University of Mosul

College of Petroleum & Mining Engineering

Industrial Chemistry

Lecture …(3)….

Petroleum and Refining Engineering Department

Catalyst Concepts in Heterogeneous Catalysis

reaction is compared to that of an uncatalyzed reaction in Figure 5.5.

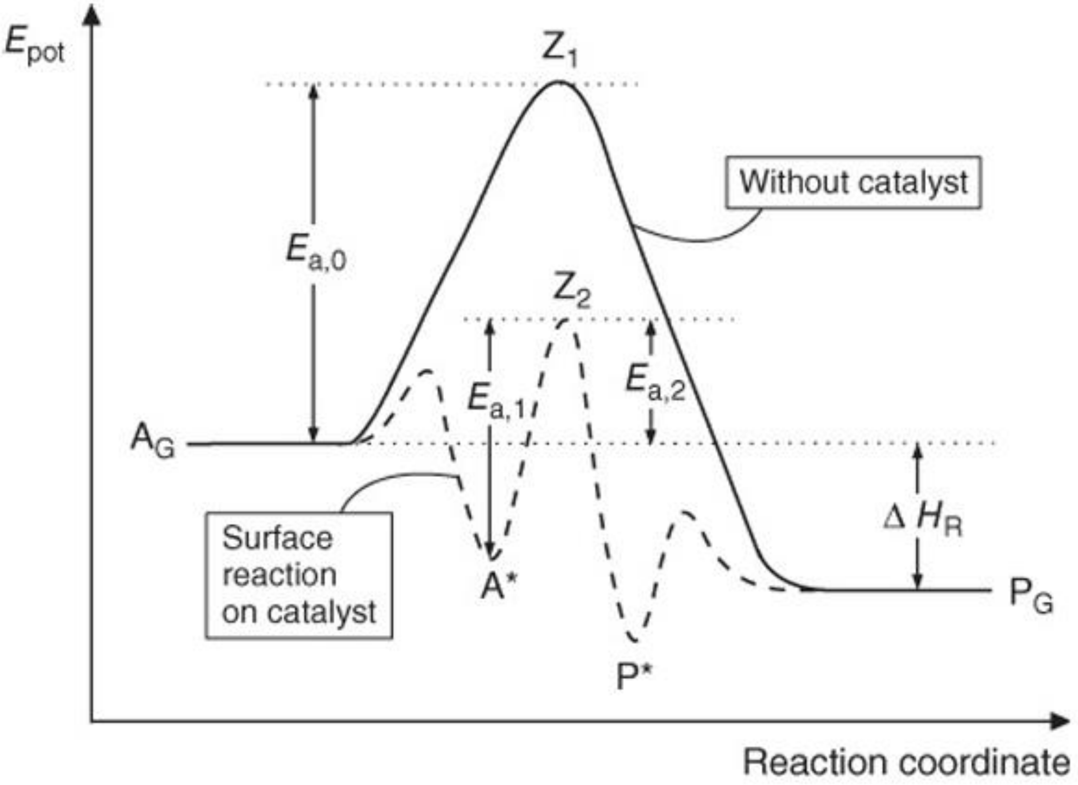


Figure 5.9 Course of a heterogeneously catalyzed gas-phase reaction $A_G \rightarrow P_G$. $E_{a,0}$ = activation energy of the homogeneous uncatalyzed gas-phase reaction; $E_{a,1}$ = true activation energy; $E_{a,2}$ = apparent activation energy of the catalyzed reaction; Z_1 = transition state of the gas-phase reaction; Z_2 = transition state of the surface reaction; and ΔH_R = reaction enthalpy.

$$\Delta G = \Delta H - T\Delta S \tag{5.22}$$

Since it can be expected that the reaction entropy values will not vary greatly from reactant to reactant, the adsorption enthalpy ΔH will depend, as a first approximation, mainly on the strength of chemical bonding between the gas molecules and the catalyst. Two fundamental types of chemisorption processes can be distinguished [8]:

- Molecular or associative chemisorption, in which all bonds of the adsorbate molecule are retained.
- Dissociative chemisorption, in which the bonds of the adsorbate molecule are cleaved and molecular fragments are adsorbed on the catalyst surface.

