)} \quad (14.7)$$

Hydrogen migration

$$CH_2CH_{2(ad)} + H_{(ad)} \rightarrow CH_3CH_{2(ad)} + S$$
(14.8)

Molecular desorption:

$$CO_{(ad)} \rightarrow CO + S$$
(14.9)

Recombinative desorption (reductive elimination)

$$CH_3CH_{2(ad)} + H_{(ad)} \rightarrow CH_3CH_3 + 2S$$
(14.10)

$$2H_{(ad)} \rightarrow H_2 + 2S$$
(14.11)

Displacement reaction

$$CH_3CH_{2(ad)} + H_2 \rightarrow CH_3CH_3 + H_{(ad)} \quad (14.12)$$

$$CO + 2\ H_{(ad)} \rightarrow H_2 + CO_{(ad)} \quad (14.13)$$

$$CO + CH_2CH_{3(ad)} + H_{(ad)} \rightarrow CH_3CH_3 + CO_{(ad)} \quad (14.14)$$

β-scission

$$R_2CDCH_{2(ad)} \rightarrow R_2C{=}CH_2 + D_{(ad)} \quad (14.15)$$

General rules for overall reactions on catalysts

- There must be bare sites on the catalyst to start the reaction.
- Then at least one of the reactants must adsorb on the bare sites.
- Then there are a series of bond dissociation reactions, fragmentations, association reactions and single atom recombinations which convert the adsorbed reactants into products
- Then the products desorb.

Catalytic reactions always go through a catalytic cycle

- Adsorption
- Reaction
- Desorption

Next mechanisms of Important reactions: Olefin hydrogenation

$$CH_2{=}CH_2 + H_2 \rightarrow CH_3CH_3 \quad (14.16)$$

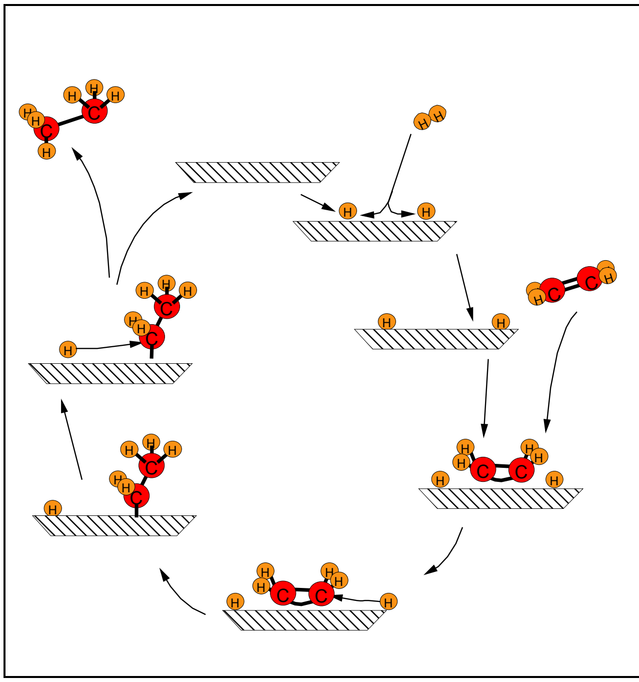


Figure 14.12 The mechanism of ethylene hydrogenation on supported platinum catalysts

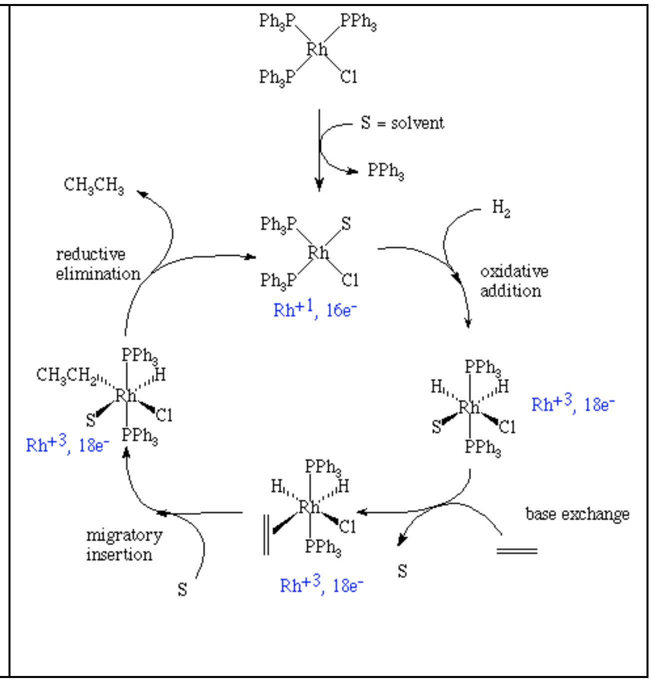


Figure 14.13 The mechanism of ethylene hydrogenation on a $RhCl(PPh_3)_3$ cluster. (Wilkinson's catalyst)

