Chapter 27

Catalysis and some industrial processes

Homogeneous catalysis: alkene (olefin) and alkyne metathesis

Homogeneous catalytic reduction of N_2 to NH_3

Homogeneous catalysts: industrial applications, development.

Heterogeneous catalysts: surfaces, interactions with adsorbates, commercial applications, and organometallic cluster models

Catalyst – a substance that alters the rate of a reaction without appearing in any of the products of that reaction; it may speed up or slow down a reaction. For a reversible reaction, a catalyst alters the rate at which equilibrium is attained; it does not alter the position of equilibrium.

Autocatalytic reaction – one of the products is able to catalyze the reaction.

Homogeneous catalyst – in the same phase as the components of the reaction that it is catalyzing.

Homogeneous catalyst – in a different phase from the components of the reaction for which it is catalyzing.

Arrhenius equation:

$$\ln k = \ln A - \frac{E_a}{RT} \quad \text{or} \quad k = Ae^{\left(\frac{-E_a}{RT}\right)}$$

$$k = \frac{k'T}{h} e^{\left(\frac{-\Delta G^{\Updownarrow}}{RT}\right)}$$

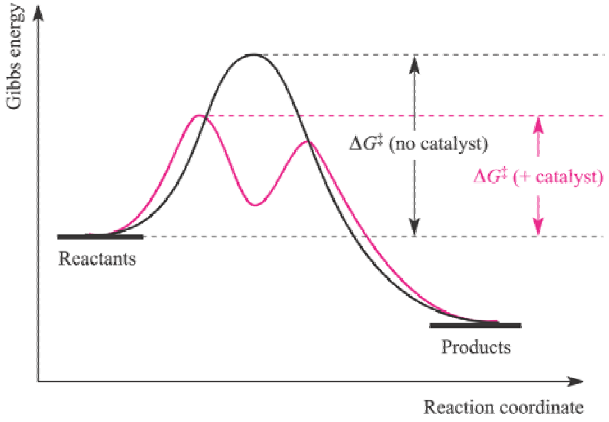

Fig. 27.1 A schematic representation of the reaction profile of a reaction without and with a catalyst. The pathway for the catalysed reaction has two steps, and the first step is rate determining.

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A catalyzed reaction pathway is usually represented by a catalytic cycle.

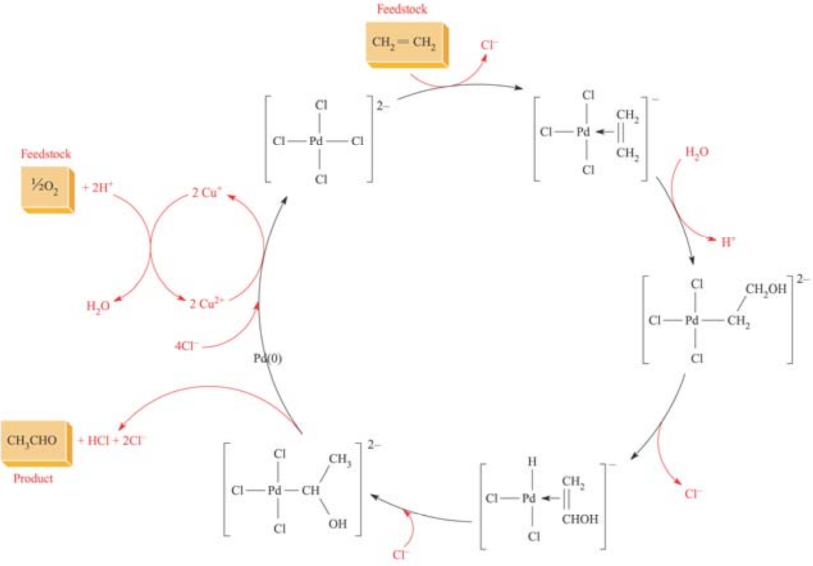

Fig. 27.2 Catalytic cycle for the Wacker process; for simplicity, we have ignored the role of coordinated H_2O, which replaces Cl^- *trans* to the alkene.

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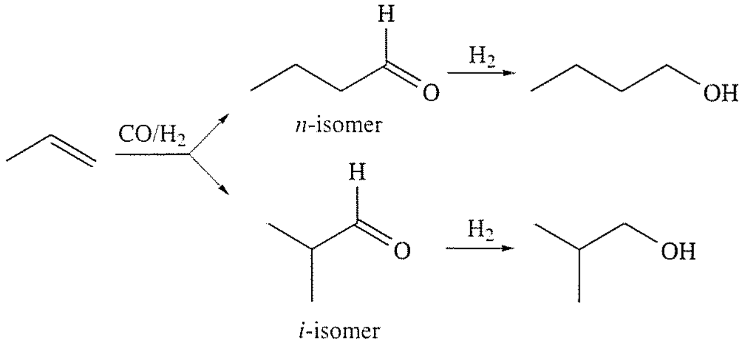
Choosing a catalyst one considers:

- Concentration of catalyst required
- Catalytic turnover
- selectivity of the catalyst to the desired product
- how often the catalyst needs renewing

Catalytic turnover number (TON) is the number of moles of product per mole of catalyst. Indicates the number of catalytic cycles for a given process, (e.g. after 1h the TON was 2500). Typically applied to batch processes.