Molecular chemisorption occurs with molecules having multiple bonds or free electron pairs. For example, on platinum surfaces, ethylene gives up two π electrons of its double bond and forms two σ bonds with Pt atoms. The resulting sp^3 hybridization results in a tetrahedral arrangement of bonds (Figure 5.10).

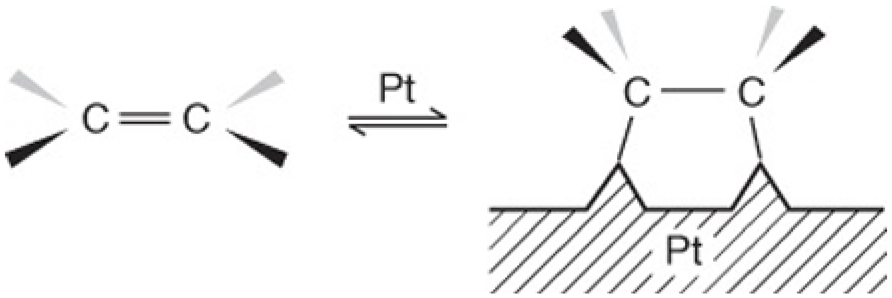


Figure 5.10 Molecular chemisorption of ethylene on a Pt surface.

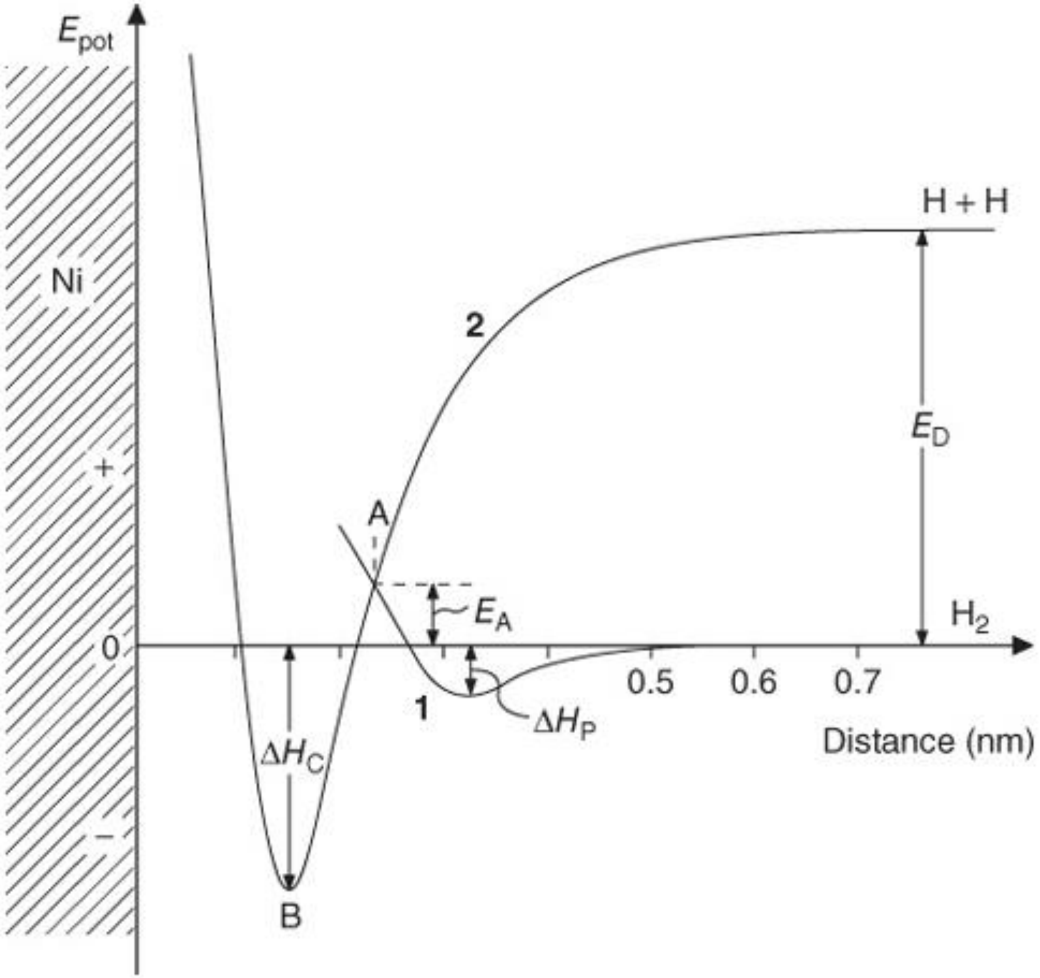


Figure 5.11 Potential energy and interatomic distances in the adsorption of hydrogen on nickel. Curve 1: physisorption (0.32 nm, $\Delta H_p = -4\ \mathrm{kJ\ mol^{-1}}$); curve 2: chemisorption (0.16 nm, $\Delta H_c = -46\ \mathrm{kJ\ mol^{-1}}$); E_D = dissociation energy of H_2 (218 kJ mol^{-1}); and E_A = activation energy for adsorption.

Catalysis Kinetics: Rate Laws and Activation Energy

- • Reaction Rate: $r = -d[A]/dt = k \cdot f(cA)$
