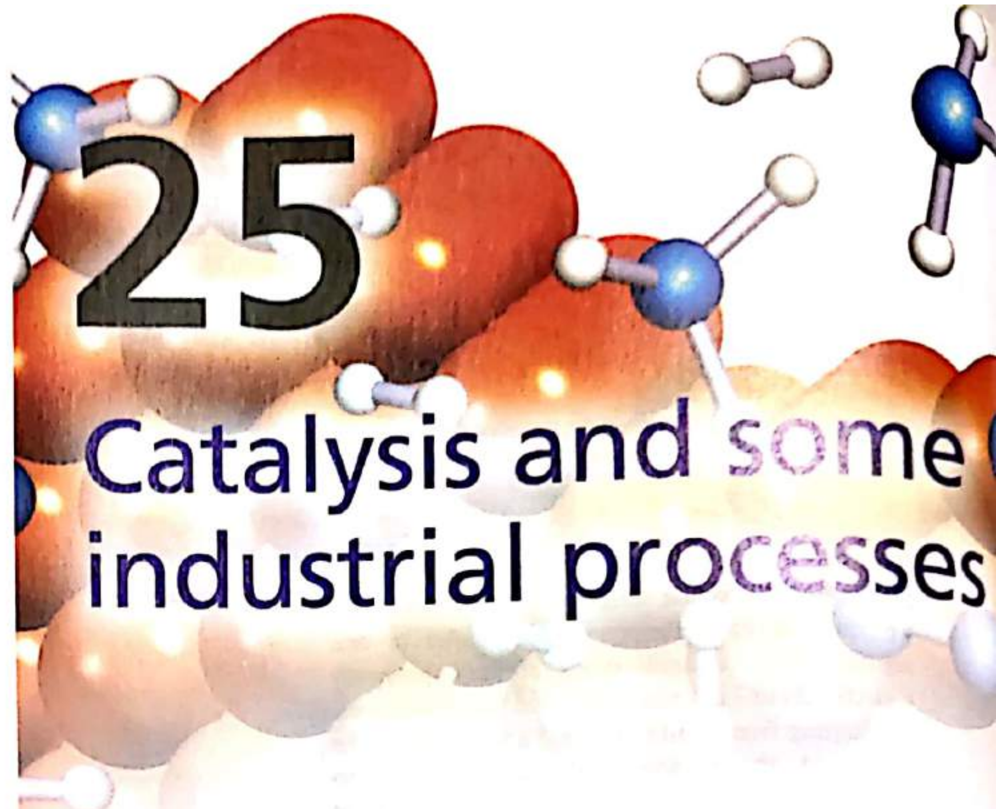
Topics

- Homogeneous catalysis
- Alkene and alkyne metathesis
- Reduction of N_2 to NH_3
- Alkene hydrogenation
- Monsanto and Cativa processes
- Hydroformylation
- Alkene oligomerization
- Developing new catalysts
- Heterogeneous catalysis
- Ziegler–Natta catalysis
- Fischer–Tropsch reactions
- Haber process
- Contact process
- Catalytic converters
- Zeolites



25

Catalysis and some industrial processes

25.1 Introduction and definitions

Numerous applications of catalysts in small-scale synthesis and the industrial production of chemicals have been described in this book. Now we discuss catalysis in detail, focusing on commercial applications. Catalysts containing *d*-block metals are of immense importance to the chemical industry: they provide cost-effective syntheses, and control the specificity of reactions that might otherwise give mixed products. The chemical industry (including fuels) is worth hundreds of billions of US dollars per year.[†] The search for new catalysts is one of the major driving forces behind organometallic research, and the chemistry in many parts of this chapter can be understood in terms of the reaction types introduced in Chapter 24. Current research also includes the development of environmentally friendly 'green chemistry', e.g. the use of supercritical CO_2 ($scCO_2$, see Section 9.13) as a medium for catalysis.[‡]

A ***catalyst*** is 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.

The term *catalyst* is often used to encompass both the *catalyst precursor* and the *catalytically active species*. A catalyst precursor is the substance added to the reaction, but it may undergo loss of a ligand such as CO or PPh_3 before it is available as the catalytically active species.

Although one tends to associate a catalyst with *increasing* the rate of a reaction, a *negative catalyst* slows down a reaction. Some reactions are internally catalysed (*autocatalysis*) once the reaction is under way, e.g. in the reaction of $[C_2O_4]^{2-}$ with $[MnO_4]^-$, the Mn^{2+} ions formed catalyse the forward reaction.

In an ***autocatalytic reaction***, one of the products is able to catalyse the reaction.

Catalysts fall into two categories, homogeneous and heterogeneous, depending on their relationship to the phase of the reaction in which they are involved.

A ***homogeneous catalyst*** is in the same phase as the components of the reaction that it is catalysing.
A ***heterogeneous catalyst*** is in a different phase from the components of the reaction for which it is acting.

25.2 Catalysis: introductory concepts

Energy profiles for a reaction: catalysed versus non-catalysed

A catalyst operates by allowing a reaction to follow a different pathway from that of the non-catalysed reaction. If the activation barrier is lowered, then the reaction proceeds more rapidly. Figure 25.1 illustrates this for a

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[†] For an overview of the growth of catalysis in industry during the 20th century, see: G.W. Parshall and R.E. Putscher (1986) *J. Chem. Educ.*, vol. 63, p. 189. For insight into the size of the chemical markets in the US and worldwide, see: W.J. Storck (2006) *Chem. Eng. News*, January 9 issue, p. 12; (2010) *Chem. Eng. News*, July 5 issue, p. 54.

[‡] For example, see: W. Leitner (2002) *Acc. Chem. Res.*, vol. 35, p. 746 – 'Supercritical carbon dioxide as a green reaction medium for catalysis'; I.P. Beletskaya and L.M. Kustov (2010) *Russ. Chem. Rev.*, vol. 79, p. 441 – 'Catalysis as an important tool of green chemistry'.

THEORY

Box 25.1 Energy and Gibbs energy of activation: E_a and $\Delta G^{\ddagger}$

The Arrhenius equation:

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

is often used to relate the rate constant, k, of a reaction to the activation energy, E_a, and to the temperature, T (in K). In this equation, A is the pre-exponential factor, and R = molar gas constant. The activation energy is often approximated to $\Delta H^{\ddagger}$, but the exact relationship is:

$$E_a = \Delta H^{\ddagger} + RT$$

The energy of activation, $\Delta G^{\ddagger}$, is related to the rate constant by the equation:

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

where k' = Boltzmann's constant, h = Planck's constant.

In Section 26.2 we discuss activation parameters, including $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, and show how these can be determined from an Eyring plot (Fig. 26.2) which derives from the equation above relating k to $\Delta G^{\ddagger}$.

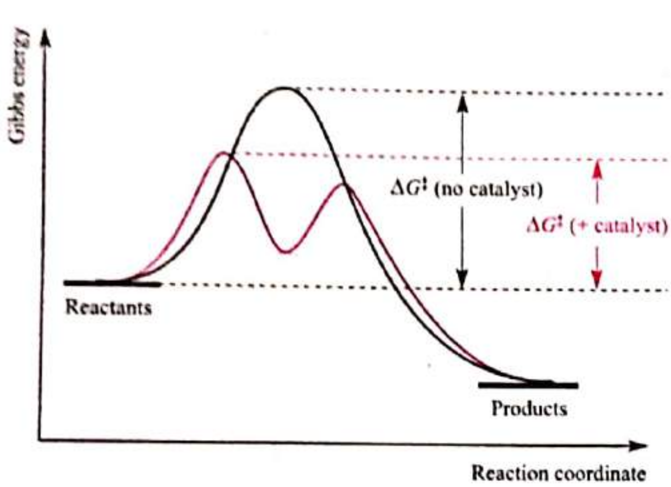


Fig. 25.1 A schematic representation of the reaction profile of a reaction without and with a catalyst. The pathway for the catalysed reaction has two steps, and the first step is rate determining.

reaction that follows a single step when it is non-catalysed, but a 2-step path when a catalyst is added. Each step in the catalysed route has a characteristic Gibbs energy of activation, $\Delta G^{\ddagger}$, but the step that matters with respect to the rate of reaction is that with the higher barrier. For the catalysed pathway in Fig. 25.1, the first step is the rate-determining step. (See Box 25.1 for the relevant equations for and relationship between E_a and $\Delta G^{\ddagger}$.) Values of $\Delta G^{\ddagger}$ for the controlling steps in the catalysed and non-catalysed routes are marked in Fig. 25.1. A crucial aspect of the catalysed pathway is that it must not pass through an energy minimum *lower* than the energy of the products. Such a minimum would be an 'energy sink', and would lead to the pathway yielding different products from those desired.

Catalytic cycles

A catalysed reaction pathway is usually represented by a *catalytic cycle*.

A ***catalytic cycle*** consists of a series of stoichiometric reactions (often reversible) that form a closed loop. The catalyst must be regenerated so that it can participate in the cycle of reactions more than once.

For a catalytic cycle to be efficient, the intermediates must be short-lived. The downside of this for understanding the mechanism is that short lifetimes make studying a cycle difficult. Experimental probes are used to investigate the kinetics of a catalytic process, isolate or trap the intermediates, attempt to monitor intermediates in solution, or devise systems that model individual steps so that the product of the model-step represents an intermediate in the cycle. In the latter, the 'product' can be characterized by conventional techniques (e.g. NMR and IR spectroscopies, X-ray diffraction, mass spectrometry). For many cycles, however, the mechanisms are not firmly established.

Self-study exercises

These exercises review types of organometallic reactions and the 18-electron rule.

1. What type of reaction is the following, and by what mechanism does it occur?

   $Mn(CO)_5Me + CO \longrightarrow Mn(CO)_5(COMe)$

   [*Ans.* See eq. 24.40]

2. Which of the following compounds contain a 16-electron metal centre: (a) $Rh(PPh_3)_3Cl$; (b) $HCo(CO)_4$; (c) $Ni(\eta^3\text{-}C_3H_5)_2$; (d) $Fe(CO)_4(PPh_3)$; (e) $[Rh(CO)_2I_2]^-$?

   [*Ans.* (a), (c), (e)]

3. Write an equation to show β-hydrogen elimination from $L_nMCH_2CH_2R$. [*Ans.* See eq. 24.44]

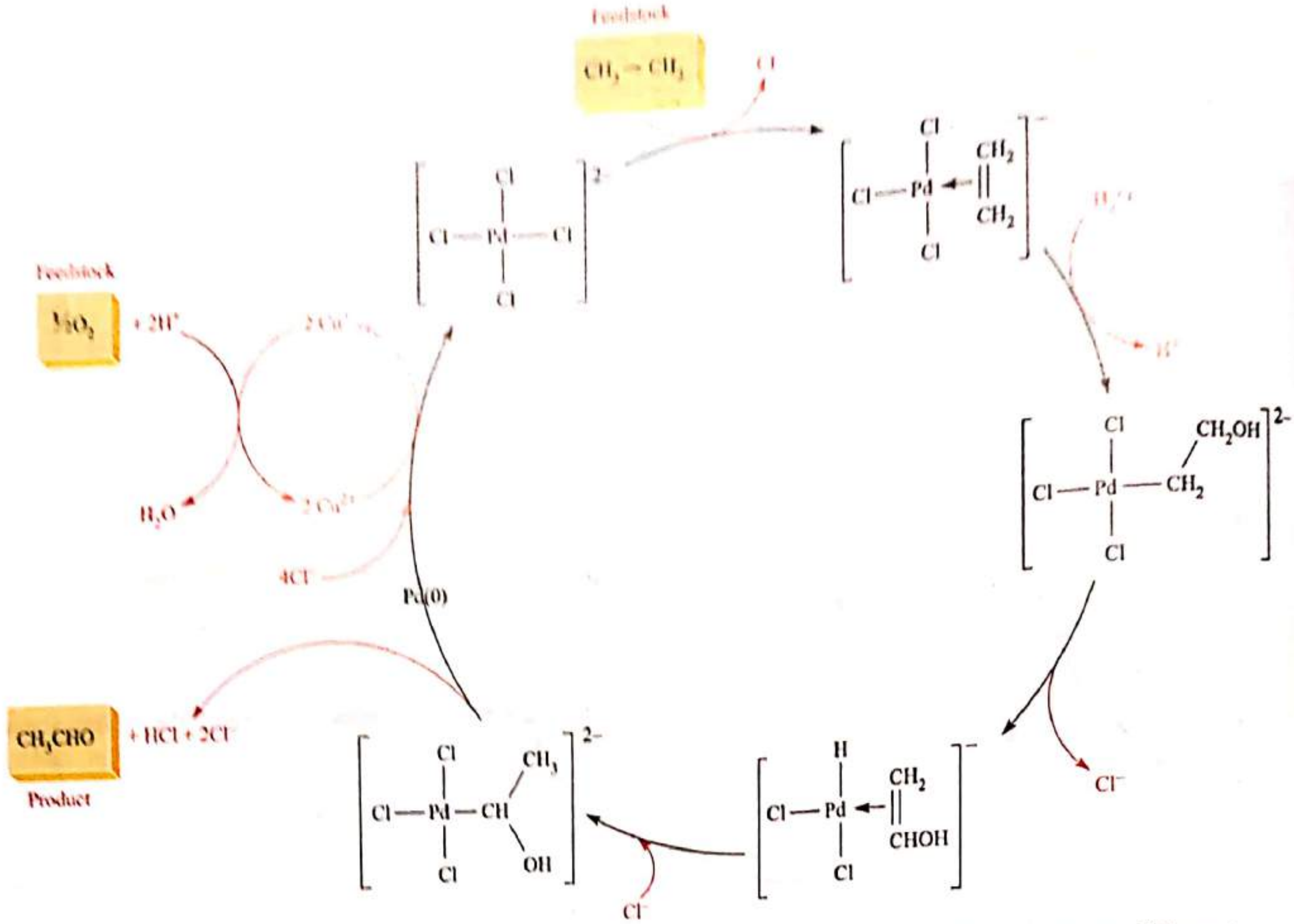


Fig. 25.2 Catalytic cycle for the Wacker process. For simplicity, we have ignored the role of coordinated H_2O, which replaces Cl^- *trans* to the alkene.

4. What is meant by 'oxidative addition'? Write an equation for the oxidative addition of H_2 to $RhCl(PPh_3)_3$.

[*Ans.* See eq. 24.34 and associated text]

5. What type of reaction is the following, and what, typically, is the mechanism for such reactions?

$$Mo(CO)_5(THF) + PPh_3 \longrightarrow Mo(CO)_5(PPh_3) + THF$$

[*Ans.* See eq. 24.29 and associated text]

We now study one cycle in detail to illustrate the notations. Figure 25.2 shows a simplified catalytic cycle for the Wacker process which converts ethene to acetaldehyde (eq. 25.1). The process was developed in the 1950s and although it is not of great industrial significance nowadays, it provides a well-studied example for close examination.

$$CH_2=CH_2 + \tfrac{1}{2}O_2 \xrightarrow{[PdCl_4]^{2-}\text{ catalyst}} CH_3CHO \qquad (25.1)$$

The *feedstocks* for the industrial process are highlighted along with the final product in Fig. 25.2. The catalyst in the Wacker process contains palladium: through most of the cycle, the metal is present as Pd(II) but is reduced to Pd(0) as CH_3CHO is produced. We now work through the cycle, considering each step in terms of the organometallic reaction types discussed in Section 24.7.