Catalytic turnover frequency (TOF) is the catalytic turnover per unit time. Indicates the number of moles of product per mole of catalyst per unit time, (e.g. TOF 20 min^{-1}). Typically applied to continuous processes (flow reactors).



Selectivity:

the n:i ratio of aldehydes (regioselectivity of the reaction)

aldehyde:alcohol ratio for a given chain (chemoselectivity of the reaction)

Alkene (olefin) metathesis

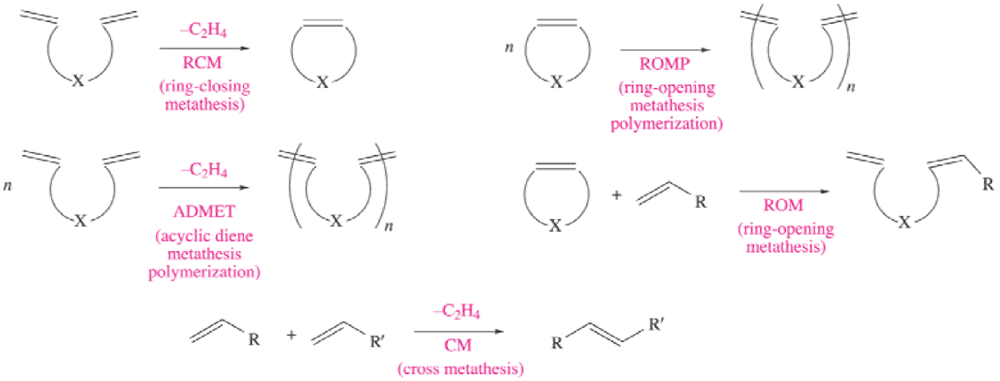


Fig. 27.3 Examples of alkene (olefin) metathesis reactions with their usual abbreviations.

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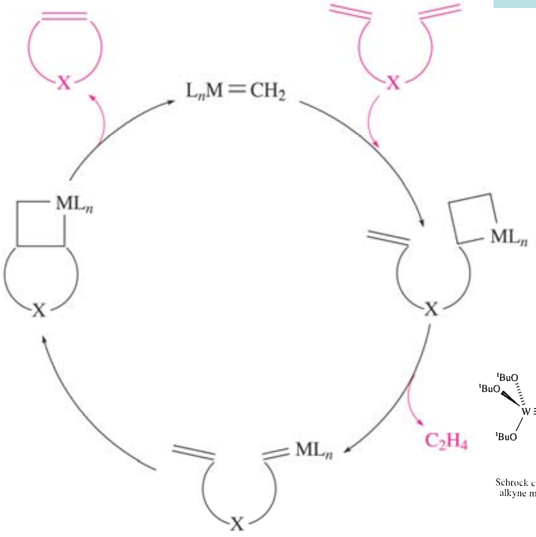
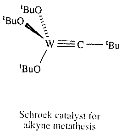
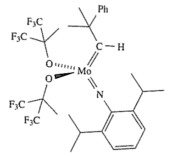
Chauvin mechanism





Schrock catalyst for alkyne metathesis



Example of a Schrock-type catalyst for alkene metathesis

Fig. 27.4 A catalytic cycle for ring-closure metathesis (RCM) showing the Chauvin m
involves [2 + 2]-cycloadditions and cycloreversions.

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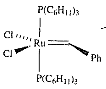
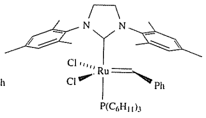


C_6H_{11} = cyclohexyl



Grubbs' catalysts

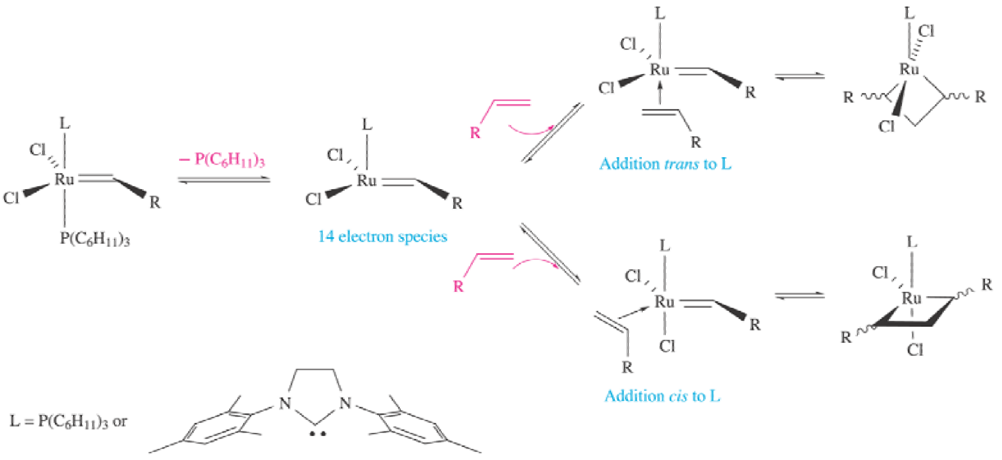


Fig. 27.5 Initial steps in the mechanism of alkene metathesis involving first and second generation Grubbs' catalysts. Two possibilities for the formation of the metallocyclobutane intermediates are shown.