Isomerization

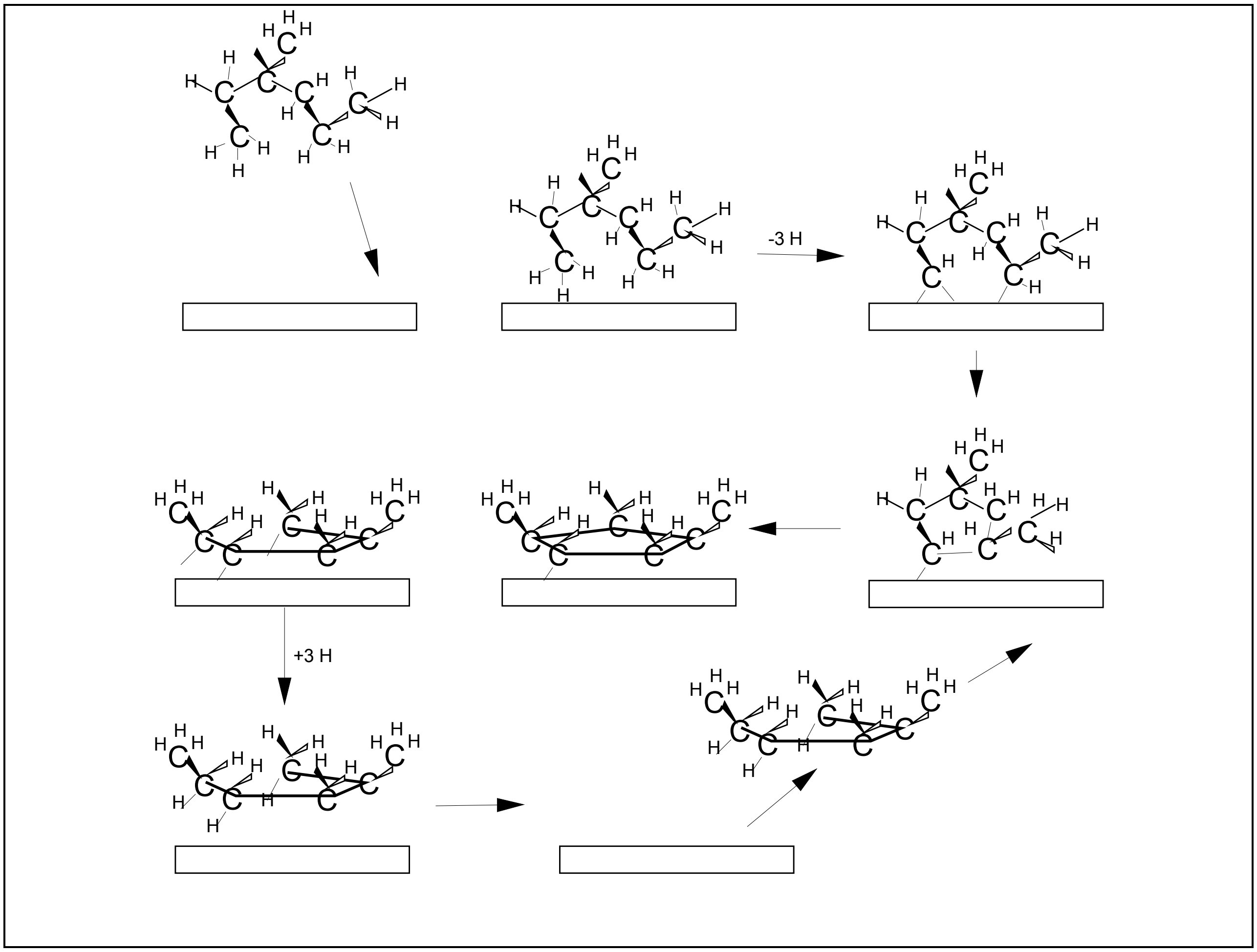


Figure 14.14 One mechanism of the 3 methyl-hexane isomerization.