1. (The first step involves substitution by $CH_2=CH_2$ in $[PdCl_4]^{2-}$ (eq. 25.2). At the top of Fig. 25.2, the arrow notation shows $CH_2=CH_2$ entering the cycle and Cl^- leaving. One Cl^- is then replaced by H_2O, but we ignore this in Fig. 25.2.

$$[PdCl_4]^{2-} + CH_2=CH_2 \longrightarrow [PdCl_3(\eta^2\text{-}C_2H_4)]^- + Cl^-) \qquad (25.2)$$

2. (The next step involves nucleophilic attack by H_2O with loss of H^+. Recall that coordinated alkenes are susceptible to nucleophilic attack)(see eq. 24.86).3(In the third step, β-elimination occurs and formation of the Pd–H bond results in loss of Cl^-).4(This is followed by attack by Cl^- with H atom migration to give a σ-bonded $CH(OH)CH_3$ group).(Elimination of CH_3CHO, H^+ and Cl^- with reduction of Pd(II) to Pd(0) occurs in the last step).(To keep the cycle going, Pd(0) is now oxidized by Cu^{2+} (eq. 25.3). The

secondary cycle in Fig. 25.2 shows the reduction of Cu^{2+} to Cu^+ and reoxidation of the latter by O_2 in the presence of H^+ (eq. 25.4).

$$Pd + 2Cu^{2+} + 8Cl^- \longrightarrow [PdCl_4]^{2-} + 2[CuCl_2]^- \qquad (25.3)$$

$$2[CuCl_2]^- + \tfrac{1}{2}O_2 + 2HCl \longrightarrow 2CuCl_2 + 2Cl^- + H_2O \qquad (25.4)$$

If the whole cycle in Fig. 25.2 is considered with species 'in' balanced against species 'out', the *net reaction* is reaction 25.1.

Choosing a catalyst

A reaction is not usually catalysed by a unique species and a number of criteria must be considered when choosing the most effective catalyst, especially for a commercial process. Moreover, altering a catalyst in an industrial plant already in operation may be costly (e.g. a new plant design may be required) and the change must be guaranteed to be financially viable. Apart from the changes in reaction conditions that the use of a catalyst may bring about (e.g. pressure and temperature), other factors that must be considered are:

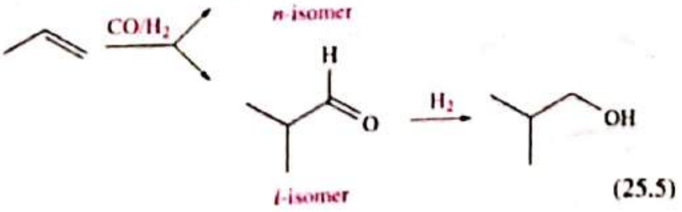
- the concentration of catalyst required;
- the catalytic turnover;
- the selectivity of the catalyst to the desired product;
- how often the catalyst needs renewing.

The *catalytic turnover number* (TON) is the number of moles of product per mole of catalyst. This number indicates the number of catalytic cycles for a given process, e.g. after 2 h, the TON was 2400.

The *catalytic turnover frequency* (TOF) is the catalytic turnover per unit time: the number of moles of product per mole of catalyst per unit time, e.g. the TOF was 20 min^{-1}.

Defining the catalytic turnover number and frequency is not without problems. For example, if there is more than one product, one should distinguish between values of the total TON and TOF for all the catalytic products, and specific values for individual products. The term catalytic turnover number is usually used for batch processes, whereas catalytic turnover frequency is usually applied to continuous processes (flow reactors).

Now we turn to the question of selectivity, and the conversion of propene to an aldehyde provides a good example. Equation 25.5 shows the four possible products that may result from the reaction of propene with CO and H_2 (*hydroformylation*; see also Section 25.5).

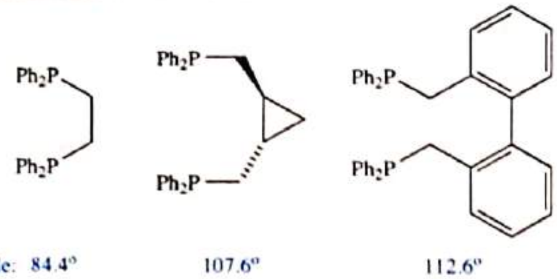


(25.5)

The following ratios are important:

- the *n* : *i* ratio of the aldehydes (*regioselectivity* of the reaction);
- the aldehyde : alcohol ratio for a given chain (*chemoselectivity* of the reaction).

The choice of catalyst can have a significant effect on these ratios. For reaction 25.5, a cobalt carbonyl catalyst (e.g. $HCo(CO)_4$) gives ≈80% C_4-aldehyde, 10% C_4-alcohol and ≈10% other products, and an *n* : *i* ratio ≈3 : 1. For the same reaction, various rhodium catalysts with phosphane co-catalysts can give an *n* : *i* ratio of between 8 : 1 and 16 : 1, whereas ruthenium cluster catalysts show a high chemoselectivity to aldehydes with the regioselectivity depending on the choice of cluster, e.g. for $Ru_3(CO)_{12}$, $n:i \approx 2:1$, and for $[HRu_3(CO)_{11}]^-$, $n:i \approx 74:1$. Where the hydroformylation catalyst involves a bisphosphane ligand (e.g. $Ph_2PCH_2CH_2PPh_2$, dppe), the ligand bite angle (see structure **7.16**) can significantly influence the product distribution. For example, the *n* : *i* ratios in the hydroformylation of hex-1-ene catalysed by a Rh(I)-bisphosphane complex are ≈2.1, 12.1 and 66.5 as the bite angle of the bisphosphane ligand increases along the series:[†]



Although a diagram such as Fig. 25.2 shows a catalyst being regenerated and passing once more around the cycle, in practice, catalysts eventually become exhausted or are *poisoned*, e.g. by impurities in the feedstock.

25.3 Homogeneous catalysis: alkene (olefin) and alkyne metathesis

In Section 24.12, we introduced *alkene (olefin) metathesis*, i.e. metal-catalysed reactions in which C=C bonds are redistributed. The importance of alkene and alkyne metathesis was recognized by the award of the 2005 Nobel Prize in Chemistry to Yves Chauvin, Robert H. Grubbs and Richard R. Schrock 'for the development of the metathesis method in organic synthesis'. Examples of alkene metathesis are shown in Fig. 25.3. The Chauvin mechanism for metal-catalysed alkene metathesis involves a metal alkylidene species and a series of [2 + 2]-cycloadditions and

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[†] For further discussion of the effects of ligand bite angles on catalyst efficiency and selectivity, see: P. Dierkes and P.W.N.M. van Leeuwen (1999) *J. Chem. Soc., Dalton Trans.*, p. 1519.

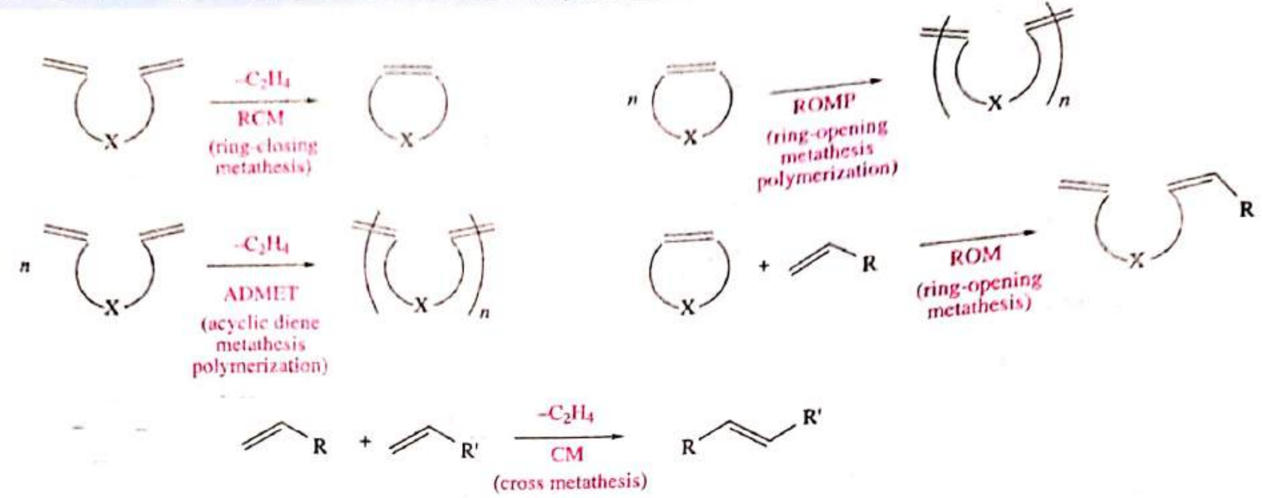
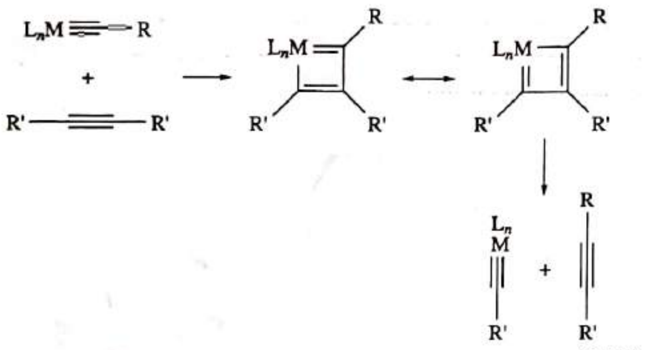


Fig. 25.3 Examples of alkene (olefin) metathesis reactions with their usual abbreviations.

cycloreversions (Fig. 25.4). Scheme 25.6 shows the mechanism for alkyne metathesis which involves a high oxidation state metal alkylidyne complex, $L_nM{\equiv}CR$.



(25.6)

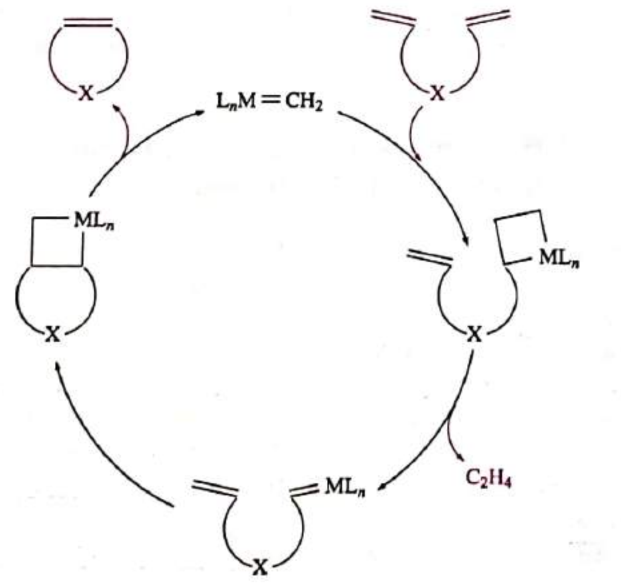
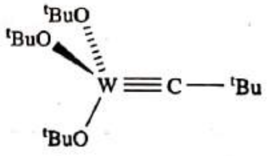


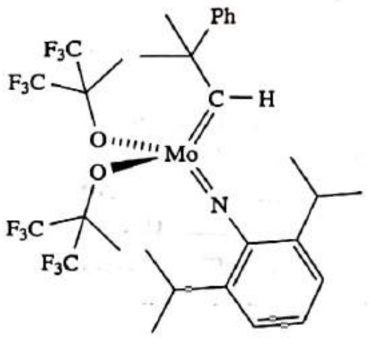
Fig. 25.4 A catalytic cycle for ring-closure metathesis (RCM) showing the Chauvin mechanism which involves [2 + 2]-cycloadditions and cycloreversions.

The catalysts that have played a dominant role in the development of this area of chemistry are those designed by Schrock (e.g. catalysts **25.1** and **25.2**) and Grubbs (catalysts **25.3** and **25.4**). Catalyst **25.3** is the traditional 'Grubbs' catalyst', and related complexes are also used. The 'second-generation' catalyst **25.4** exhibits higher catalytic activities in alkene metathesis reactions. Catalysts **25.1–25.4** are commercially available. There are around 15 modifications of Grubbs' catalysts which are optimized for different catalytic roles. This includes the recent 'third-generation' catalyst (see structure **24.68**).



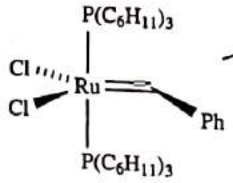
Schrock catalyst for alkyne metathesis

(25.1)



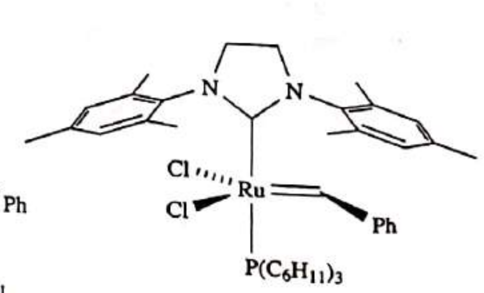
Example of a Schrock-type catalyst for alkene metathesis

(25.2)



C_6H_{11} = cyclohexyl

(25.3)



(25.4)

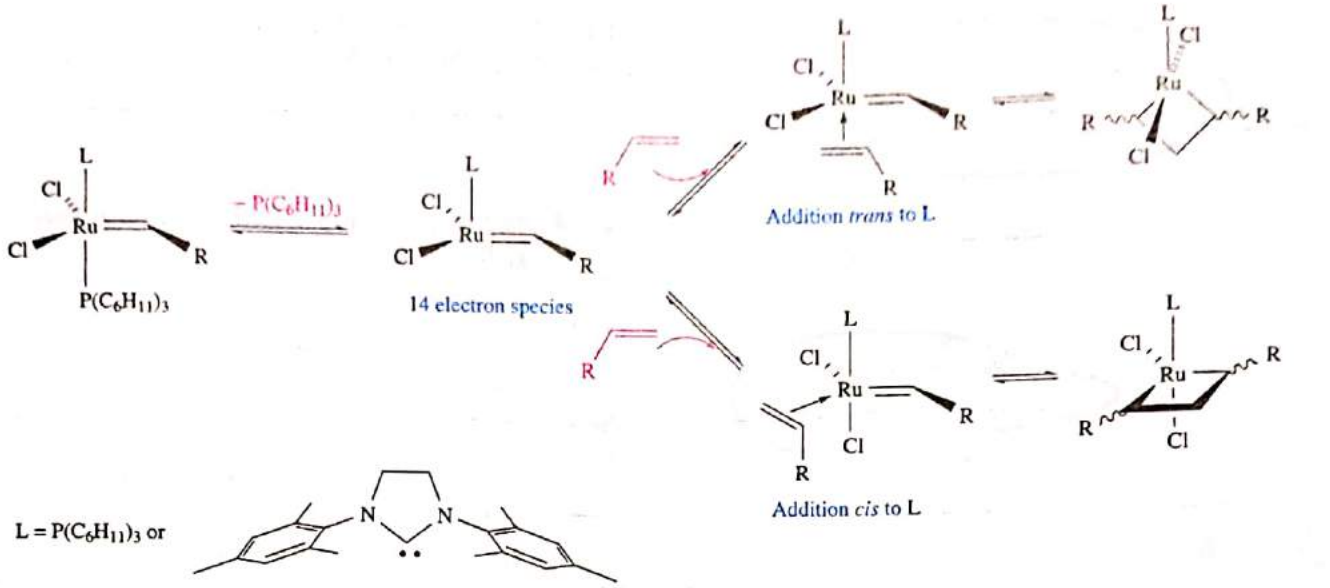


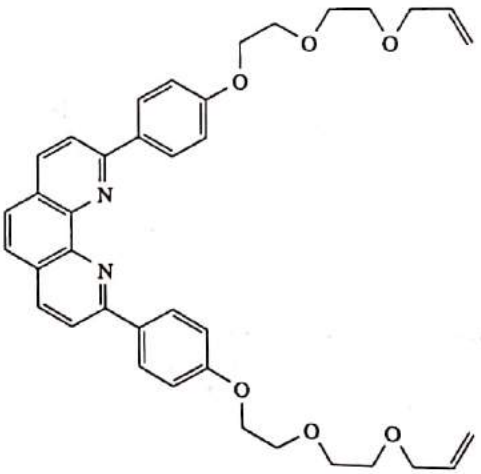
Fig. 25.5 Initial steps in the mechanism of alkene metathesis involving first and second generation Grubbs' catalysts. Two possibilities for the formation of the metallocyclobutane intermediates are shown.