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Homogeneous catalytic reduction of N_2 to NH_3

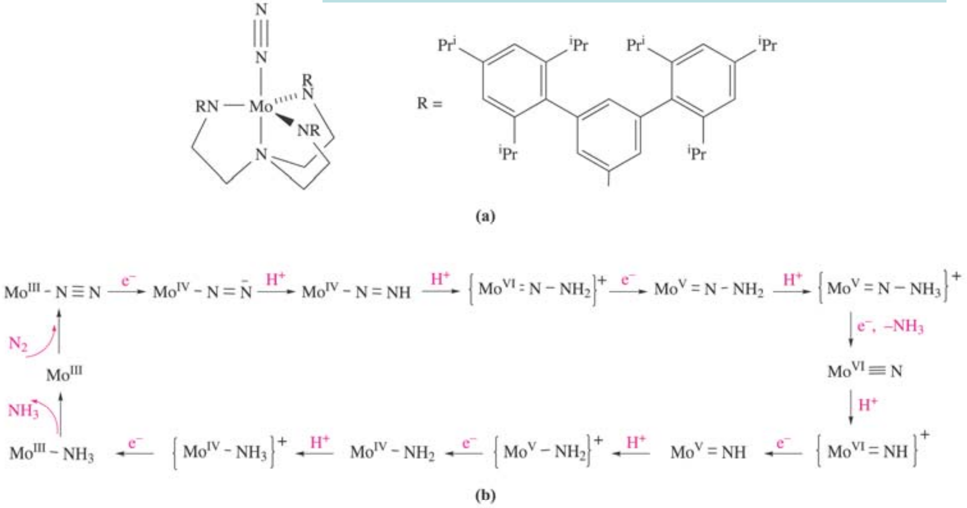

Fig. 27.6 (a) Dinitrogen bound to the single Mo(III) centre in the complex that is the starting point for the catalytic conversion of N_2 in NH_3 at room temperature and pressure. (b) The proposed scheme in which six protons and six electrons generate two equivalents of NH_3 from one equivalent of N_2. The complex shown in part (a) is abbreviated to $Mo^{III}N_2$, and so on.

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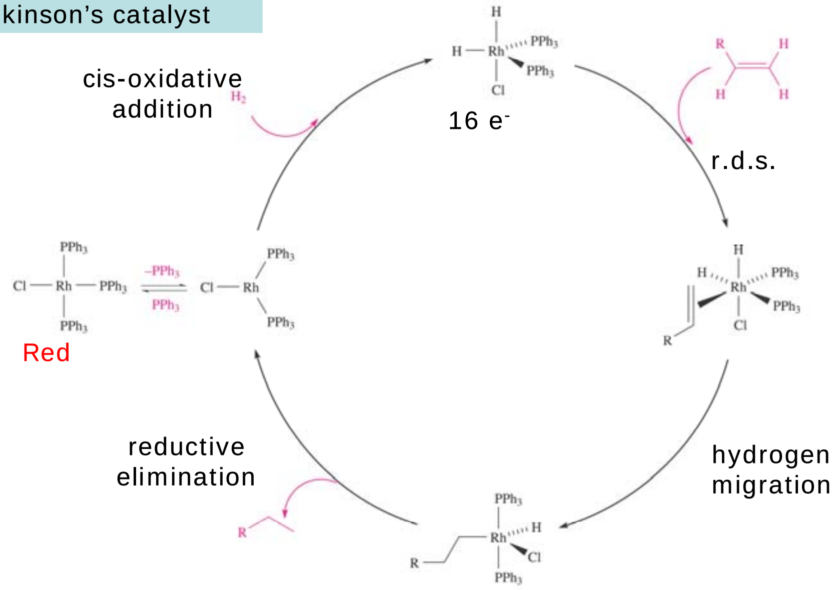
Wilkinson's catalyst



cis-oxidative addition

16 e$^-$

r.d.s.

Red

hydrogen migration

reductive elimination

Fig. 27.7 Catalytic cycle for the hydrogenation of $RCH{=}CH_2$ using Wilkinson's catalyst, $RhCl(PPh_3)_3$.

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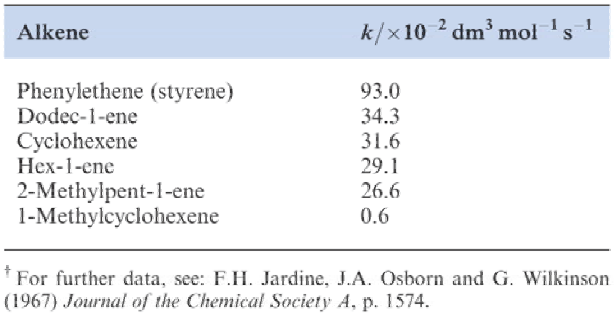

Alkene	$k / \times 10^{-2}$ dm^3 mol^{-1} s^{-1}
Phenylethene (styrene)	93.0
Dodec-1-ene	34.3
Cyclohexene	31.6
Hex-1-ene	29.1
2-Methylpent-1-ene	26.6
1-Methylcyclohexene	0.6

[†] For further data, see: F.H. Jardine, J.A. Osborn and G. Wilkinson (1967) *Journal of the Chemical Society A*, p. 1574.