Requires at least 5 carbons in the chain so called 5 center isomerization

3-centered isomerization also possible but may require a metallocarbocytron

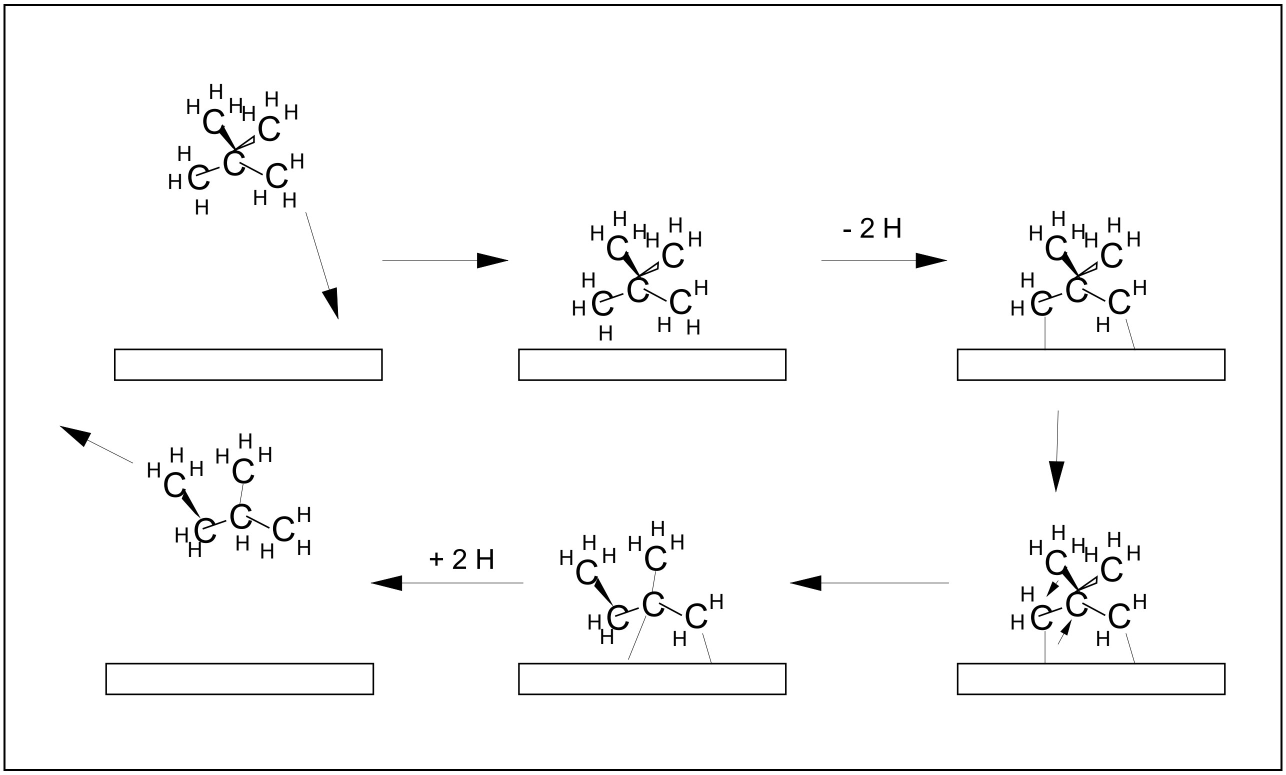


Figure 14.15 One of the proposed mechanisms of neopentane isomerization.

CO oxidation

$$CO + 1/2\ O_2 \Rightarrow CO_2$$
(14.27)

$$O_2 \ + \ 2\ S \rightarrow 2O_{(ad)}$$
(14.28)

$$CO + S \rightarrow CO_{(ad)}$$
(14.29)

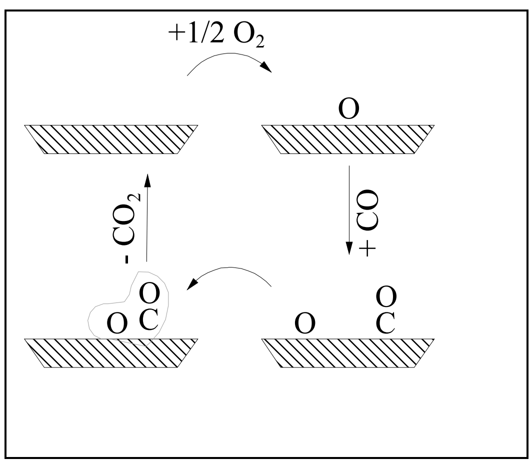


Figure14.16 **The catalytic cycle for CO oxidation**

Partial oxidation of ethylene

$$O_2 + 2\,S \rightarrow 2O_{(ad)}$$

(14.31)

$$CH_2 = CH_2 \; + \; S \rightarrow CH_2 = CH_{2(ad)}$$

(14.32)

$$CH_2 = CH_{2(ad)} + O_{(ad)} \rightarrow CH_2 \overset{O}{\acute{} - \grave{}} CH_{2(ad)}$$

(14.33)

$$CH_2 \overset{O}{\acute{} - \grave{}} CH_{2(ad)} \rightarrow CH_2 \overset{O}{\acute{} - \grave{}} CH_2$$

(14.34)

$$CH_2CH_2 \; + \; 3\,O_2 \Rightarrow \; 2CO_2 + 2\,H_2O$$

(14.35)

Hydroformulation

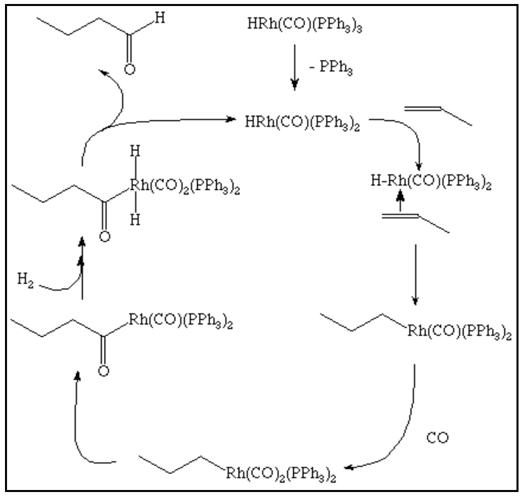


Figure 14.17 **The catalytic cycle for hydroformylation over a rhodium hydride cluster.**

$$CO + RCH = CH_2 + H_2 \Rightarrow RCH_2CH_2CHO \quad (14.36)$$

$$RCH = CH_2 + S \rightarrow RCH = CH_{2(ad)} \quad (14.37)$$

$$CO + RCH = CH_{2(ad)} + H_{(ad)} \rightarrow RCH_2CH_{2(ad)} + CO_{(ad)} \quad (14.38)$$

$$RCH_2CH_{2(ad)} + CO_{(ad)} \rightarrow RCH_2CH_2CO_{(ad)}$$
(14.39)

$$RCH_2CH_2CO_{(ad)} + H_2 \rightarrow RCH_2CH_2COH + H_{(ad)}$$
(14.40)

Principles of catalytic reaction

- Metals can help initiate reactions
- Metals can stabilize the intermediates of a reaction
- Metals can hold the reactants in close proximity and in the right configuration to react
- Metals can stretch bonds and otherwise make bonds easier to break
- Metals can donate and accept electrons

Metals are solvents for radicals. They lower the energy of radical species which allows initiation-propagation reactions to occur.