In Grubbs' catalysts, tricyclohexylphosphane is chosen in preference to other PR_3 ligands because its steric hindrance and strongly electron-donating properties lead to enhanced catalytic activity. The first step in the mechanism of alkene metathesis involving Grubbs' catalysts is the dissociation of a $P(C_6H_{11})_3$ ligand to give a coordinatively unsaturated, 14-electron species (Fig. 25.5). The choice of the phosphane ligand is crucial for this initiation step: PR_3 ligands that are less sterically demanding than $P(C_6H_{11})_3$ bind too strongly to Ru, whereas those that are more bulky than $P(C_6H_{11})_3$ are too labile and a stable starting complex is not formed. The activated complex now enters the catalytic cycle by binding an alkene. This may coordinate to the Ru centre either *cis* or *trans* to $P(C_6H_{11})_3$ (first generation catalyst) or the *N*-heterocyclic carbene ligand (second generation catalyst). In keeping with the general Chauvin mechanism, the next step involves formation of metallocyclic intermediates (Fig. 25.5).[†]

A great advantage of Grubbs' catalysts is that they are tolerant of a large range of functional groups, thus permitting their widespread application. We highlight a laboratory example that combines coordination chemistry with the use of catalyst **25.3**: the synthesis of a *catenate*.

A *catenand* is a molecule containing two interlinked chains. A *catenate* is a related molecule that contains a coordinated metal ion.

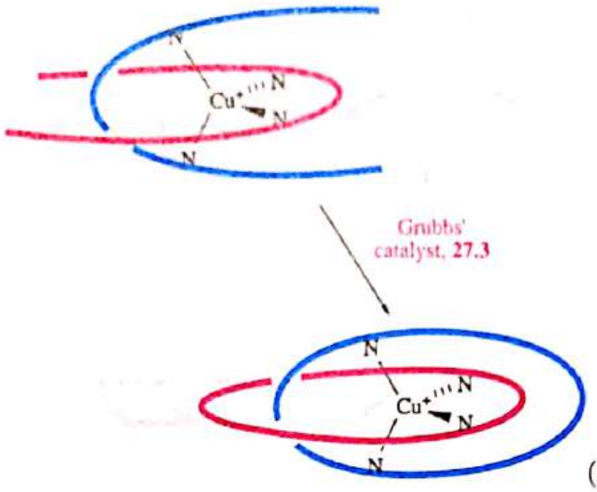
Topologically, the chemical assembly of a catenand is non-trivial because it requires one molecular chain to be threaded through another. Molecule **25.5** contains two terminal alkene functionalities and can also act as a bidentate ligand by using the *N*,*N'*-donor set.



(25.5)

The complex $[Cu(\mathbf{25.5})_2]^+$ is shown schematically at the top of eq. 25.7. The tetrahedral Cu^+ centre acts as a template, fixing the positions of the two ligands with the central phenanthroline units orthogonal to one another. Ring closure of *each* separate ligand can be achieved by treating $[Cu(\mathbf{25.5})_2]^+$ with Grubbs' catalyst, and the result is the formation of a catenate, shown schematically as the product in eq. 25.7. The relative orientations of the two coordinated ligands in $[Cu(\mathbf{25.5})_2]^+$ is important if competitive reactions between *different* ligands are to be minimized.

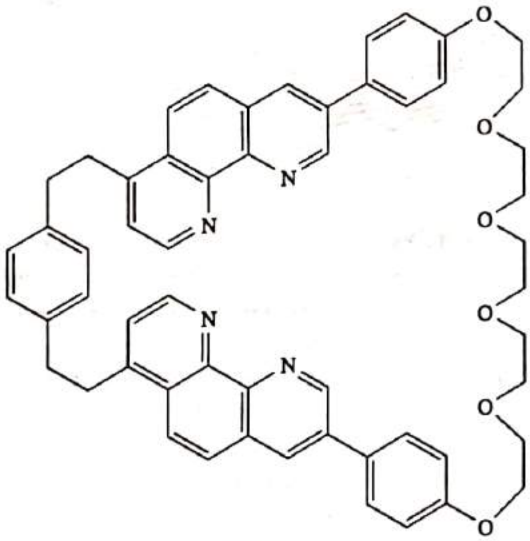
[†] For elucidation of the mechanisms see, for example: R.H. Grubbs (2004) *Tetrahedron*, vol. 60, p. 7117; D.R. Anderson, D.D. Hickstein, D.J. O'Leary and R.H. Grubbs (2006) *J. Am. Chem. Soc.*, vol. 128, p. 8386; A.G. Wenzel and R.H. Grubbs (2006) *J. Am. Chem. Soc.*, vol. 128, p. 16048.



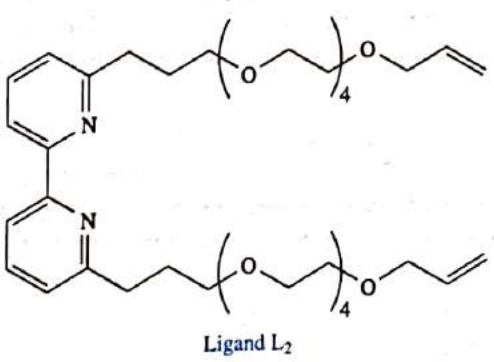
(25.7)

Self-study exercise

Ligand L_1 reacts with $Ru(DMSO)_4Cl_2$ in MeCN to give $[RuL_1(NCMe)_2]^{2+}$. Reaction of this complex with ligand L_2, followed by treatment with first generation Grubbs' catalyst, results in the formation of a catenate. (a) Draw a scheme for the reaction, paying attention to the coordination environment and stereochemistry of the Ru centre. (b) What type of alkene metathesis reaction is involved in the last step? (c) What complications can arise in this type of reaction?



Ligand L_1



Ligand L_2

[*Ans*: See P. Mobian *et al.* (2003) *J. Am. Chem. Soc.*, vol. 125, p. 2016; P. Mobian *et al.* (2003) *Helv. Chim. Acta*, vol. 86, p. 4195]

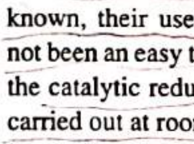
25.4 Homogeneous catalytic reduction of N_2 to NH_3

In nature, the fixation of nitrogen by bacteria involves the reduction of N_2 to NH_3 (eq. 25.8) catalysed by an iron- and molybdenum-containing nitrogenase (see Section 29.4). In contrast to this natural process, the industrial production of NH_3 (eq. 25.9) requires harsh conditions and a heterogeneous catalyst (see Section 25.8). Given the massive scale on which NH_3 is manufactured, the conversion of N_2 to NH_3 using a homogeneous catalyst under ambient conditions is a goal that many chemists have tried to achieve.

$$N_2 + 8H^+ + 8e^- \rightleftharpoons 2NH_3 + H_2 \qquad (25.8)$$

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad (25.9)$$

Since nature depends on FeMo-nitrogenase, complexes containing these metals are of particular interest in terms of investigating N_2 to NH_3 conversion. Complexes of type **25.6** have been a starting point for a number of studies involving intermediates such as **25.7** and **25.8**. However, such interconversions produce only moderate yields of NH_3 when **25.8** is protonated.



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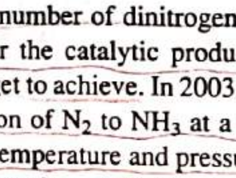
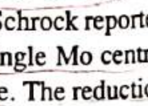
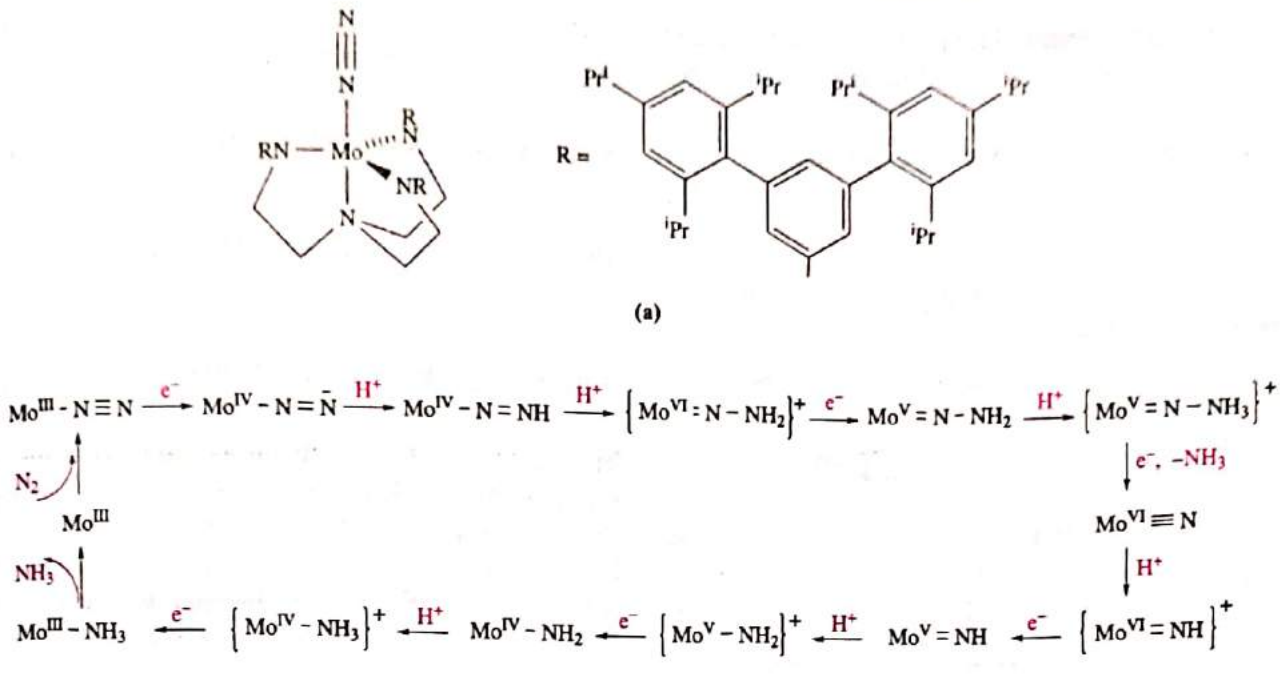


(25.7)



(25.8)

Despite the large number of dinitrogen metal complexes known, their use for the catalytic production of NH_3 has not been an easy target to achieve. In 2003, Schrock reported the catalytic reduction of N_2 to NH_3 at a single Mo centre, carried out at room temperature and pressure. The reduction is selective (it does not give any N_2H_4). The catalyst is represented in Fig. 25.6a in the state in which N_2 is bound. The tripodal ligand $[N(CH_2CH_2NR)_3]^{3-}$ shown bound to the Mo(III) centre is designed to maximize steric crowding around the active metal site, creating a pocket in which small-molecule transformations occur. The substituents R increase the solubility of the complexes shown in Fig. 25.6b. Each step in the proposed catalytic cycle involves either proton or electron transfer. Of the intermedi-

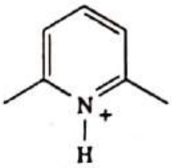


(a)

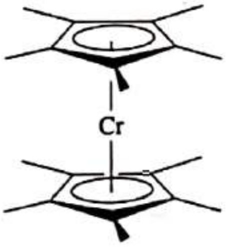
(b)

Fig. 25.6 (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.

ates shown, eight have been fully characterized.[†] In practice, a heptane solution of the complex $Mo^{III}N_2$ (defined in Fig. 25.6) is treated with an excess of 2,6-dimethylpyridinium ion (**25.9**) as the proton source and $(\eta^5\text{-}C_5Me_5)_2Cr$ (**25.10**) as the electron source. Decamethylchromocene is a very strong reducing agent, undergoing 1-electron oxidation to $[(\eta^5\text{-}C_5Me_5)_2Cr]^+$. The reagents must be added in a slow and controlled manner. Under these conditions, the efficiency of NH_3 formation from N_2 is ≈60%.



(25.9)



(25.10)

Although this example of the catalytic conversion of N_2 to NH_3 under ambient conditions in a well-defined molecular system remains at the research stage, it establishes that such conversions are possible.

25.5 Homogeneous catalysis: industrial applications

In this section, we describe selected homogeneous catalytic processes that are of industrial importance. Many more processes are applied in industry and detailed accounts can be found in the suggested reading at the end of the chapter. Two advantages of homogeneous over heterogeneous catalysis are the relatively mild conditions under which many processes operate, and the selectivity that can be achieved. A disadvantage is the need to separate the catalyst at the end of a reaction in order to recycle it, e.g. in the hydroformylation process, volatile $HCo(CO)_4$ can be removed by flash evaporation. The use of polymer supports or biphasic systems (Section 25.6) makes catalyst separation easier, and the development of such species is an active area of current research.

Throughout this section, the role of *coordinatively unsaturated 16-electron species* (see Section 24.7) and the ability of the metal centre to change coordination number (essential requirements of an active catalyst) should be noted.