- • Arrhenius Equation: $k = k_0 \cdot \exp(-Ea / RT)$

- Where:
- k = rate constant
- Ea = activation energy
- R = gas constant
- T = temperature (Kelvin)

$$\Delta G = -46 + (300 \times 0.068) = -25.6\ \text{kJ mol}^{-1}$$

The probability of reaction is thus extremely high. The diagram also shows that the idea that the H_2 molecule dissociates and is then chemisorbed on the Ni surface is purely hypothetical, and that in fact physisorption precedes chemisorption. The total process can be described schematically as shown in Figure 5.12.

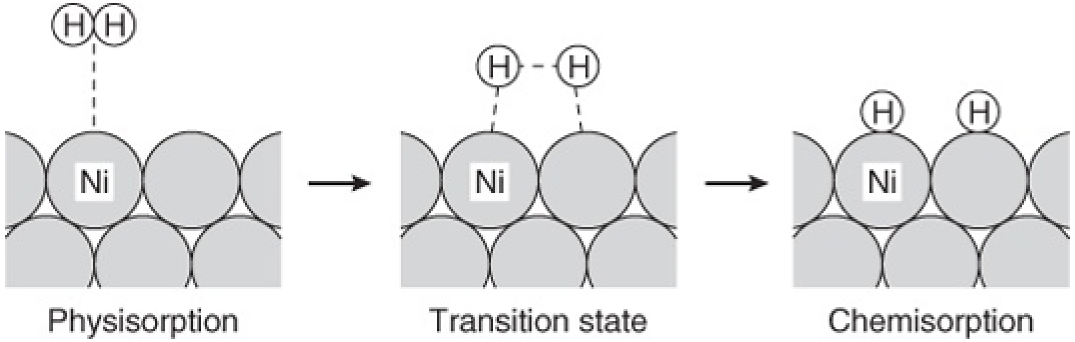
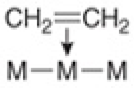


Figure 5.12 Dissociative adsorption of hydrogen on nickel surfaces.

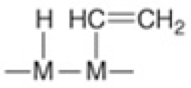
For both types of chemisorption, there are numerous examples that exhibit parallels to organometallic chemistry and therefore homogeneous catalysis.