Metals Initiate reactions

consider

$$CH_2 = CH_2 + H_2 \Rightarrow CH_3CH_3$$
(14.41)

In the gas phase

$$H_2 \rightarrow 2H$$
(14.42)

$$CH_2CH_2 + H \rightarrow CH_3CH_2$$
(14.43)

$$CH_3CH_2 + H_2 \rightarrow CH_3CH_3 + H$$
(14.44)

$$2H \rightarrow H_2$$
(14.45)

reaction 14.42 is 104 kcal/mole endothermic

On a surface

$$H_2 + 2\,S \leftrightarrows 2H_{(ad)}$$

(14.46)

$$CH_2 = CH_2 + S \rightarrow CH_2 = CH_{2(ad)}$$

(14.47)

$$CH_2CH_{2(ad)} + H_{(ad)} \rightarrow CH_3CH_{2(ad)} + S$$

(14.48)

$$CH_3CH_{2(ad)} + H_2 \rightarrow CH_3CH_3 + H_{(ad)}$$

(14.49)

reaction 14.46 is 13 kcal/mole exothermic

Metals stabilize intermediates

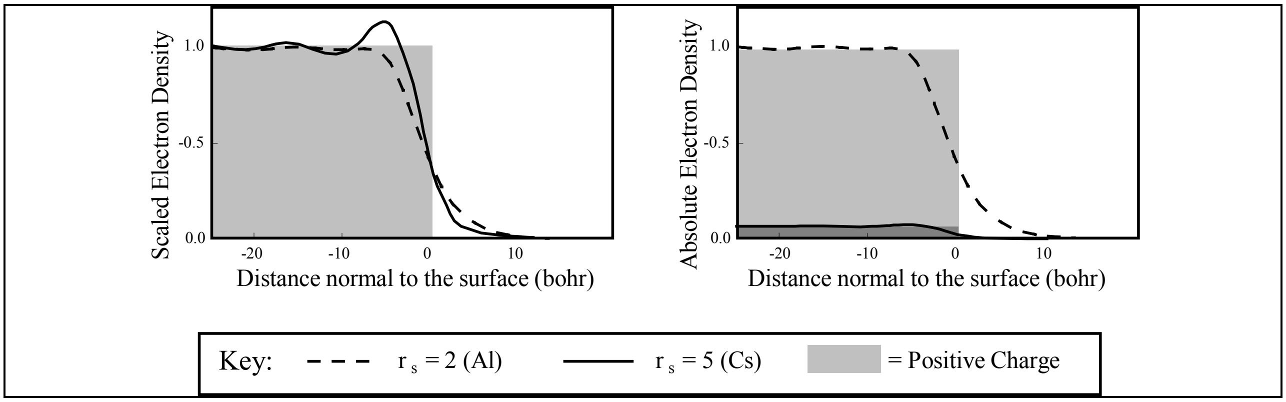


Figure 14.18 **The electron density extending out from a metal surface. (Note 1 bohr =0.52Å)**