Alkene hydrogenation

The most widely used procedures for the hydrogenation of alkenes nearly all employ heterogeneous catalysts, but for certain specialized purposes, homogeneous catalysts are used. Although addition of H_2 to a double bond is thermodynamically favoured (eq. 25.10), the kinetic barrier is

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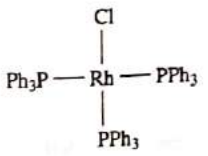
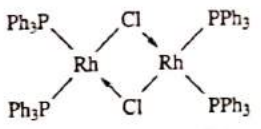
[†] For further details, see: R.R. Schrock (2005) *Acc. Chem. Res.*, vol. 38, 955; W.W. Weare *et al.* (2006) *Proc. Nat. Acad. Sci.*, vol. 103, p. 17099; T. Kupfer and R.R. Schrock (2009) *J. Am. Chem. Soc.*, vol. 131, p. 12829; M.R. Reithofer, R.R. Schrock and P. Müller (2010) *J. Am. Chem. Soc.*, vol. 132, p. 8349; T. Munisamy and R.R. Schrock (2012) *Dalton Trans.*, vol. 41, p. 130.

high and a catalyst is required for the reaction to be carried out at a viable rate without the need for high temperatures and pressures.

$$CH_2{=}CH_2 + H_2 \longrightarrow C_2H_6 \quad \Delta G^\circ = -101\,\text{kJ mol}^{-1} \qquad (25.10)$$



(25.11)



(25.12)

Wilkinson's catalyst (**25.11**) has been widely studied, and in its presence alkene hydrogenation can be carried out at 298 K and 1 bar H_2 pressure. The red, 16-electron Rh(I) complex **25.11** can be prepared from $RhCl_3$ and PPh_3, and is commonly used in benzene/ethanol solution, in which it dissociates to some extent (equilibrium 25.11). A solvent molecule (solv) fills the fourth site in $RhCl(PPh_3)_2$ to give $RhCl(PPh_3)_2(solv)$. The 14-electron $RhCl(PPh_3)_2$ (or its solvated analogue) is the active catalyst for the hydrogenation of alkenes. Dimerization of $RhCl(PPh_3)_2$ to **25.12** leads to a catalytically inactive species, and may occur when the concentrations of H_2 and alkene are low (e.g. at the end of a batch process).

$$RhCl(PPh_3)_3 \rightleftharpoons RhCl(PPh_3)_2 + PPh_3 \quad K = 1.4 \times 10^{-4} \qquad (25.11)$$

The *cis*-oxidative addition of H_2 to $RhCl(PPh_3)_3$ (left-hand side of Fig. 25.7) yields a coordinatively unsaturated 16-electron species (eq. 25.12).

$$\underset{\text{14-electron}}{RhCl(PPh_3)_2} + H_2 \rightleftharpoons \underset{\text{16-electron}}{RhCl(H)_2(PPh_3)_2} \qquad (25.12)$$

The addition of an alkene to $RhCl(H)_2(PPh_3)_2$ is probably the rate-determining step of the catalytic cycle shown in Fig. 25.7. The stereochemistry of octahedral $RhCl(H)_2(PPh_3)_2(\eta^2\text{-alkene})$ is such that the alkene is *cis* with respect to the two *cis*-hydrido ligands. Hydrogen migration then occurs to give a σ-bonded alkyl ligand, followed by reductive elimination of an alkane and regeneration of the active catalyst. The process is summarized in Fig. 25.7, the role of the solvent being ignored. The scheme shown should not be taken as being unique. For example, for some alkenes, experimental data suggest that $RhCl(PPh_3)_2(\eta^2\text{-alkene})$ is an intermediate. Other catalysts

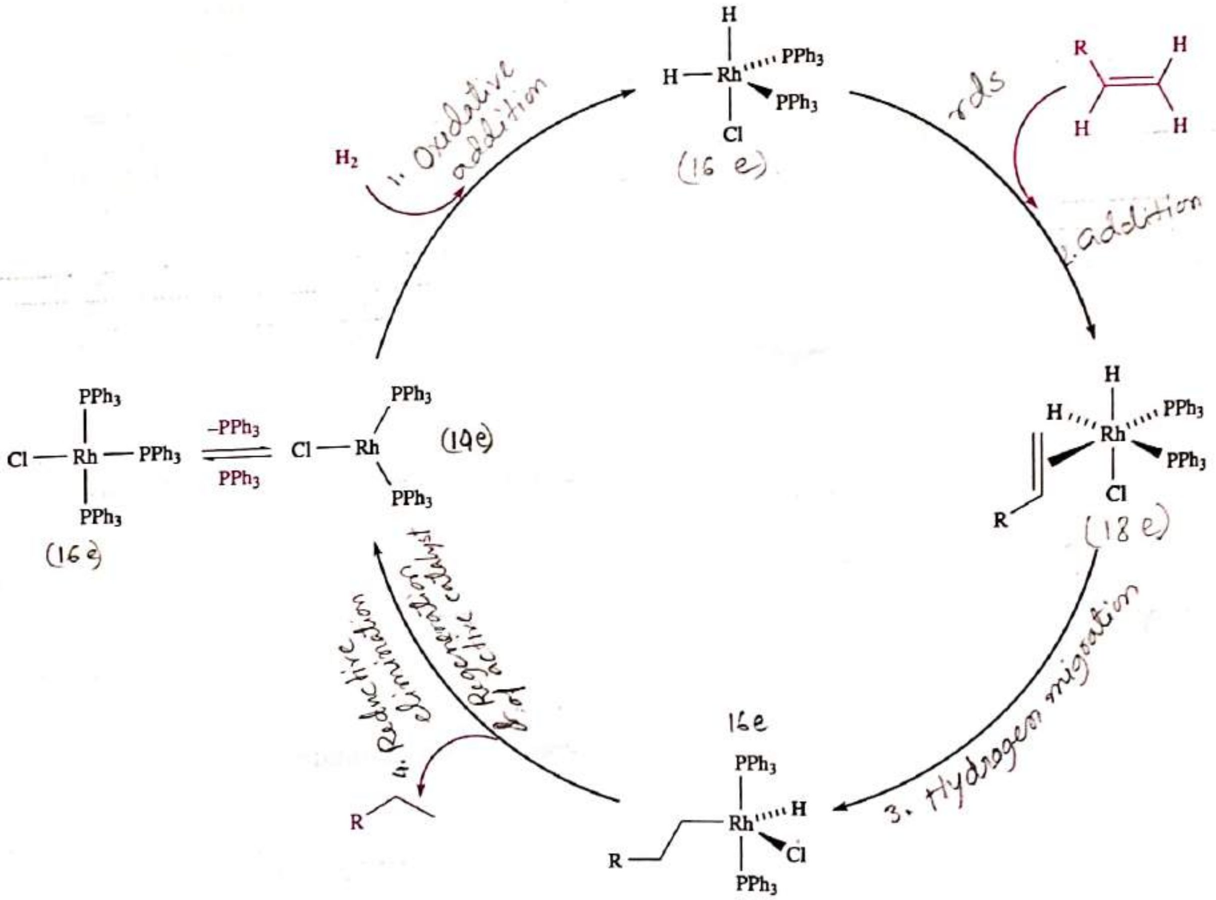


Fig. 25.7 Catalytic cycle for the hydrogenation of $RCH{=}CH_2$ using Wilkinson's catalyst, $RhCl(PPh_3)_3$.

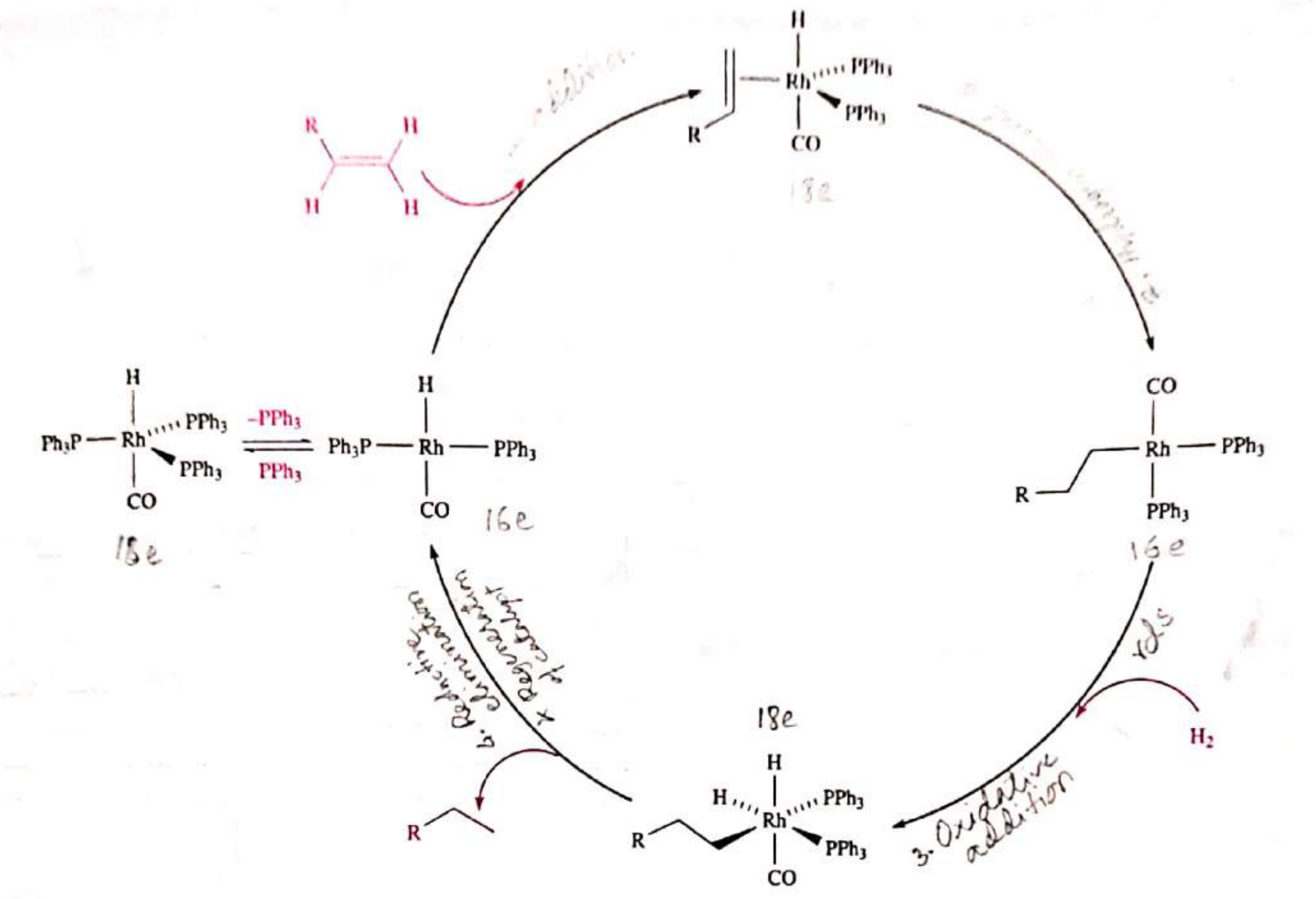


Fig. 25.8 Catalytic cycle for the hydrogenation of $RCH{=}CH_2$ using $HRh(CO)(PPh_3)_3$ as catalyst.

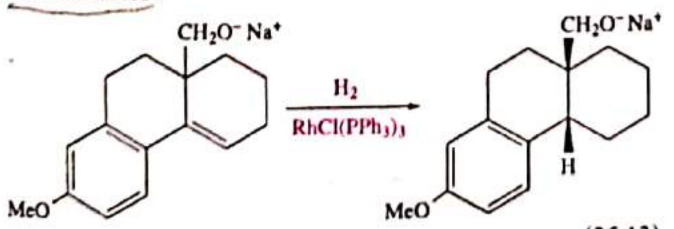
such as $HRuCl(PPh_3)_3$ and $HRh(CO)(PPh_3)_3$ (which loses PPh_3 to give an active 16-electron complex) react with alkene, rather than H_2, in the first step in the catalytic cycle. Figure 25.8 summarizes the route by which $HRh(CO)(PPh_3)_3$ catalyses the hydrogenation of an alkene. The rate-determining step is the oxidative addition of H_2 to the σ-bonded alkyl complex.

Substrate

Substrates for hydrogenation catalysed by Wilkinson's catalyst include alkenes, dienes, allenes, terpenes, butadiene rubbers, antibiotics, steroids and prostaglandins. Significantly, ethene actually poisons its own conversion to ethane, and catalytic hydrogenation using $RhCl(PPh_3)_3$ cannot be applied in this case. For effective catalysis, the size of the alkene is important. The rate of hydrogenation is hindered by sterically demanding alkenes (Table 25.1). Many useful *selective* hydrogenations can be achieved, e.g. reaction 25.13.

Size

Selectivity



(25.13)

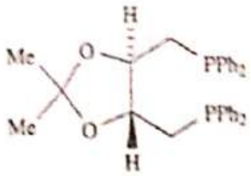
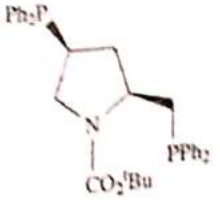
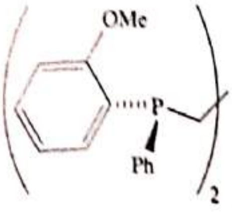
Biologically active compounds usually have at least one *asymmetric centre* and dramatic differences in the activities of different enantiomers of chiral drugs are commonly observed. Whereas one enantiomer may be an effective therapeutic drug, the other may be inactive or highly toxic as was the case with

Table 25.1 Rate constants for the hydrogenation of alkenes (at 298 K in C_6H_6) in the presence of Wilkinson's catalyst.[†]

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) *J. Chem. Soc. A*, p. 1574.

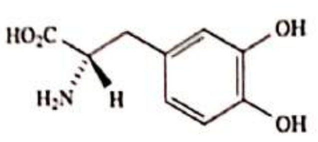
Table 25.2 Observed % ee of the product of the hydrogenation of $CH_2{=}C(CO_2H)(NHCOMe)$ using Rh(I) catalysts containing different chiral bisphosphanes.

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

thalidomide.[†] *Asymmetric synthesis* is therefore an active field of research.

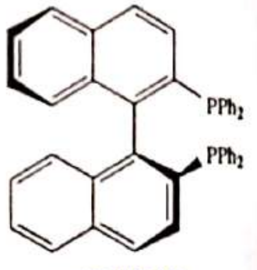
> ***Asymmetric synthesis*** is an enantioselective synthesis and its efficiency can be judged from the ***enantiomeric excess*** (ee):
>
> $$\%\ \text{ee} = \left(\frac{|R - S|}{|R + S|}\right) \times 100$$
>
> where R and S = relative quantities of *R* and *S* enantiomers.
>
> An enantiomerically pure compound has 100% enantiomeric excess (100% ee). In ***asymmetric catalysis***, the catalyst is chiral.

If hydrogenation of an alkene can, in principle, lead to enantiomeric products, then the alkene is *prochiral* (see end-of-chapter problem 25.6a). If the catalyst is *achiral* (as $RhCl(PPh_3)_3$ is), then the product of hydrogenation of the prochiral alkene is a racemate: i.e. starting from a prochiral alkene, there is an equal chance that the σ-alkyl complex formed during the catalytic cycle (Fig. 25.7) will be an *R*- or an *S*-enantiomer. If the catalyst is *chiral*, it should favour the formation of one or other of the *R*- or *S*-enantiomers, thereby making the hydrogenation enantioselective. *Asymmetric hydrogenations* can be carried out by modifying Wilkinson's catalyst, introducing a chiral phosphane or chiral bidentate bisphosphane, e.g. (*R,R*)-DIOP (defined in Table 25.2). By varying the chiral catalyst, hydrogenation of a given prochiral alkene proceeds with differing enantiomeric selectivities as exemplified in Table 25.2. An early triumph of the application of asymmetric alkene hydrogenation to drug manufacture was the production of the alanine derivative L-DOPA (**25.13**), which is used in the treatment of Parkinson's disease.[‡] The anti-inflammatory drug Naproxen (active in the (*S*)-form) is prepared by chiral resolution or by asymmetric hydrogenation of a prochiral alkene (reaction 25.14); enantiopurity is essential, since the (*R*)-enantiomer is a liver toxin.