Table 27.1 Rate constants for the hydrogenation of alkenes (at 298K in C_6H_6) in the presence of Wilkinson's catalyst.[†]

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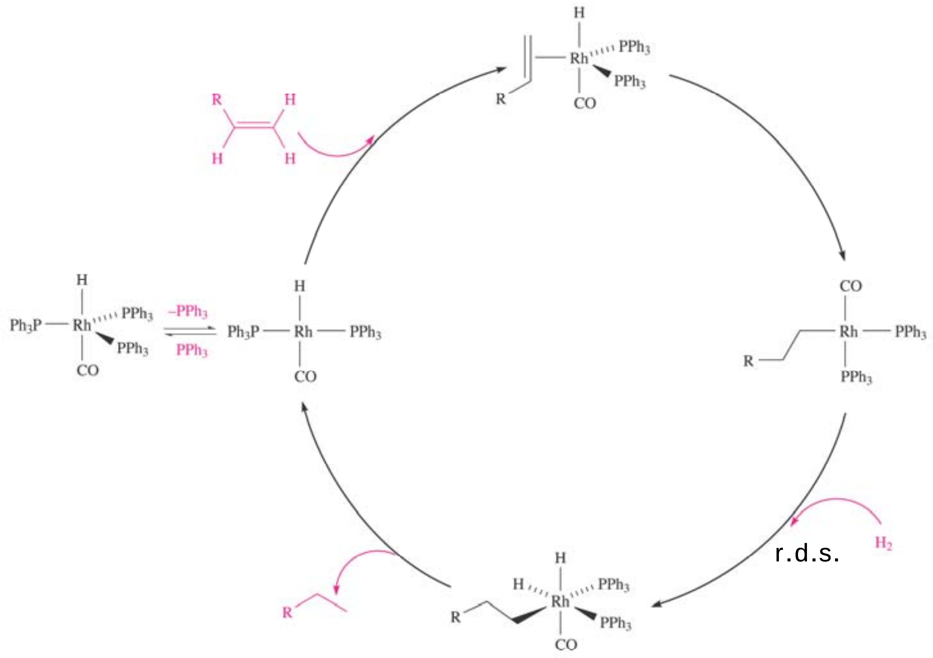

Fig. 27.8 Catalytic cycle for the hydrogenation of $RCH=CH_2$ using $HRh(CO)(PPh_3)_3$ as catalyst.

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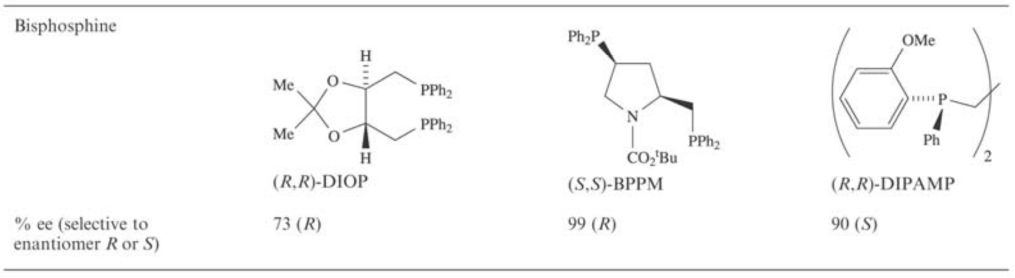
Asymmetric synthesis

$$\% \text{ ee} = \left(\frac{|R - S|}{|R + S|} \right) \times 100$$



Bisphosphine	(*R*,*R*)-DIOP	(*S*,*S*)-BPPM	(*R*,*R*)-DIPAMP
% ee (selective to enantiomer *R* or *S*)	73 (*R*)	99 (*R*)	90 (*S*)

Table 27.2 Observed % ee of the product of the hydrogenation of $CH_2=C(CO_2H)(NHCOMe)$ using Rh(I) catalysts containing different chiral bisphosphines.

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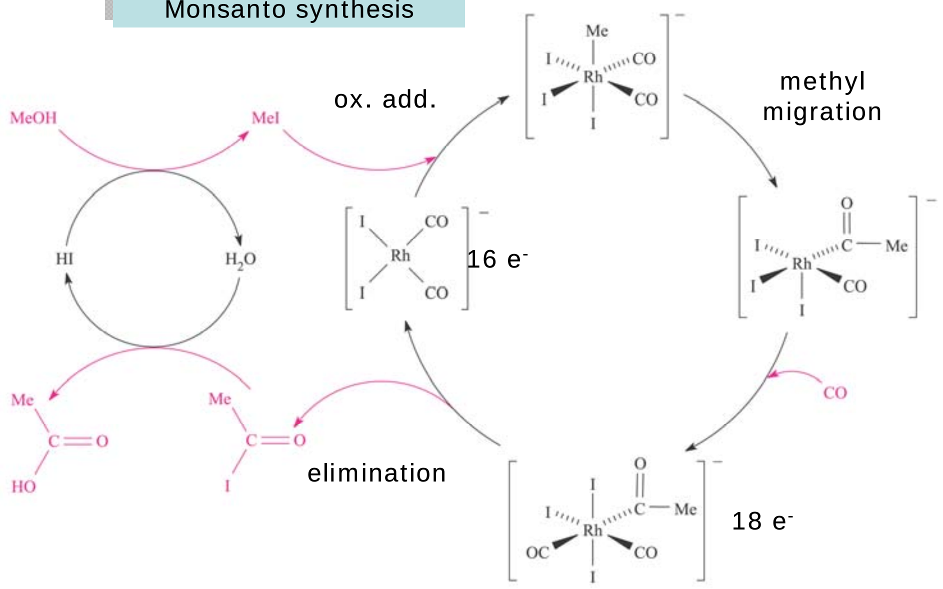
Monsanto synthesis



ox. add.

methyl migration

$16\ e^-$

$18\ e^-$

elimination

Fig. 27.9 The Monsanto acetic acid process involves two interrelated catalytic cycles.