Surface provides many free d-electrons to stabilize radicals

D-band effect

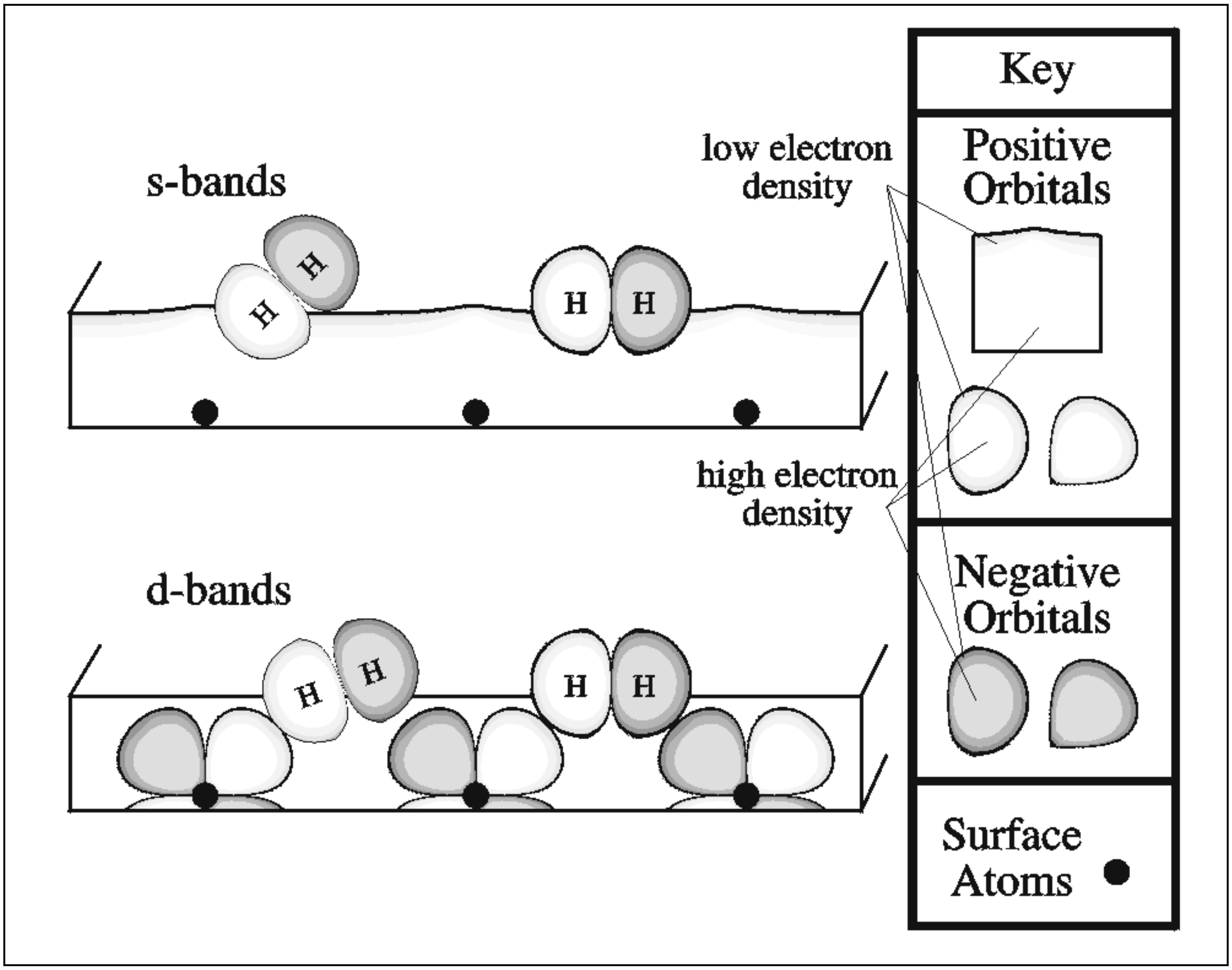


Figure 14.19 A side view of the interaction of the antibonding orbitals in H_2 with the s- and d-bands at the Γ-point in Pt(100).

Positive attracts positive, negative attracts negative

Allows four centered reactions like

$$H_2 + 2S \rightarrow \begin{matrix} H - H \\ / \quad \backslash \\ S - S \end{matrix} \rightarrow \begin{matrix} H\ H \\ |\ | \\ S - S \end{matrix} \qquad (14.51)$$

to occur.

Redox chemistry

$$C_6H_5CH_3 + O_2 \Rightarrow C_6H_5\overset{H}{C} = O + H_2O$$

(14.52)

$$Co^{3+} + C_6H_5CH_3 \rightarrow Co^{2+} + H^+ + C_6H_5\underset{H}{\overset{H}{C}}\bullet$$

(14.53)

$$C_6H_5\underset{H}{\overset{H}{C}}\bullet + O_2 \rightarrow C_6H_5\underset{H}{\overset{H}{C}}OO\bullet$$

(14.54)

$$C_6H_5\underset{H}{\overset{H}{C}}OO\bullet + Co^{2+} \rightarrow C_6H_5\overset{H}{C} = O + Co^{3+} + OH^-$$

(14.55)

$$OH^- + H^+ \rightarrow H_2O$$

(14.56)

Metals hold reactants in close proximity

$$3\ HC \equiv CH \Rightarrow C_6H_6$$

(14.58)

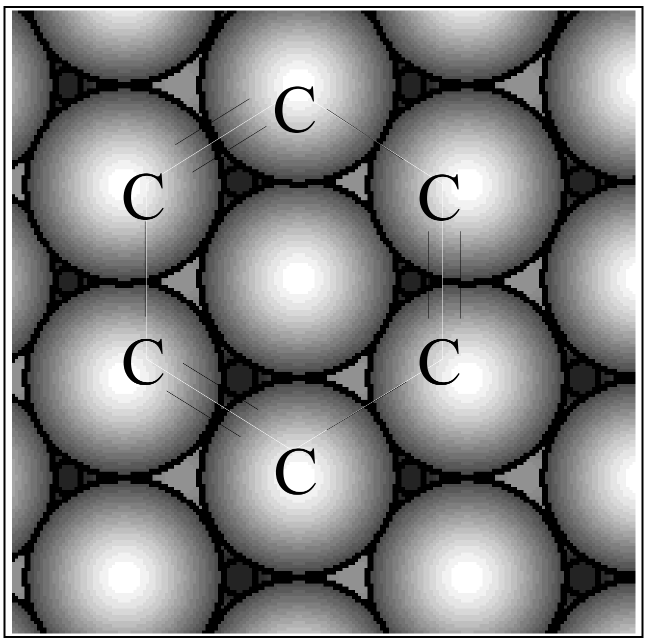


Figure 12.16 The active site for reaction (12.91) on a palladium catalyst.