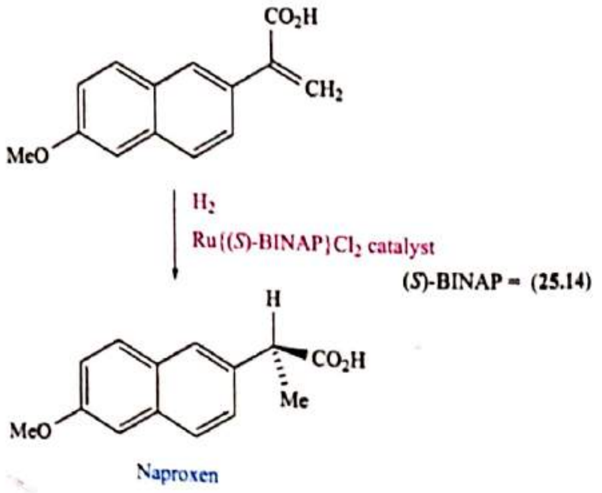
L-DOPA

(25.13)



(*S*)-BINAP

(25.14)



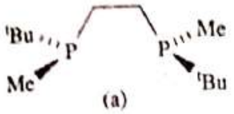
(25.14)

[†] See, for example: E. Thall (1996) *J. Chem. Educ.*, vol. 73, p. 481 – 'When drug molecules look in the mirror'; S.C. Stinson (1998) *Chem. Eng. News*, 21 Sept. issue, p. 83 – 'Counting on chiral drugs'; H. Caner, E. Groner, L. Levy and I. Agranat (2004) *Drug Discovery Today*, vol. 9, p. 105 – 'Trends in the development of chiral drugs'.

[‡] For further details, see: W.A. Knowles (1986) *J. Chem. Educ.*, vol. 63, p. 222 – 'Application of organometallic catalysis to the commercial production of L-DOPA'.

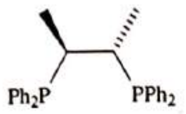
Self-study exercise

Which of the following ligands are chiral? For each chiral ligand, explain how the chirality arises.

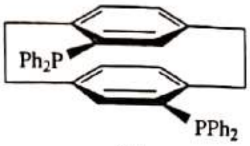


(a)

(b)



(c)

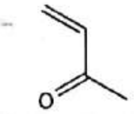


(d)

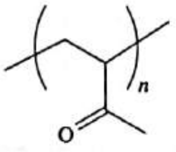
[*Ans.* (a), (c), (d)]

Monsanto and Cativa acetic acid syntheses

The conversion of MeOH to $MeCO_2H$ (eq. 25.15) is carried out on a huge industrial scale, and 60% of the world's acetyls are manufactured using the Monsanto and Cativa processes. Currently, ≈7 Mt per year of acetic acid are consumed worldwide, with the formation of vinyl acetate (**25.15**) being the most important commercial end use. Vinyl acetate is the precursor to polyvinylacetate (PVA, **25.16**).



(25.15)

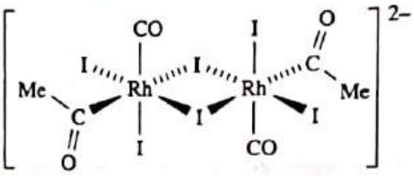


PVA

(25.16)

$$MeOH + CO \longrightarrow MeCO_2H \qquad (25.15)$$

Before 1970, acetic acid was manufactured by the BASF process utilizing cobalt-based catalysts, and high temperatures and pressures. Replacement of this procedure by the Monsanto process brought advantages of milder conditions and greater selectivity (Table 25.3). The Monsanto process uses a rhodium-based catalyst, and involves two interrelated catalytic cycles (Fig. 25.9 with M = Rh). In the left-hand cycle in Fig. 25.9, MeOH is converted to MeI, which then enters the right-hand cycle by oxidative addition to the catalyst, *cis*-$[Rh(CO)_2I_2]^-$, which is a 16-electron complex. This addition is the rate-determining step in the process. It 2. is followed by methyl migration and Fig. 25.9 shows the product of this step to be a 5-coordinate, 16-electron species. However, it is more likely to be an 18-electron complex, either dimer **25.17**, or $[Rh(CO)(COMe)I_3(solv)]$ where solv represents a solvent molecule. EXAFS studies (see Box 25.2) in THF solution indicate a dimer is present at 253 K, but a solvated monomer at 273 K. The next step 3. in the cycle in Fig. 25.9 is addition of CO (or replacement of the solvent molecule in $[Rh(CO)(COMe)I_3(solv)]$ by CO) to give an 18-electron, octahedral complex which elim- 4. inates MeCOI. This enters the left-hand cycle in Fig. 25.9 and is converted to $MeCO_2H$.



(25.17)

The yields of products in any industrial manufacturing process must be optimized. One difficulty in the Monsanto process is the oxidation of *cis*-$[Rh(CO)_2I_2]^-$ by HI (eq. 25.16). The product easily loses CO, precipitating RhI_3 thereby removing the catalyst from the system (eq. 25.17). Operating under a pressure of CO prevents this last detrimental step and, as eq. 25.18 shows, reverses the effects of reaction 25.16. Adding small amounts of H_2 prevents oxidation of Rh(I) to Rh(III).

Disadvantage of Monsanto process

$$[Rh(CO)_2I_2]^- + 2HI \longrightarrow [Rh(CO)_2I_4]^- + H_2 \qquad (25.16)$$

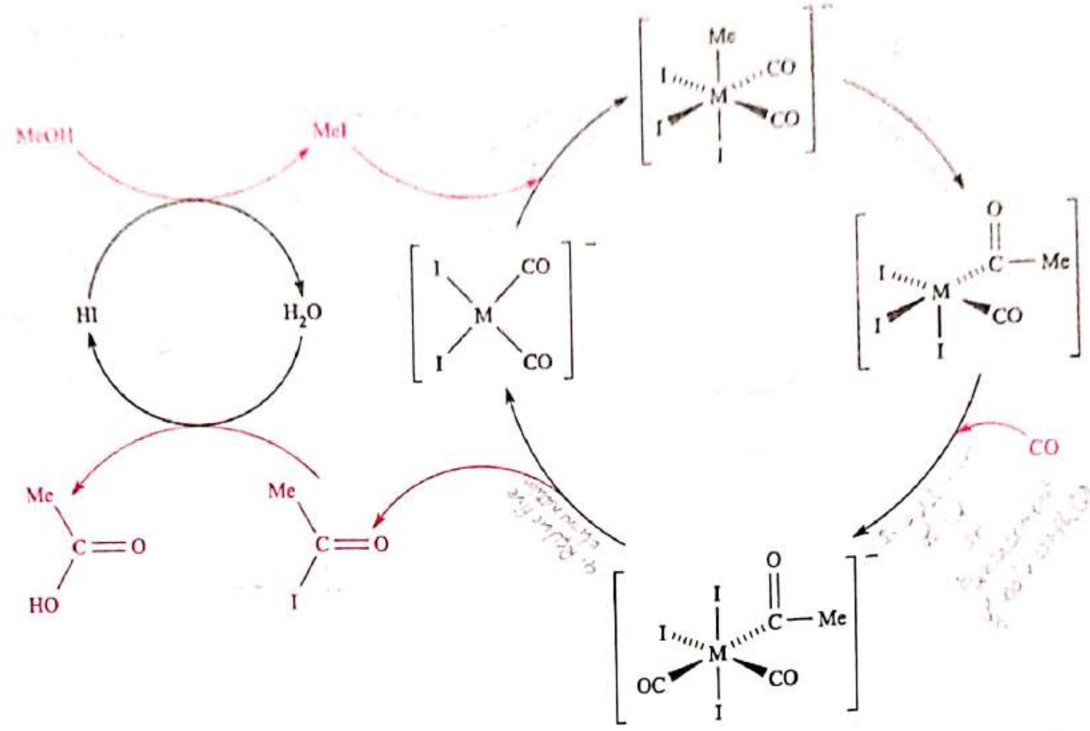
$$[Rh(CO)_2I_4]^- \longrightarrow RhI_3(s) + 2CO + I^- \qquad (25.17)$$

$$[Rh(CO)_2I_4]^- + CO + H_2O \longrightarrow [Rh(CO)_2I_2]^- + 2HI + CO_2 \qquad (25.18)$$

Between 1995 and 2000, BP Chemicals commercialized and began to operate the Cativa process for the production of acetic acid. The catalyst is *cis*-$[Ir(CO)_2I_2]^-$ in the presence of a ruthenium-based promoter (e.g. $Ru(CO)_4I_2$) or an iodide promoter (a molecular iodide, e.g. InI_3). Catalyst

Table 25.3 Comparison of conditions and selectivities of the BASF, Monsanto and Cativa processes for the manufacture of acetic acid (eq. 25.15).

Conditions	BASF (Co-based catalyst)	Monsanto (Rh-based catalyst)	Cativa (Ir-based catalyst)
Temperature / K	500	453	453
Pressure / bar	500–700	35	20–40
Selectivity / %	90	>99	>99



solvated or dimeric 25.17

Fig. 25.9 The two interrelated catalytic cycles in the Monsanto (M = Rh) and Cativa (M = Ir) acetic acid manufacturing processes.

Comparison of Monsanto and Cativa

precursors include $IrCl_3$ and H_2IrCl_6. 1. (The catalytic cycle for the Cativa process (Fig. 25.9 with M = Ir) is essentially the same as for the Monsanto process. However, oxidative addition of MeI to *cis*-$[Ir(CO)_2I_2]^-$ is faster than to *cis*-$[Rh(CO)_2I_2]^-$, and this step is not rate-determining in the Cativa process (compare discussion above for the Monsanto process). The increased strength of the metal–ligand bonds on going from Rh to Ir (see exercise below) results in the rate-determining step being methyl migration. The rate of this step can be increased by the addition of an I^- abstractor, and this results in methyl migration occurring in the 5-coordinate $[Ir(CO)_2I_2Me]$ rather than in the 6-coordinate $[Ir(CO)_2I_3Me]^-$.)

Self-study exercise

On going from Rh to Ir, metal–ligand bonding becomes stronger. Explain how the following data provide evidence for this.

	ν_{CO} / cm^{-1}	
cis-$[Rh(CO)_2I_2]^-$	2059	1988
cis-$[Ir(CO)_2I_2]^-$	2046	1968
cis,fac-$[Rh(CO)_2I_3Me]^-$	2104	2060
cis,fac-$[Ir(CO)_2I_3Me]^-$	2098	2045

2. (An important advantage of the Cativa over Monsanto process is the fact that precipitation of $IrCl_3$ does not occur as readily as precipitation of $RhCl_3$ (see eq. 25.17).) 3. (A second advantage is that CO_2 emissions are ≈30% lower in the Cativa than in the Monsanto process. (The similarities between the two routes (Fig. 25.9) means that acetic acid manufacturing plants built to operate the Monsanto process can be retrofitted so as to switch production to the more advantageous Cativa process.) 4.

Tennessee–Eastman acetic anhydride process

The Tennessee–Eastman acetic anhydride process converts methyl acetate to acetic anhydride (eq. 25.19) and has been in commercial use since 1983.

$$MeCO_2Me + CO \longrightarrow (MeCO)_2O \checkmark \qquad (25.19)$$

(It closely resembles the Monsanto process but uses $MeCO_2Me$ in place of MeOH. *cis*-$[Rh(CO)_2I_2]^-$ remains the catalyst and the oxidative addition of MeI to *cis*-$[Rh(CO)_2I_2]^-$ is still the rate-determining step. One pathway can be described by adapting Fig. 25.9 with M = Rh, replacing:

- MeOH by $MeCO_2Me$;
- H_2O by $MeCO_2H$;
- $MeCO_2H$ by $(MeCO)_2O$.

However, (a second pathway (Fig. 25.10) in which LiI replaces HI is extremely important for efficiency of the process.) (The final product is formed by the reaction of acetyl iodide and lithium acetate.) (Other alkali metal iodides do not function as well as LiI, e.g. replacing LiI by NaI slows the reaction by a factor of ≈2.5.)

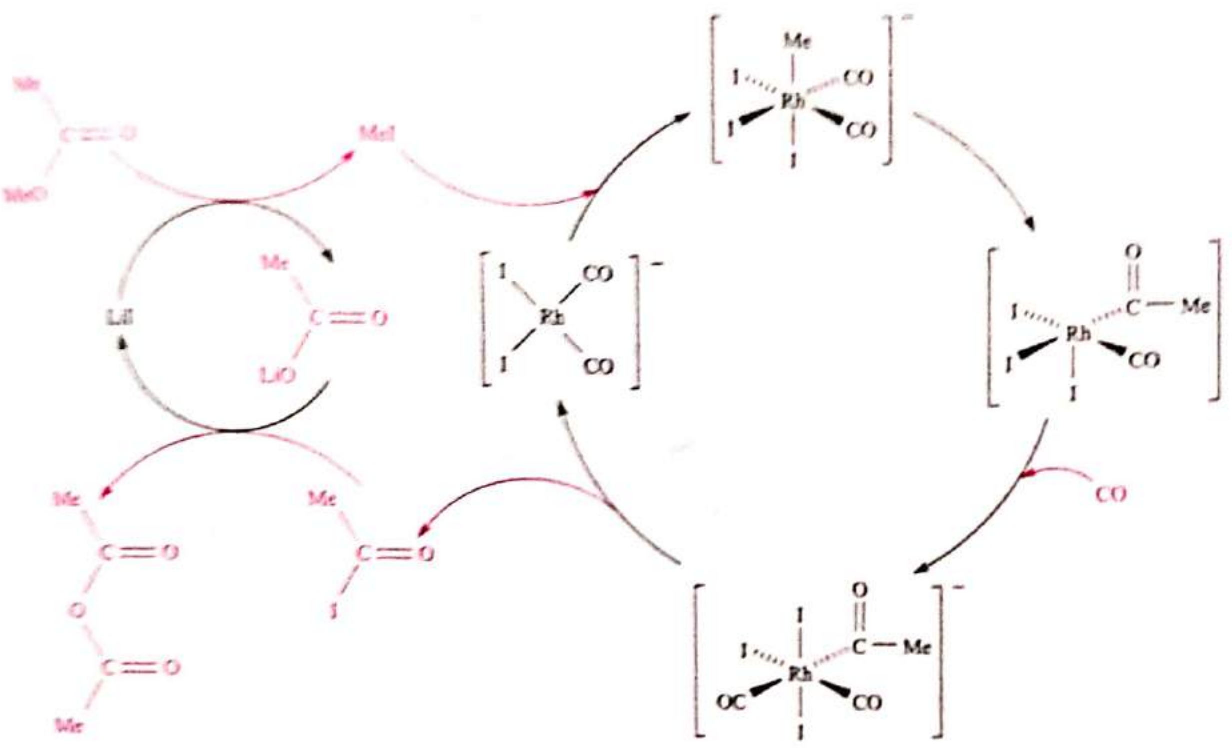


Fig. 25.10 Catalytic cycle for the Tennessee–Eastman acetic anhydride process.