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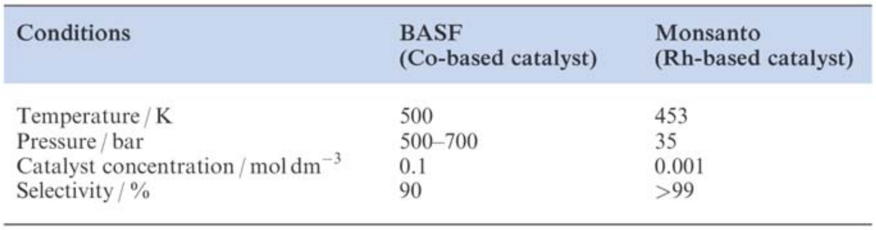

Conditions	BASF (Co-based catalyst)	Monsanto (Rh-based catalyst)
Temperature / K	500	453
Pressure / bar	500–700	35
Catalyst concentration / mol dm^{-3}	0.1	0.001
Selectivity / %	90	>99

Table 27.3 Major advantages of the Monsanto process over the BASF process for the manufacture of acetic acid (equation 27.15) can be seen from the summary in this table.

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Tennessee-Eastman acetic anhydride

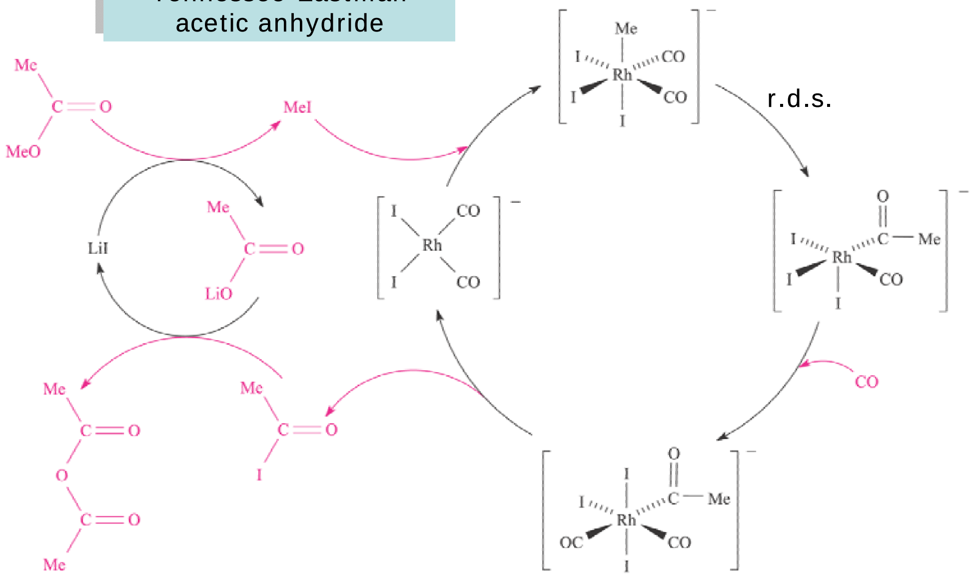

Fig. 27.10 Catalytic cycle for the Tennessee–Eastman acetic anhydride process.

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Competitive Catalytic cycle

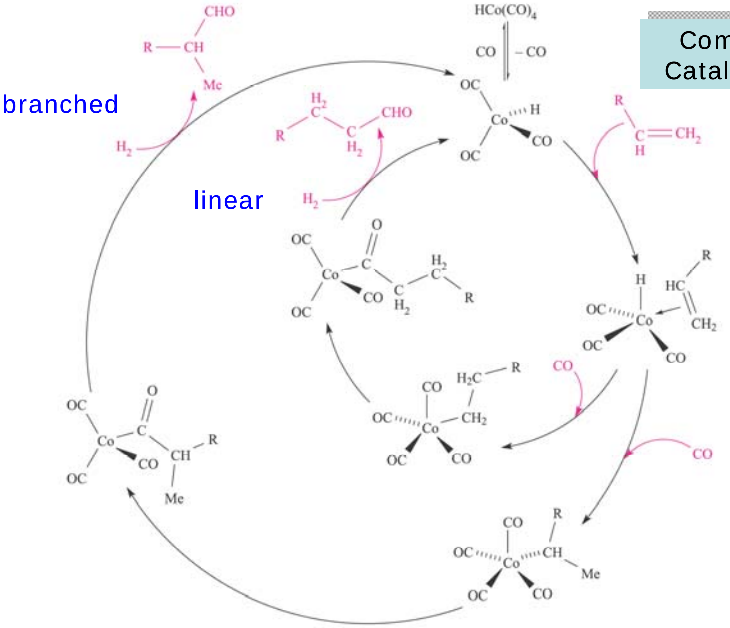

Fig. 27.11 Competitive catalytic cycles in the hydroformylation of alkenes to give linear (inner cycle) and branched (outer cycle) aldehydes.