In the chemisorption of alkenes, other surface complexes can occur, for example, π complexes with a donor–acceptor bond and dissociatively bound complexes:



$$\begin{array}{c} CH_2{=}CH_2 \\ \downarrow \\ M{-}M{-}M \end{array}$$

Metal π complex



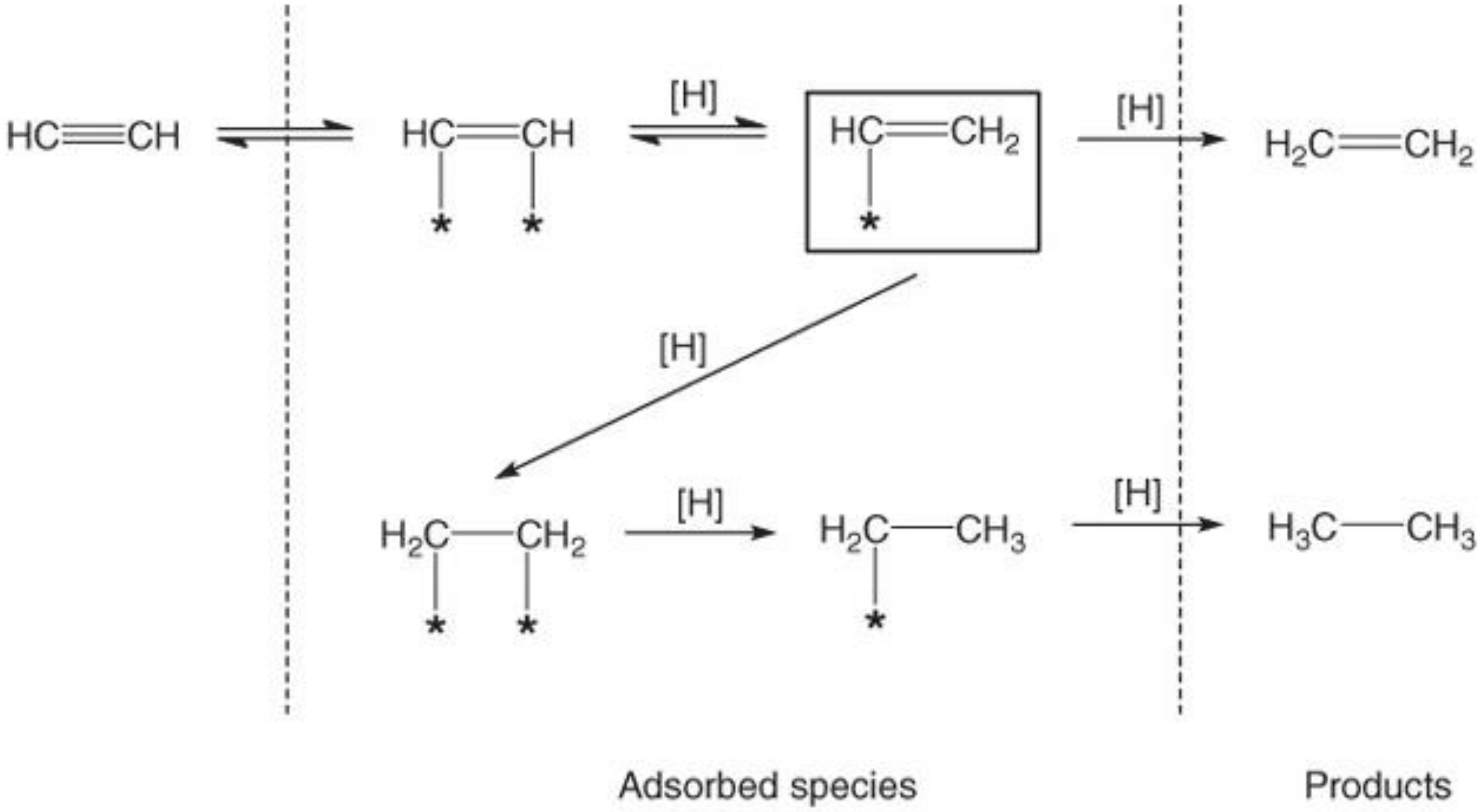
$$\begin{array}{cc} H & HC{=}CH_2 \\ | & | \\ {-}M{-} & M{-} \end{array}$$

Dissociatively chemisorbed ethylene

Dissociative chemisorption occurs preferably with alkenes in which the allylic methyl group is highly activated (e.g., propene). Hydrogen abstraction gives an allyl radical, which can be bound as follows:

Table 5.6 Relative reaction rates on transition metal catalysts

Row	Reaction		Metals and relative reaction rates					
1	Hydrogenation of ethylene (metal catalysts)		Cr		Fe	$\boxed{\text{Co}}$	Ni	Cu
			0.95		15	100	36	1.2
2	Hydrodesulfurization of dibenzo-thiophene (metal sulfide catalysts)	Nb	Mo	Tc	$\boxed{\text{Ru}}$	Rh	Pd	
		0.5	2	13	100	26	3	
3	Hydrogenolysis of CH_3NH_2 to methane (metal catalysts)			Re	Os	$\boxed{\text{Ir}}$	Pt	Au
				0.008	0.9	100	11	0.5



Scheme 5.2 Mechanism for the hydrogenation of acetylene.

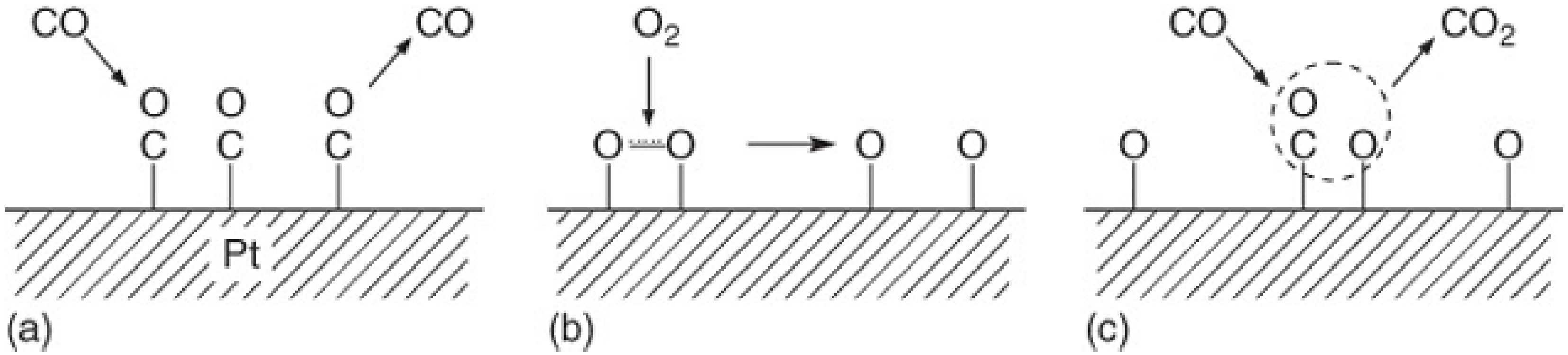


Figure 5.18 Oxidation of CO on platinum surfaces.

The O_2 is initially adsorbed in molecular form as a peroxide-like compound, which rapidly dissociates with the release of energy (Figure 5.18b). Since the oxygen atoms require several free centers for adsorption, saturation coverage with oxygen is rapidly reached.

Table 5.11 Classification of solid-state catalysts

	Conductors	Semiconductors	Insulators
Conductivity range, Ω^{-1} cm^{-1}	10^6 to 10^4	10^3–10^{-9}, increases with increasing temperature	10^{-9} to 10^{-20}
Electron transfer	Electron exchange metal/adsorbate	Electron transfer at high temperatures	—
Examples	Numerous metals, mostly transition metals and alloys	Metalloids (Si, Ge, etc.); nonstoichiometric oxides and sulfides (ZnO, Cu_2O, NiO, ZnS, Ni_2S_3, etc.)	Stoichiometric oxides (Al_2O_3, SiO_2, B_2O_3, MgO, SiO_2/MgO, SiO_2/Al_2O_3, etc.), salts, solid acids

Having discussed the electronic properties of the catalyst, let us now turn our attention to electron transfer between substrate and catalyst. The following classification is relative to the substrate:

- *Acceptor reactions*: electrons flow from catalyst to substrate; the adsorbate acts as an acceptor (examples: starting materials with high electron affinity; reactions in which oxygen is mobilized).
- *Donor reactions*: electrons flow from substrate to catalyst (examples: substrates that readily release electrons), that is, reducing agents with low ionization energies; reactions in which H_2 or CO is mobilized.