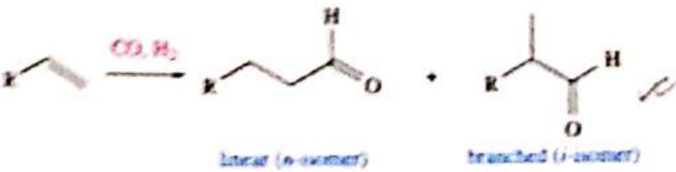
Self-study exercises

1. With reference to Fig. 25.10, explain what is meant by the term 'coordinatively unsaturated'.
2. What features of $[Rh(CO)_2I_2]^-$ allow it to act as an active catalyst?
3. In Fig. 25.10, which step is an oxidative addition?

[*Answers*: Refer to the discussion of the Monsanto process, and Section 24.7]

Hydroformylation (Oxo-process)

Hydroformylation (or the Oxo-process) is the conversion of alkenes to aldehydes (reaction 25.20). It is catalysed by cobalt and rhodium carbonyl complexes and has been exploited as a manufacturing process since World War II.



(25.20)

Cobalt-based catalysts were the first to be employed. Under the conditions of the reaction (370–470 K, 100–400 bar), $Co_2(CO)_8$ reacts with H_2 to give $HCo(CO)_4$. The latter is usually represented in catalytic cycles as the precursor to the coordinatively unsaturated (i.e. active) species $HCo(CO)_3$. As eq. 25.20 shows, hydroformylation can generate a mixture of linear and branched aldehydes, and the catalytic cycle in Fig. 25.11 accounts for both products. All steps (except for the final release of the aldehyde) are reversible. To interpret the catalytic cycle, start with $HCo(CO)_3$ at the top of Fig. 25.11. Addition of the alkene is the first step and this is followed by CO addition and accompanying H migration and formation of a σ-bonded alkyl group. At this point, the cycle splits into two routes depending on which C atom is involved in Co–C bond formation. The two pathways are shown as the inner and outer cycles in Fig. 25.11. In each, the next step is alkyl migration, followed by oxidative addition of H_2 and the transfer of one H atom to the alkyl group to give elimination of the aldehyde. The inner cycle eliminates a linear aldehyde, while the outer cycle produces a branched isomer. Two major complications in the process are the hydrogenation of aldehydes to alcohols, and alkene isomerization (which is also catalysed by $HCo(CO)_3$). The first of these problems (see eq. 25.5) can be controlled by using H_2 : CO ratios greater than 1 : 1 (e.g. 1.5 : 1). The isomerization problem (regioselectivity) can be addressed by using other catalysts (see below) or can be turned to advantage by purposely preparing mixtures of isomers for separation at a later stage. Scheme 25.21 illustrates the distribution of products formed when oct-1-ene undergoes

1.
cycle
3.
4.
problem
2 problem

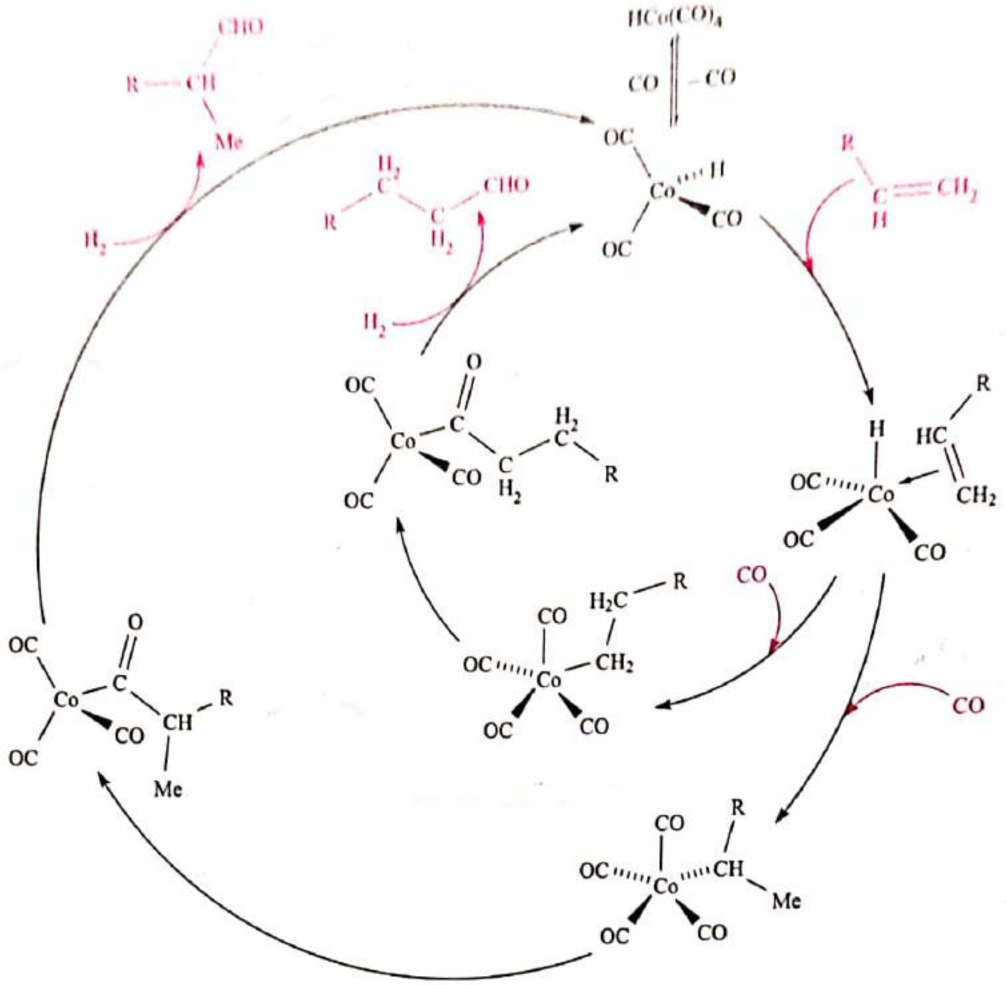
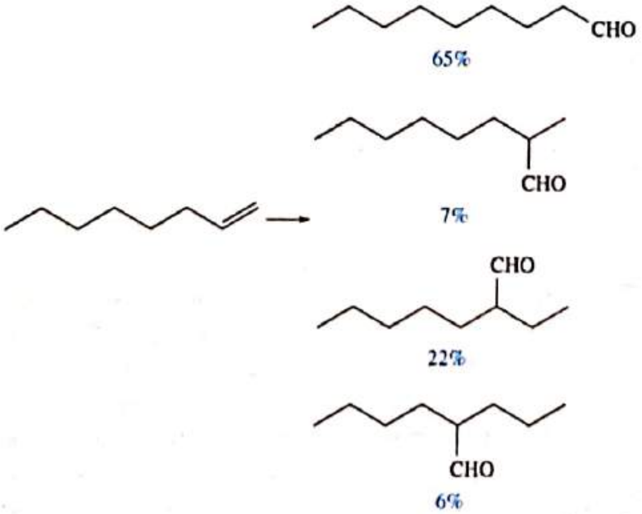


Fig. 25.11 Competitive catalytic cycles in the hydroformylation of alkenes to give linear (inner cycle) and branched (outer cycle) aldehydes.

hydroformylation at 423 K, 200 bar, and with a 1 : 1 H_2 : CO ratio.



(25.21)

Table 25.4 Rate constants for the hydroformylation of selected alkenes at 383 K in the presence of the active catalytic species $HCo(CO)_3$.

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

Just as we saw that the rate of hydrogenation was hindered by sterically demanding alkenes (Table 25.1), so too is the rate of hydroformylation affected by steric constraints, as is illustrated by the data in Table 25.4.

Other hydroformylation catalyst precursors that are used industrially are $HCo(CO)_3(PBu_3)$ (which, like $HCo(CO)_4$, must lose CO to become coordinatively unsaturated)

Table 25.5 A comparison of the operating conditions for and selectivities of three commercial hydroformylation catalysts. The formulae given are for the catalyst precursors.

	$HCo(CO)_4$	$HCo(CO)_3(PBu_3)$	$HRh(CO)(PPh_3)_3$
Temperature / K	410–450	450	360–390
Pressure / bar	250–300	50–100	30
Regioselectivity $n:i$ ratio (see eq. 25.5)	≈3 : 1	≈9 : 1	>10 : 1
Chemoselectivity (aldehyde predominating over alcohol)	High	Low	High

comparison

and $HRh(CO)(PPh_3)_3$ (which loses PPh_3 to give the catalytically active $HRh(CO)(PPh_3)_2$). Data in Table 25.5 compare the operating conditions for, and selectivities of, these catalysts with those of $HCo(CO)_4$. The Rh(I) catalyst is particularly selective towards aldehyde formation, and under certain conditions the $n:i$ ratio is as high as 20:1. An excess of PPh_3 prevents reactions 25.22 which occur in the presence of CO. The products of reactions 25.22 are also hydroformylation catalysts, but lack the selectivity of $HRh(CO)(PPh_3)_2$. The parent phosphane complex, $HRh(PPh_3)_3$, is inactive towards hydroformylation, and while $RhCl(PPh_3)_3$ is active, Cl^- acts as an inhibitor.

$$\left.\begin{array}{l} HRh(CO)(PPh_3)_2 + CO \rightleftharpoons HRh(CO)_2(PPh_3) + PPh_3 \\ HRh(CO)_2(PPh_3) + CO \rightleftharpoons HRh(CO)_3 + PPh_3 \end{array}\right\} \quad (25.22)$$

Self-study exercises

1. Interpret the data in eq. 25.21 into a form that gives an $n:i$ ratio for the reaction. [*Ans.* ≈1.9 : 1]
2. Draw out a catalytic cycle for the conversion of pent-1-ene to hexanal using $HRh(CO)_4$ as the catalyst precursor. [*Ans.* See inner cycle in Fig. 25.11, replacing Co by Rh]

Alkene oligomerization

The Shell Higher Olefins Process (SHOP) uses a nickel-based catalyst to oligomerize ethene. The process is designed to be flexible, so that product distributions meet consumer demand. The process is complex, but Fig. 25.12 gives a simplified catalytic cycle and indicates the form in which the nickel catalyst probably operates. 1. Alkene addition is followed by hydrogen (first step) or alkyl (later steps) migration and formation of a σ-bonded alkyl group. 2. This leaves a coordinatively unsaturated metal centre that can again undergo alkene addition. 3. If β-hydride elimination occurs, an alkene that contains a longer carbon chain than the starting alkene is produced.

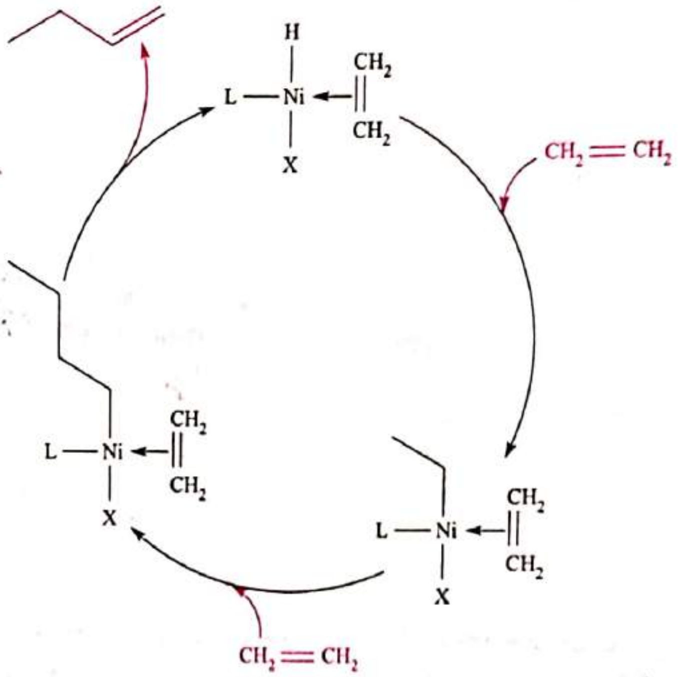


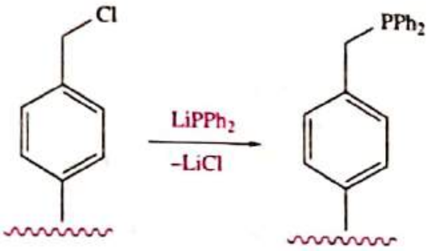
Fig. 25.12 Simplified catalytic cycle illustrating the oligomerization of ethene using a nickel-based catalyst; L = phosphane, X = electronegative group.

25.6 Homogeneous catalyst development

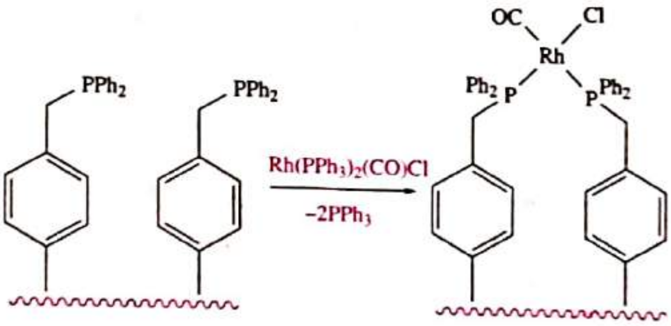
The development of new catalysts is an important research topic, and in this section we briefly introduce some areas of current interest.

Polymer-supported catalysts

Attaching homogeneous metal catalysts to polymer supports retains the advantages of mild operating conditions and selectivity usually found for conventional homogeneous catalysts, while aiming to overcome the difficulties of catalyst separation. Types of support include polymers with a high degree of cross-linking and with large surface areas, and microporous polymers (low degree of cross-linking) which swell when they are placed in solvents. A common method of attaching the catalyst to the polymer is to functionalize the polymer with a ligand that can then be used to coordinate to, and hence bind, the catalytic metal centre. Equation 25.23 gives a schematic representation of the use of a chlorinated polymer to produce phosphane groups supported on the polymer surface. Scheme 25.24 illustrates application of the phosphane-functionalized surface to attach a Rh(I) catalyst. This system catalyses the carbonylation of MeOH in the presence of a MeI promoter, and therefore has relevance to the Monsanto process (Fig. 25.9).

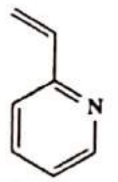


(25.23)

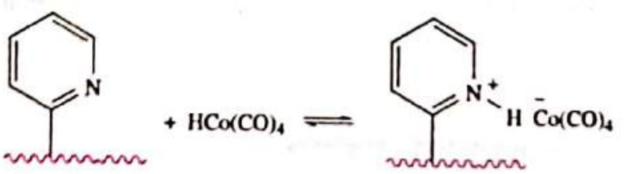


(25.24)

Alternatively, some polymers can bind the catalyst directly, e.g. poly-2-vinylpyridine (made from monomer **25.18**) is suitable for application in the preparation of hydroformylation catalysts (eq. 25.25).