Structure sensitive reactions

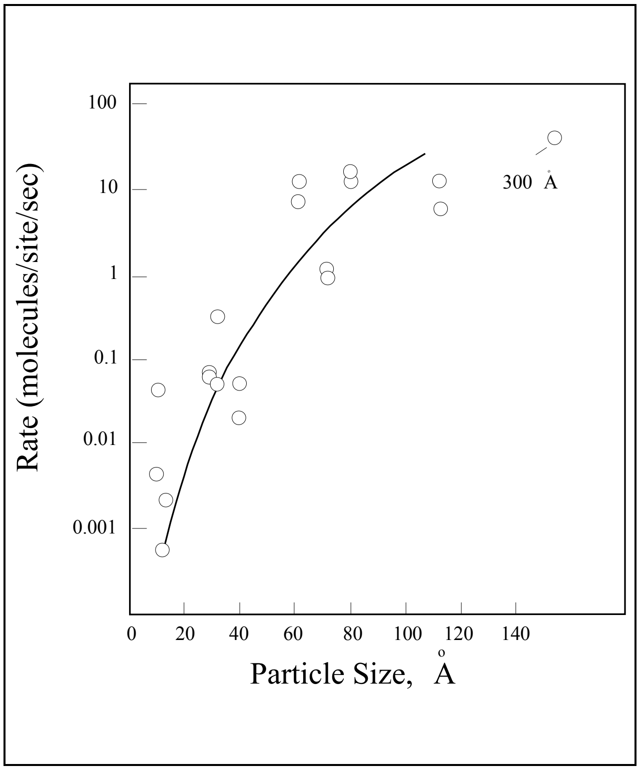


Figure 14.21 The rate of the reaction

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

over an iron catalyst as a function of size of the iron particles in the catalyst. Data of Boudart et al [1975]

Group VIII metals - host of reactions

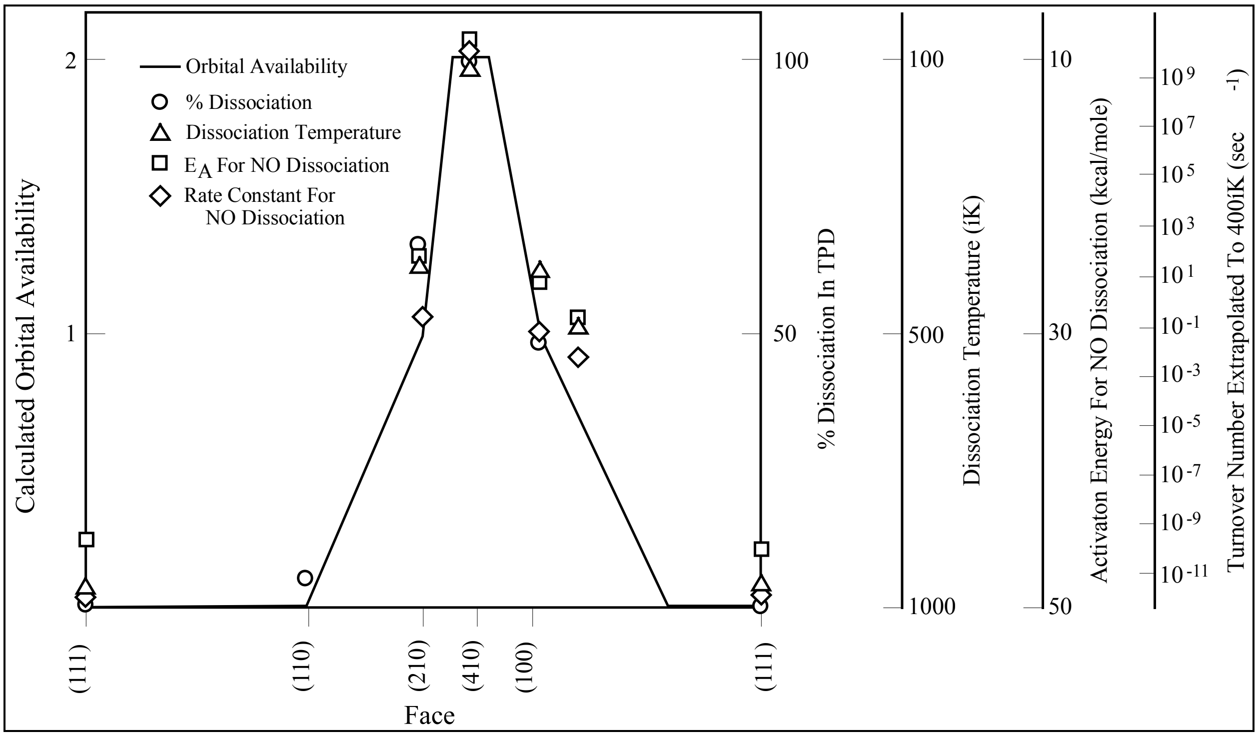
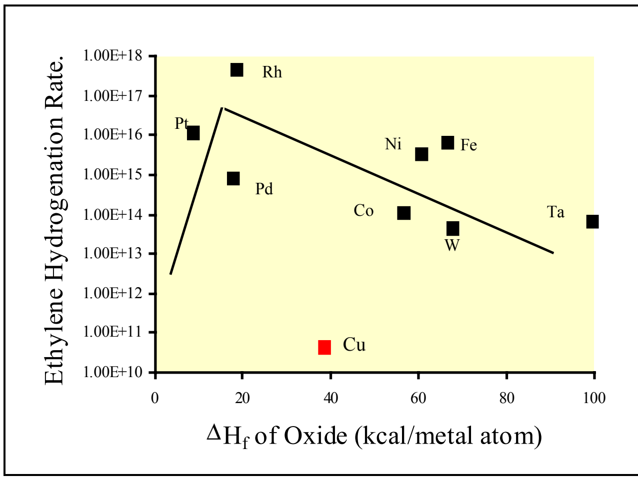