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Alkene	**$k / \times 10^{-5}\ s^{-1}$**
Hex-1-ene	110
Hex-2-ene	30
Cyclohexene	10
Oct-1-ene	109
Oct-2-ene	31
2-Methylpent-2-ene	8

Table 27.4 Rate constants for the hydroformylation of selected alkenes at 383K in the presence of the active catalytic species $HCo(CO)_3$.

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	$HCo(CO)_4$	**$HCo(CO)_3(PBu_3)$**	**$HRh(CO)(PPh_3)_3$**
Temperature / K	410–450	450	360–390
Pressure / bar	250–300	50–100	30
Regioselectivity $n:i$ ratio	$\approx 3:1$	$\approx 9:1$	$>10:1$
Chemoselectivity (aldehyde predominating over alcohol)	High	Low	High

Table 27.5 A comparison of the operating conditions for and selectivities of three commercial hydroformylation catalysts.

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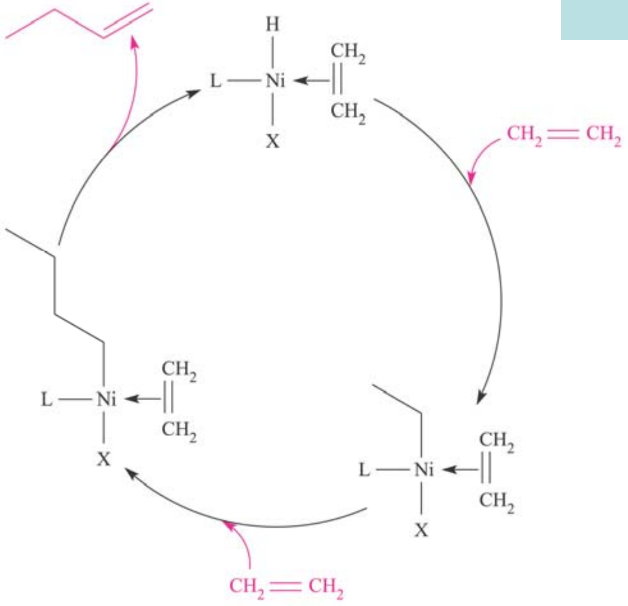

Fig. 27.12 Simplified catalytic cycle illustrating the oligomerization of ethene using a nickel-based catalyst; L = phosphine, X = electronegative group.

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Homogeneous catalysts: cationic clusters

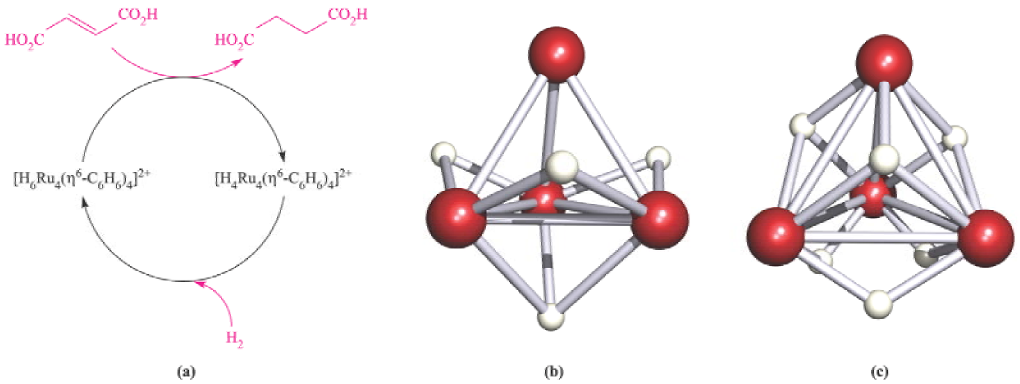

Fig. 27.13 (a) Catalytic cycle for the hydrogenation of fumaric acid by $[H_4(\eta^6\text{-}C_6H_6)_4Ru_4]^{2+}$; (b) H_4Ru_4 core of $[H_4(\eta^6\text{-}C_6H_6)_4Ru_4]^{2+}$, and (c) H_6Ru_4 core of $[H_6(\eta^6\text{-}C_6H_6)_4Ru_4]^{2+}$, both determined by X-ray diffraction [G. Meister *et al.* (1994) *J. Chem. Soc., Dalton Trans.*, p. 3215]. ^1H NMR spectroscopic data suggest that $[H_6(\eta^6\text{-}C_6H_6)_4Ru_4]^{2+}$ may contain an H_2 ligand and four hydrido ligands. Colour code in (b) and (c): Ru, red; H, white.

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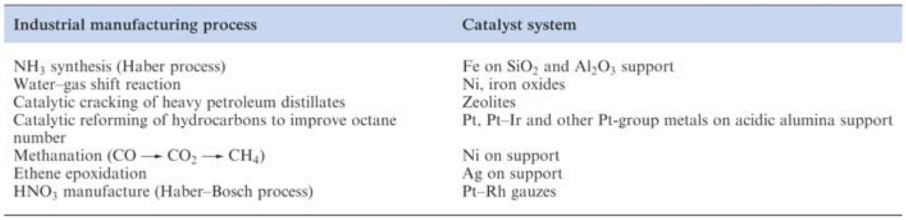
Heterogeneous catalysts



Industrial manufacturing process	Catalyst system
NH_3 synthesis (Haber process)	Fe on SiO_2 and Al_2O_3 support
Water–gas shift reaction	Ni, iron oxides
Catalytic cracking of heavy petroleum distillates	Zeolites
Catalytic reforming of hydrocarbons to improve octane number	Pt, Pt–Ir and other Pt-group metals on acidic alumina support
Methanation ($CO \longrightarrow CO_2 \longrightarrow CH_4$)	Ni on support
Ethene epoxidation	Ag on support
HNO_3 manufacture (Haber–Bosch process)	Pt–Rh gauzes

Physisorption – involves weak van der Waals interactions between the surface and the adsorbate.