(25.18)



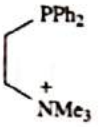
(25.25)

Hydroformylation catalysts can also be made by attaching the cobalt or rhodium carbonyl residues to a phosphane-functionalized surface through phosphane-for-carbonyl substitution. The chemo- and regioselectivities observed for the supported homogeneous catalysts are typically quite different from those of their conventional analogues.

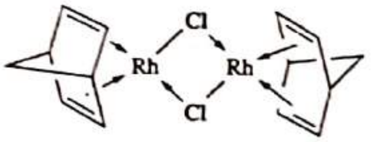
While much progress has been made in this area, leaching of the metal into solution (which partly defeats the advantages gained with regard to catalyst separation) is a common problem.

Biphasic catalysis

Biphasic catalysis addresses the problem of catalyst separation. One strategy uses a water-soluble catalyst. This is retained in an aqueous layer that is immiscible with the organic medium in which the reaction takes place. Intimate contact between the two solutions is achieved during the catalytic reaction, after which the two liquids are allowed to settle and the catalyst-containing layer separated by decantation. Many homogeneous catalysts are hydrophobic and so it is necessary to introduce ligands that will bind to the metal but that carry hydrophilic substituents. Among ligands that have met with success is **25.19**: e.g. the reaction of an excess of **25.19** with $[Rh_2(nbd)_2(\mu\text{-}Cl)_2]$ (**25.20**) gives a species, probably $[RhCl(\mathbf{25.19})_3]^{3+}$, which catalyses the hydroformylation of hex-1-ene to aldehydes (at 40 bar, 360 K) in 90% yield with an $n:i$ ratio of 4:1. An excess of the ligand in the aqueous phase stabilizes the catalyst and increases the $n:i$ ratio to ≈10:1.

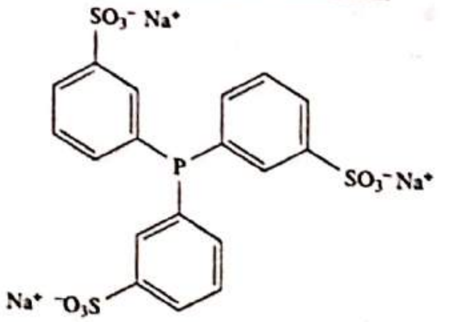


(25.19)

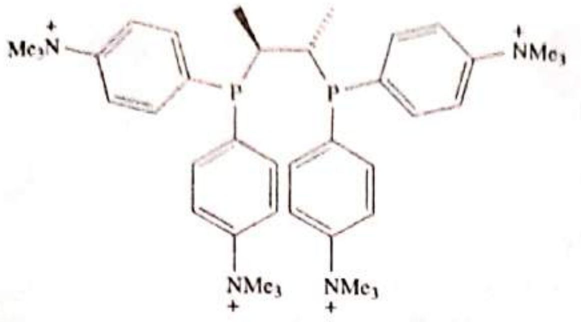


(25.20)

Much work has been carried out with the *P*-donor ligand **25.21** which can be introduced into a variety of organometallic complexes by carbonyl or alkene displacement. For example, the water-soluble complex $HRh(CO)(\mathbf{25.21})_3$ is a hydroformylation catalyst precursor. Conversion of hex-1-ene to heptanal proceeds with 93% selectivity for the *n*-isomer, a higher selectivity than is shown by $HRh(CO)(PPh_3)_3$ under conventional homogeneous catalytic conditions. A range of alkene hydrogenations are catalysed by $RhCl(\mathbf{25.21})_3$ and it is particularly efficient and selective for the hydrogenation of hex-1-ene.



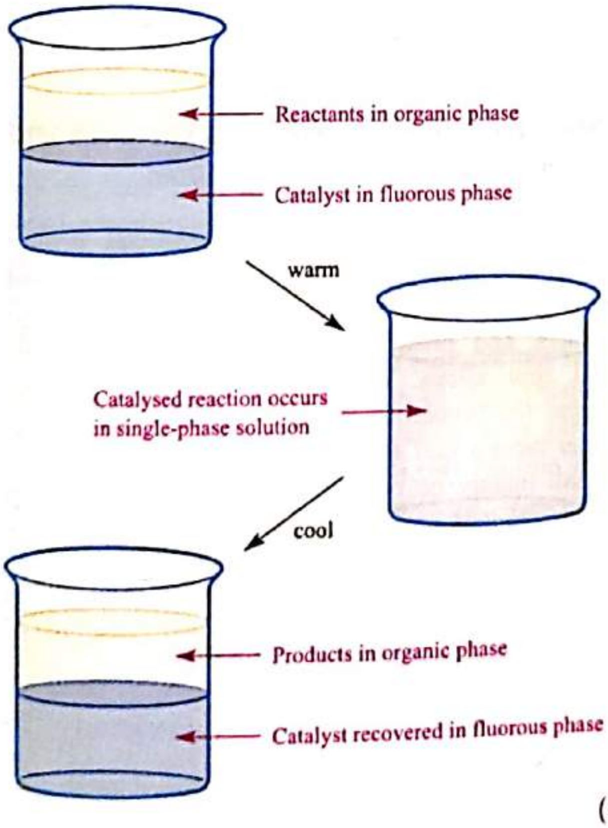
(25.21)



(25.22)

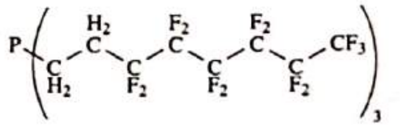
Biphasic asymmetric hydrogenation has also been developed using water-soluble chiral bisphosphanes such as **25.22** coordinated to Rh(I). With $PhCH{=}C(CO_2H)(NHC(O)Me)$ as substrate, hydrogenation takes place with 87% ee, and similar success has been achieved for related systems.

A second approach to biphasic catalysis uses a fluorous (i.e. perfluoroalkane) phase instead of an aqueous phase. There is an important difference between the higher C_n perfluoroalkanes used in fluorous biphasic catalysis and the low-boiling CFCs that have been phased out under the Montreal Protocol (see Box 14.6). The principle of fluorous biphasic catalysis is summarized in scheme 25.26.

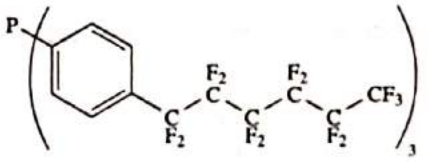


(25.26)

At room temperature, most fluorous solvents are immiscible with other organic solvents, but an increase in temperature typically renders the solvents miscible. The reactants are initially dissolved in a non-fluorinated, organic solvent and the catalyst is present in the fluorous phase. Raising the temperature of the system creates a single phase in which the catalysed reaction occurs. On cooling, the solvents, along with the products and catalyst, separate. Catalysts with suitable solubility properties can be designed by incorporating fluorophilic substituents such as C_6F_{13} or C_8F_{17}. For example, the hydroformylation catalyst $HRh(CO)(PPh_3)_3$ has been adapted for use in fluorous media by using the phosphane ligand **25.23** in place of PPh_3. Introducing fluorinated substituents alters the electronic properties of the ligand. If the metal centre in the catalyst 'feels' this change, its catalytic properties are likely to be affected. Placing a spacer between the metal and the fluorinated substituent can minimize these effects. Thus, in phosphane ligand **25.24** (which is a derivative of PPh_3), the aromatic ring helps to shield the P atom from the effects of the electronegative F atoms. Although the use of the biphasic system allows the catalyst to be recovered and recycled, leaching of the Rh into the non-fluorous phase occurs over a number of catalytic cycles.



(25.23)



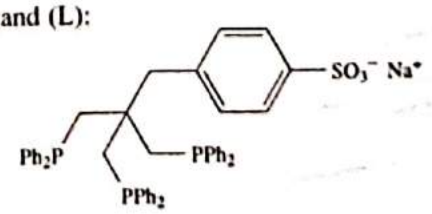
(25.24)

Although the biphasic catalysts described above appear analogous to those discussed in Section 25.5, it does not follow that the mechanisms by which the catalysts operate for a given reaction are similar.

Self-study exercises

1. Give an example of how PPh_3 can be converted into a hydrophilic catalyst.

2. The ligand (L):



forms the complex $[Rh(CO)_2L]^+$, which catalyses the hydrogenation of styrene in a water/heptane system.

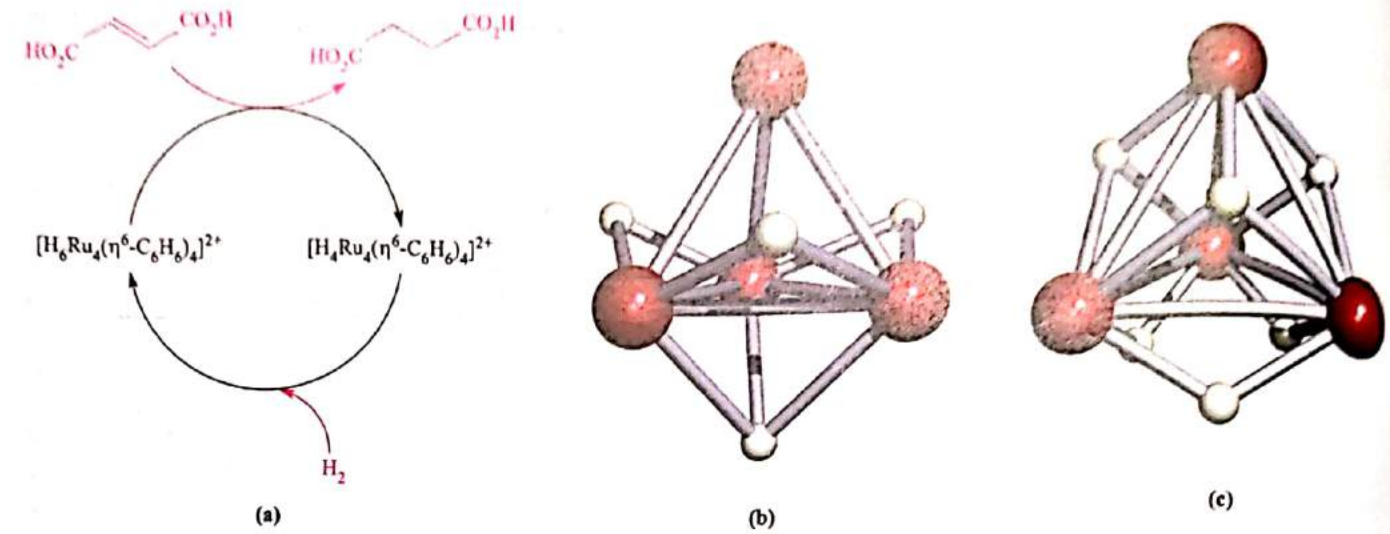


Fig. 25.13 (a) Catalytic cycle for the hydrogenation of fumaric acid by $[H_4(\eta^6\text{-}C_6H_6)_4Ru_4]^{2+}$; (b) H_4Ru_4 core of $[H_4(\eta^6\text{-}C_6H_6)_4Ru_4]^{2+}$; and (c) H_6Ru_4 core of $[H_6(\eta^6\text{-}C_6H_6)_4Ru_4]^{2+}$, both determined by X-ray diffraction [G. Meister *et al.* (1994) *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.

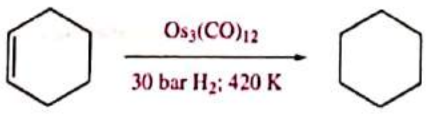
Suggest how L coordinates to the Rh centre. Explain how the catalysed reaction would be carried out, and comment on the advantages of the biphasic system over using a single solvent.

[*Ans.* See C. Bianchini *et al.* (1995) *Organometallics*, vol. 14, p. 5458]

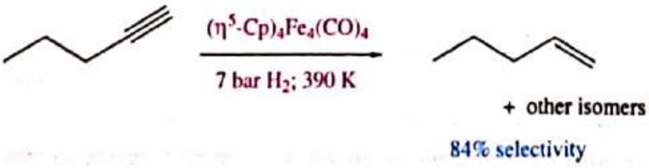
d-Block organometallic clusters as homogeneous catalysts

Over the past 40 years, much effort has been put into investigating the use of *d*-block organometallic clusters as homogeneous catalysts, and eqs. 25.27–25.29 give examples of small-scale catalytic reactions. Note that in reaction 25.27, insertion of CO is into the O–H bond. In contrast, in the Monsanto process using $[Rh(CO)_2I_2]^-$ catalyst, CO insertion is into the C–OH bond (eq. 25.15).

$$\mathrm{MeOH + CO \xrightarrow[400\ bar,\ 470\ K]{Ru_3(CO)_{12}} \underset{90\%\ selectivity}{MeOCHO}} \qquad (25.27)$$



(25.28)



(25.29)

A promising development in the area is the use of *cationic* clusters. $[H_4(\eta^6\text{-}C_6H_6)_4Ru_4]^{2+}$ catalyses the reduction of fumaric acid, the reaction being selective to the C=C bond and leaving the carboxylic acid units intact (Fig. 25.13).

Despite the large of amount of work that has been carried out in the area and the wide range of examples now known, it would appear that there are no industrial applications of molecular cluster catalysts.

25.7 Heterogeneous catalysis: surfaces and interactions with adsorbates

The majority of industrial catalytic processes involve *heterogeneous catalysis* and Table 25.6 gives selected examples. Conditions are generally harsh, with high temperatures and pressures. Before describing specific industrial applications, we introduce some terminology and discuss the properties of metal surfaces and zeolites that render them useful as heterogeneous catalysts.

Condition

We shall mainly be concerned with reactions of gases over heterogeneous catalysts. Molecules of reactants are *adsorbed* on to the catalyst surface, undergo reaction and the products are *desorbed*. Interaction between the adsorbed species and surface atoms may be of two types: physisorption or chemisorption.

interactions

✓ ***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.

The process of adsorption activates molecules, either by cleaving bonds or by weakening them. The dissociation of a diatomic molecule such as H_2 on a metal surface is

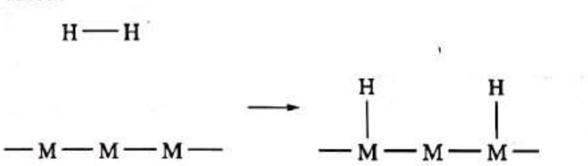
Table 25.6 Examples of industrial processes that use heterogeneous catalysts.