Figure 14.22 The rate of nitric oxide dissociation on several of the faces of platinum along the principle zone axes of the stereographic triangle. Adapted from Masel[1983].

Table 14.3 **The structure sensitivity of a series of reactions**	
Reaction	Largest variation in rate with geometry observed prior to 1999
$2CO+O_2 \rightarrow 2CO_2$	6
$C_2H_4+H_2 \rightarrow C_2H_6$	12
$CH_3OH \rightarrow CH_{2(ad)}+H_2O$	>100
$C_2H_6+H_2 \rightarrow 2CH_4$	10^4
$N_2+3H_2 \rightarrow 2NH_3$	10^5
$2NO+2H_2 \rightarrow N_2+2H_2O$	$\sim 10^{21}$

Trends over the periodic table

Copper-silver gold - partial oxidation, partial hydrogenation, possibly water gas shift



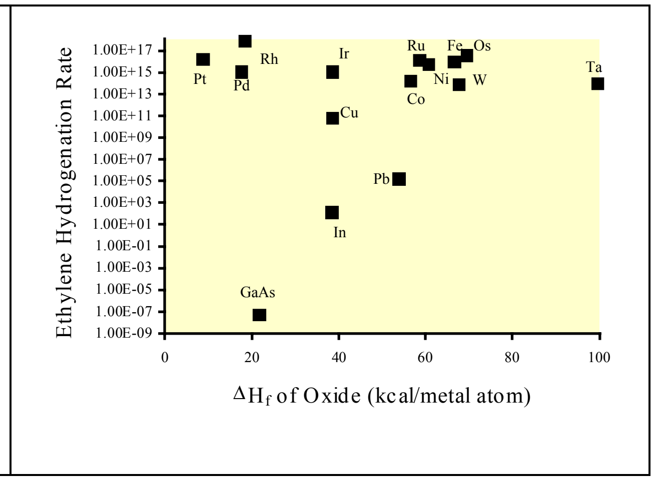


Figure 14.23 A volcano plot for the variations in the rate of ethylene hydrogenation over a subset of the transition metals

Figure 14.24 A repeat of Figure 14.20 with a larger data set.

Problem 14.A - Using the Blowers-Masel approximation to find feasible catalysts

The production of ammonia from nitrogen and hydrogen is one of the largest chemical processes worldwide. The overall reaction is $N_2 + 3\ H_2 \Rightarrow NH_3$

a) Find a feasible mechanism for the reaction on a metal catalyst.

b) Look carefully at Figure 5.12 and decide which metals are likely catalysts. Assume that all of the steps in the mechanism have to either inactivated or have a small activation barrier. Which metals will be active for the key dissociation processes during the mechanism?