Chemisorption – involves the formation of chemical bonds between surface atoms and the adsorbed species.

Table 27.6 Examples of industrial processes that use heterogeneous catalysts.

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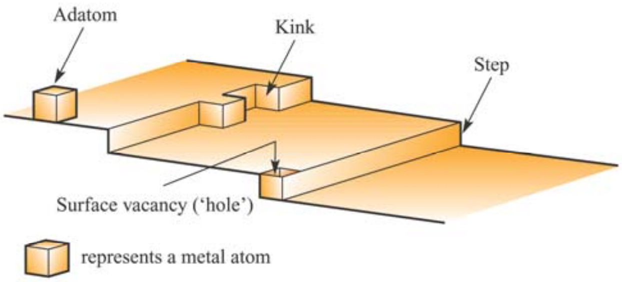

Fig. 27.14 A schematic representation of typical features of a metal surface. [Based on a figure from *Encyclopedia of Inorganic Chemistry* (1994), ed. R.B. King, vol. 3, p. 1359, Wiley, Chichester.]

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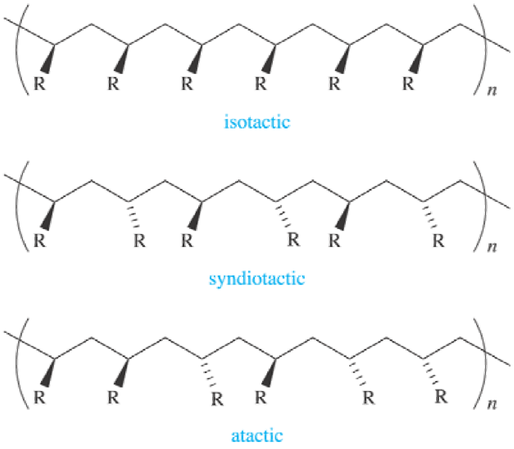

Fig. 27.15 The arrangement of R substituents in isotactic, syndiotactic and atactic linear polymers.

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Ziegler-Natta catalyst

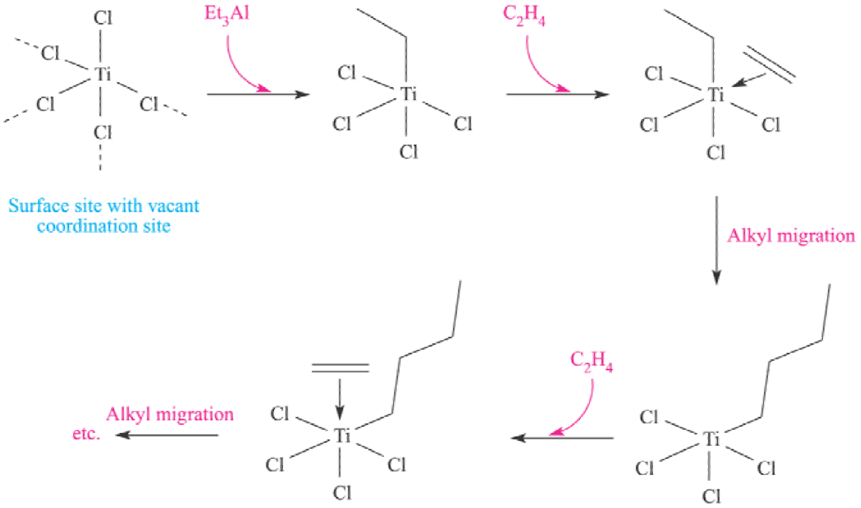

Fig. 27.16 A schematic representation of alkene polymerization on the surface of a Ziegler–Natta catalyst; the vacant coordination site must be *cis* to the coordinated alkyl group.

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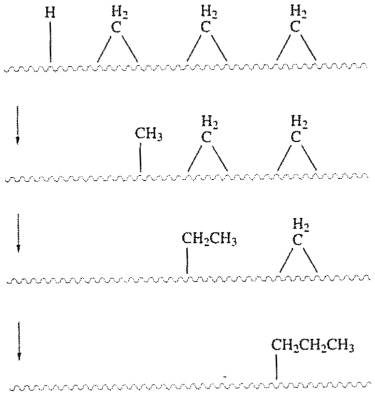
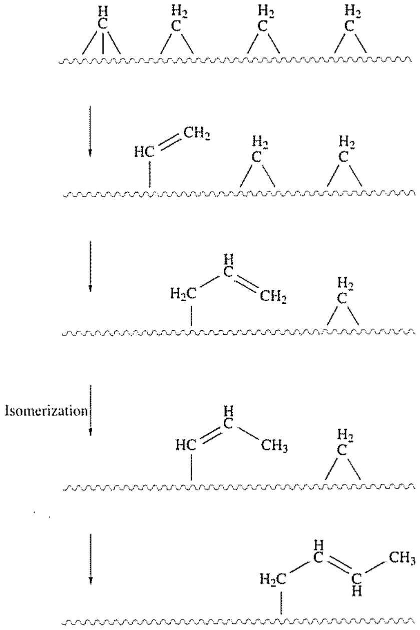
Fischer-Tropsch carbon chain growth