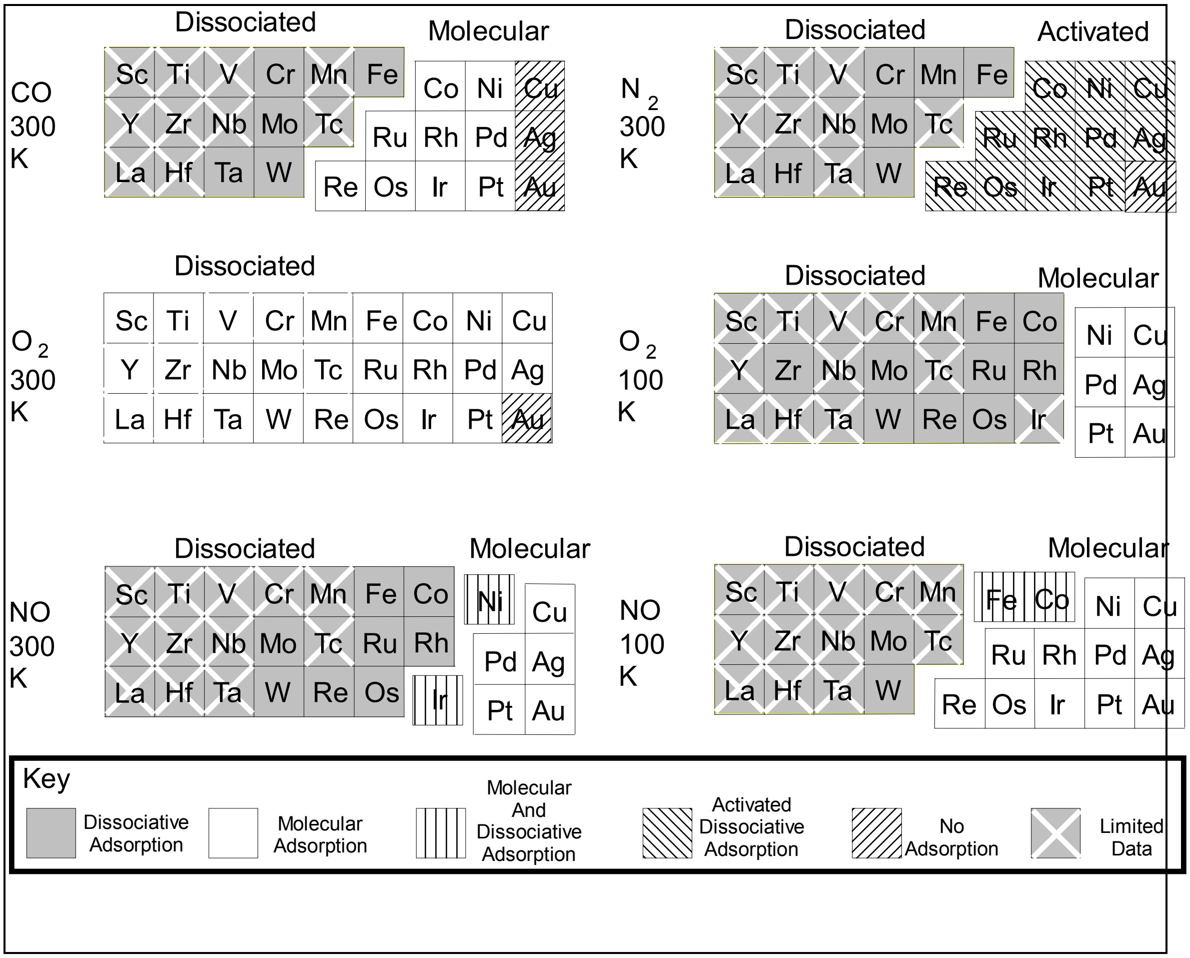


Figure 5.12 **The metals which dissociate CO, NO, H_2, O_2 and CO at various temperatures.**

c) Now think about the recombination steps. If a recombination step is too endothermic, it will not be feasible. Use the data in Table 6.5 to estimate the heat of reaction for each of the steps.

d) From your results choose a possible metal catalyst.

Table 6.5 **Approximate contributions of metal surface bond to ΔH_f kcal/mole . The data in the table is calculated from results in Benziger [1991] and results in Masel [1996]. Most of the numbers are ±5–10 kcal/mole. The numbers in brackets are based on extrapolations. Consequently, those numbers may have larger errors.**								
	Group							
	IVA	VA	VIA	VIIA	VIII	VIII	VIII	IB
Element	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**
H(M-C)	[-62]	[-56]	-53	-50	-49	-48	-50	-41
H(M-N)	[-77]	[-61]	[-44]	[-36]	-14	[-1]	-10	-3
H(M-O)	-68	-55	-58	-44	-45	-40	-38	-30
H(M-H)	-19	-15	-14	-12	-11	-12	-12	-5
Element	**Zr**	**Nb**	**Mo**	**Tc**	**Ru**	**Rh**	**Pd**	**Ag**
H(M-C)	-62	-59	-53.1	-49	-43	-40	-40	-25
H(M-N)	-34	-23	-19	[-12]	[-10]	[-9]	[-7]	+10
H(M-O)	-78	-58	[-41]	-[37]	[-36]	-28	-24	-22
H(M-H)	-20	-13	-13	-12	-11	-10	-10	0
Element	**Hf**	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**
H(M-C)	-65	-81	-72.5	-52.5	-43	-40	-40	-20
H(M-N)	-34	-26	-13	-15	[-11]	[-8]	[-5]	+10
H(M-O)	-80	-61	-47	-33	-24	-29	-24.5	-19.5
H(M-H)	?	-19	-16	-12	-11	-8	-6	+10

Table 6.1 **The contribution of various bonds to key thermodynamic properties. Data of Benson[1976].**							
Bond	C_p, cal/mole° K	S cal/mole° K	ΔH_f, kcal/mole	Bond	C_p, cal/mole° K	S cal/mole° K	ΔH_f, kcal/mole
C—H	1.74	12.90	-3.83	C_D—C	2.6	-14.3	6.7
C—C	1.98	-16.40	2.73	C_D—H	2.6	13.8	3.2
C—F	3.34	16.9	-52.5	C_D—F	4.6	18.6	-3.9
C—O	2.7	-4.0	-12.0	C_D—C_D	—	—	7.5
O—H	2.7	24.0	-27.0	CO—H	4.2	26.8	-13.9
C—N	2.1	-12.8	9.3	CO—N	3.7	-0.6	-14.4
N—H	2.3	17.7	-2.6	C_B—H	3.0	11.7	3.25
C_B—C_B	—	—	10.0	C_B—C	4.5	-17.4	7.25

<u>Solution</u>

a) The approach is to
   1) Postulate a feasible mechanism.
   2) Use Tables 6.1 and 6.5 to estimate ΔH_r for each of the steps in the mechanism.
   3) Use the Blowers-Masel approximation to estimate E_a for the reaction.
   4) E_A must be less than 34 kcal/mole, and preferably below 30 kcal/mole for every step in the mechanism.

See detailed solution in the textbook