$CO + H_2$ → Fe →
Hydrocarbons (linear + branched alkanes and alkenes)
Oxygenates (linear alcohols, aldeydes, esters and ketones)
CO_2

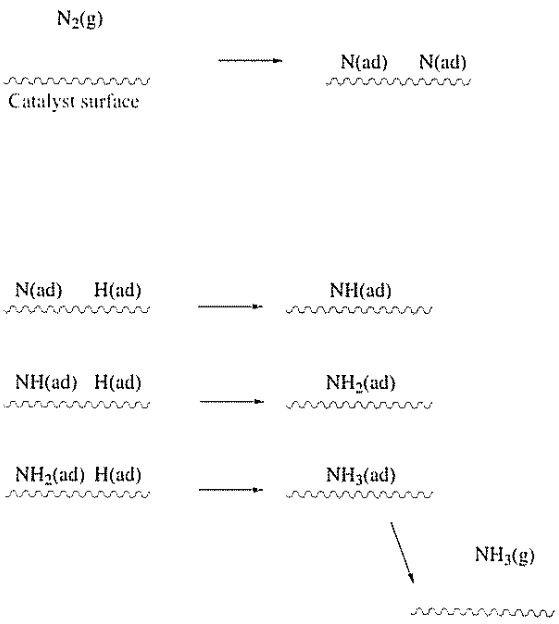
$CO + H_2$ → Co →
Hydrocarbons (linear + alkanes and alkenes)
H_2O



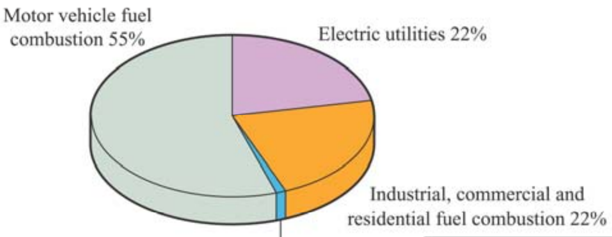
Fischer-Tropsch carbon chain growth



Haber Process



Catalytic Converters



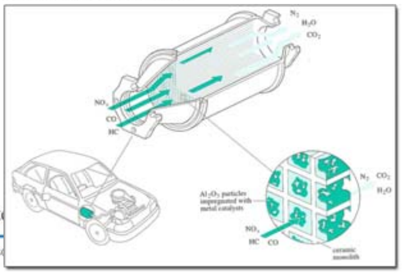


Fig. 27.17 Sources of NO_x emissions in the US. [Data: Environmental Prot

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Zeolites

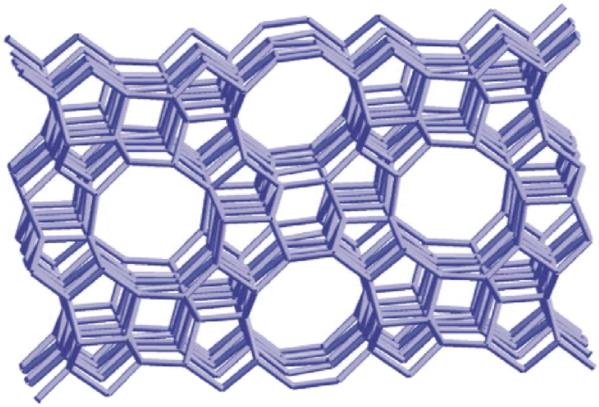

Fig. 27.18 Part of the aluminosilicate framework of synthetic zeolite ZSM-5 (structure-type MFI).

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Organometallic cluster models

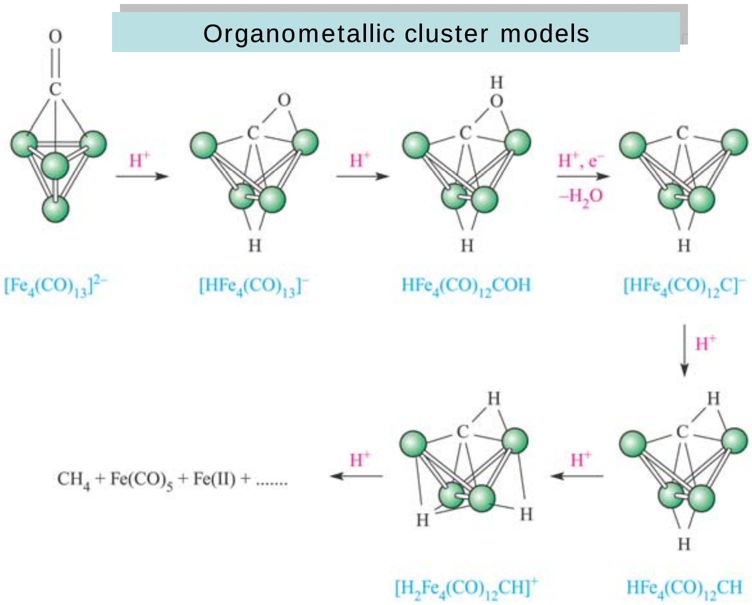

Fig. 27.19 The proton-induced conversion of a cluster-bound CO ligand to CH_4: a cluster model for catalysed hydrogenation of CO on an Fe surface. Each green sphere represents an $Fe(CO)_3$ unit.

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