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 (see Section 25.8)
Catalytic reforming of hydrocarbons to improve octane number[**]	Pt, Pt–Ir and other Pt-group metals on acidic alumina support
Methanation ($CO \rightarrow CO_2 \rightarrow CH_4$)	Ni on support
Ethene epoxidation	Ag on support
HNO_3 manufacture (Haber–Bosch process)[***]	Pt–Rh gauzes

[‡] See Section 15.5.
[*] See eqs. 10.13 and 10.14.
[**] The octane number is increased by increasing the ratio of branched or aromatic hydrocarbons to straight-chain hydrocarbons. The 0–100 octane number scale assigns 0 to *n*-heptane and 100 to 2,2,4-trimethylpentane.
[***] See Section 15.9.

represented schematically in eq. 25.30. Bond formation does not have to be with a single metal atom as we illustrate later. Bonds in molecules, e.g. C–H, N–H, are similarly activated.

metal adsorbate bond



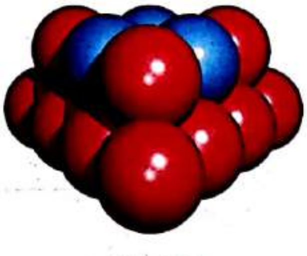
$$\text{H—H} + \text{—M—M—M—} \longrightarrow \text{—}\overset{\text{H}}{\overset{|}{\text{M}}}\text{—M—}\overset{\text{H}}{\overset{|}{\text{M}}}\text{—} \qquad (25.30)$$

The balance between the contributing bond energies is a factor in determining whether or not a particular metal will facilitate bond fission in the adsorbate. However, if metal–adsorbate bonds are especially strong, it becomes energetically less favourable for the adsorbed species to leave the surface, and this blocks adsorption sites, reducing catalytic activity.

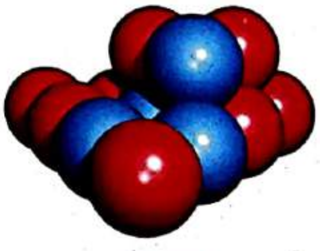
surface coverage

The adsorption of CO on metal surfaces has been thoroughly investigated. Analogies can be drawn between the interactions of CO with metal atoms on a surface and those in organometallic complexes (see Section 24.2), i.e. both terminal and bridging modes of attachment are possible, and IR spectroscopy can be used to study adsorbed CO. Upon interaction with a surface metal atom, the C–O bond is weakened in much the same way as shown in Fig. 24.1. The extent of weakening depends not only on the mode of interaction with the surface but also on the surface coverage. In studies of the adsorption of CO on a Pd(111)[†] surface, it is found that the enthalpy of adsorption of CO becomes less negative as more of the surface is covered with adsorbed molecules. An abrupt decrease in the amount of heat evolved per mole of adsorbate is observed when the surface is half-occupied by a *monolayer*. At this point, significant reorganization of the adsorbed molecules is needed to accommodate still more. Changes in the mode of attachment of CO molecules to the surface alter the strength of the C–O bond and the extent to which the molecule is activated.

Diagrams of hcp, fcc or bcc metal lattices such as we showed in Fig. 6.2 imply 'flat' metal surfaces. In practice, a surface contains imperfections such as those illustrated in Fig. 25.14. The *kinks* on a metal surface are extremely important for catalytic activity, and their presence increases the rate of catalysis. In a close-packed lattice, sections of 'flat' surface contain M_3 triangles (**25.25**), while a step possesses a line of M_4 'butterflies' (see Table 24.5), one of which is shown in blue in structure **25.26**. Both can accommodate adsorbed species in sites which can be mimicked by discrete metal clusters. This has led to the *cluster-surface analogy* (see Section 25.9).



(25.25)



(25.26)

The design of metal catalysts has to take into account not only the available surface but also the fact that the catalytically active platinum-group metals (see Section 22.2) are rare and expensive. There can also be the problem that extended exposure to the metal surface may result in side reactions. In many commercial catalysts, including motor

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[†] The notations (111), (110), (101)... are Miller indices and define the crystal planes in the metal lattice.

THEORY

Box 25.2 Some experimental techniques used in surface science

In much of this book, we have been concerned with studying species that are soluble and subjected to solution techniques (see Chapter 4) such as NMR and electronic spectroscopy, or with structural data obtained from X-ray or neutron diffraction studies of *single crystals* or electron diffraction studies of gases. The investigation of solid surfaces requires specialist techniques, many of which have been developed relatively recently. Selected examples are listed in the table below.

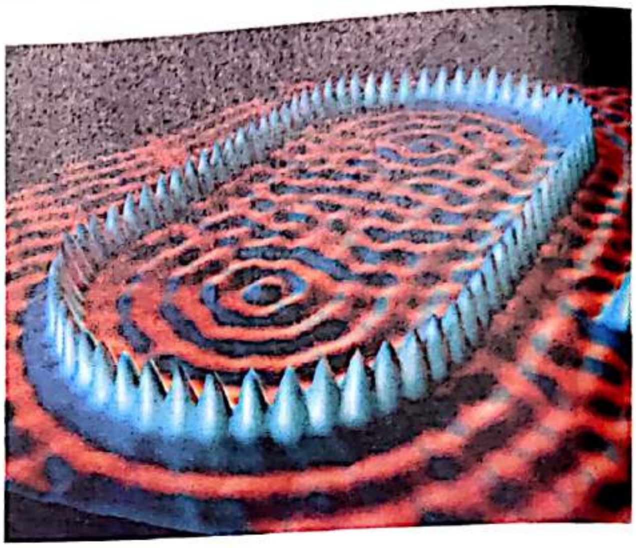
For further details of solid state techniques, see:

J. Evans (1997) *Chem. Soc. Rev.*, vol. 26, p. 11 – 'Shining light on metal catalysts'.

J. Evans (2006) *Phys. Chem. Chem. Phys.*, vol. 8, p. 3045 – 'Brilliant opportunities across the spectrum'.

G.A. Somorjai and Y. Li (2010) *Introduction to Surface Chemistry and Catalysis*, 2nd edn, Wiley, New Jersey.

A.R. West (1999) *Basic Solid State Chemistry*, 2nd edn, Wiley, Chichester.



A false colour image obtained using scanning tunnelling microscopy (STM) of iron atoms arranged in an oval on a corrugated copper surface.

Acronym	Technique	Application and description of technique
AES	Auger electron spectroscopy	Study of surface composition
EXAFS	Extended X-ray absorption fine structure	Estimation of internuclear distances around a central atom
FTIR	Fourier transform infrared spectroscopy	Study of adsorbed species
HREELS	High-resolution electron energy loss spectroscopy	Study of adsorbed species
LEED	Low-energy electron diffraction	Study of structural features of the surface and of adsorbed species
SIMS	Secondary ion mass spectrometry	Study of surface composition
STM	Scanning tunnelling microscopy	Obtaining images of a surface and adsorbed species at an atomic level
XANES	X-ray absorption near edge spectroscopy	Study of oxidation states of surface atoms
XRD	X-ray diffraction	Investigation of phases and particle sizes
XPS (ESCA)	X-ray photoelectron spectroscopy (electron spectroscopy for chemical analysis)	Study of surface composition and oxidation states of surface atoms

vehicle catalytic converters, small metal particles (e.g. 1600 pm in diameter) are dispersed on a support such as γ-alumina (*activated alumina*, see Section 13.7) which has a large surface area. Using a support of this type means that a high percentage of the metal atoms are available for catalysis. In some cases, the support itself may beneficially modify the properties of the catalyst. For example, in hydrocarbon reforming (Table 25.6), the metal and support operate together:

support

- the platinum-group metal catalyses the conversion of an alkane to alkene;
- isomerization of the alkene is facilitated by the acidic alumina surface;
- the platinum-group metal catalyses the conversion of the isomerized alkene to an alkane which is more highly branched than the starting hydrocarbon.

As well as having roles as supports for metals, silica and alumina are used directly as heterogeneous catalysts. A major application is in the catalytic cracking of heavy petroleum distillates. Very fine powders of silica and γ-alumina possess a huge surface area of $\approx 900\,m^2\,g^{-1}$. Large surface areas are a key property of zeolite catalysts (see Section 14.9), the selectivity of which can be tuned by varying the sizes, shapes and Brønsted acidity of their cavities and channels. We discuss these properties more fully in Section 25.8.

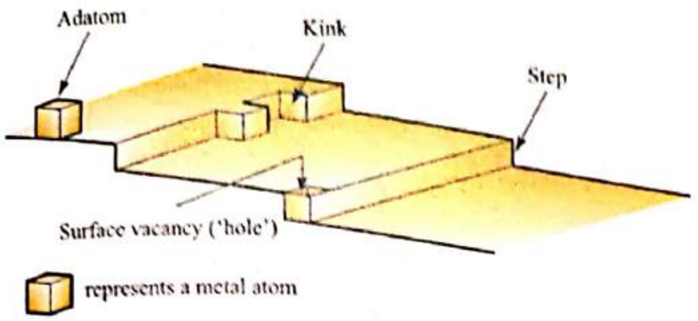


Fig. 25.14 A schematic representation of typical features of a metal surface. [Based on a figure from *Encyclopedia of Inorganic Chemistry* (1994), ed. R.B. King, vol. 3, p. 1359, Wiley, Chichester.]

25.8 Heterogeneous catalysis: commercial applications

In this section, we describe selected commercial applications of heterogeneous catalysts. The examples have been chosen to illustrate a range of catalyst types, as well as the development of motor vehicle catalytic converters.

Alkene polymerization: Ziegler–Natta catalysis and metallocene catalysts

polymer types

The 1963 the Nobel Prize in Chemistry was awarded to Karl Ziegler and Giulio Natta 'for their discoveries in the field of the chemistry and technology of high polymers'. The polymerization of alkenes by heterogeneous Ziegler–Natta catalysis is of vast importance to the polymer industry. In 1953, Ziegler discovered that, in the presence of certain heterogeneous catalysts, ethene was polymerized to high-molecular-mass polyethene at relatively low pressures. In 1954, Natta showed that polymers formed using these catalytic conditions were *stereoregular*. When a terminal alkene, $RCH{=}CH_2$, polymerizes, the R groups in a linear polymer can be arranged as shown in Fig. 25.15. Consider polypropene in which R = Me. In the *isotactic* polymer, the methyl groups are all on the same side of the carbon chain. This gives a stereoregular polymer in which the chains pack efficiently, giving a crystalline material. *Syndiotactic* polypropene (Fig. 25.15, R = Me) is also of commercial value: the Me groups are regularly arranged on alternating sides of the carbon backbone. In contrast, *atactic* polymer contains a random arrangement of R groups and is soft and elastic.

catalyst choice

First generation Ziegler–Natta catalysts were made by reacting $TiCl_4$ with Et_3Al to precipitate $\beta\text{-}TiCl_3\cdot xAlCl_3$ which was converted to $\gamma\text{-}TiCl_3$. While the latter catalysed the production of isotactic polypropene, its selectivity and efficiency required significant improvement. A change in the method of catalyst preparation generated the δ-form of $TiCl_3$ which is stereoselective below 373 K. The co-catalyst, Et_2AlCl, in these systems is essential, its role being to alkylate Ti atoms on the catalyst surface. In third generation catalysts (used since the 1980s), $TiCl_4$ is supported on anhydrous $MgCl_2$, and Et_3Al is used for alkylation. Surface Ti(IV) is reduced to Ti(III) before coordination of the alkene (see below). The choice of $MgCl_2$ as the substrate arises from the close similarity between the crystal structures of $MgCl_2$ and $\beta\text{-}TiCl_3$. This allows *epitaxial* growth of $TiCl_4$ (or $TiCl_3$ after reduction) on $MgCl_2$.

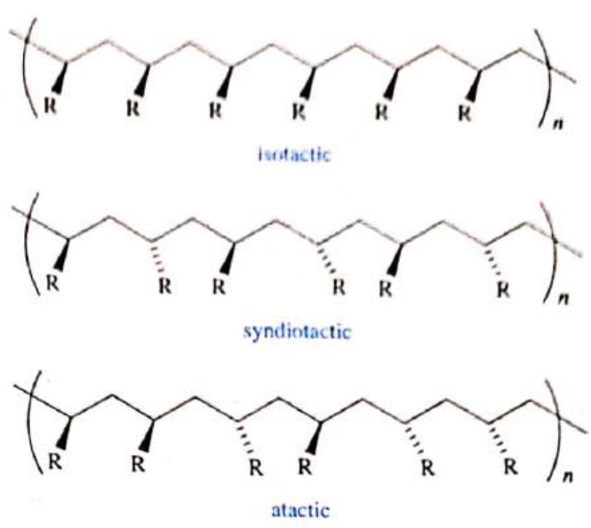


Fig. 25.15 The arrangement of R substituents in isotactic, syndiotactic and atactic linear polymers.

Epitaxial **growth of a crystal on a substrate crystal is such that the growth follows the crystal axis of the substrate.**

mechanism

Alkene polymerization is catalysed at a surface Ti(III) centre in which there is a terminal Cl atom and a vacant coordination site. The *Cossee–Arlman mechanism* is the accepted pathway of the catalytic process and a simplified representation of the mechanism is shown in Fig. 25.16. Coordinatively unsaturated $TiCl_5$ units are the catalytically active sites. In the first step, the surface Cl atom is replaced by an ethyl group. It is crucial that the alkyl group is *cis* to the vacant coordination site to facilitate alkyl migration in the third step. In the second step, the alkene binds to Ti(III) and this is followed by alkyl migration. The repetition of these last two steps results in polymer growth. In propene polymerization, the stereoselective formation of isotactic polypropene is thought to be controlled by the catalyst's surface structure which imposes restrictions on the possible orientations of the coordinated alkene relative to the metal-attached alkyl group. Growth of the polymer is terminated by β-hydride elimination (the metal-bound H atom produced is transferred to an incoming alkene molecule to give a surface-bound alkyl group), or by reaction with H_2. The latter can be used to control the length

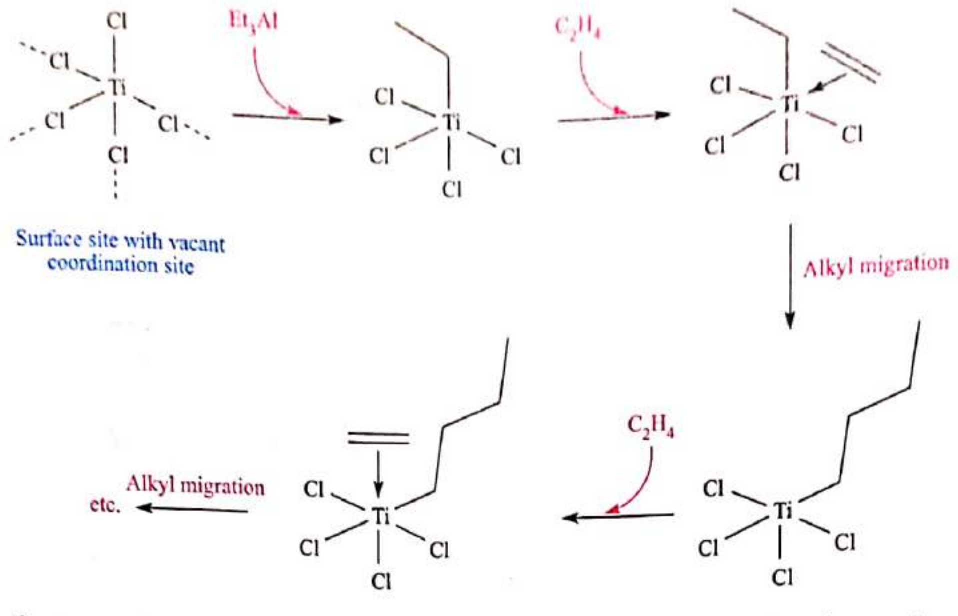
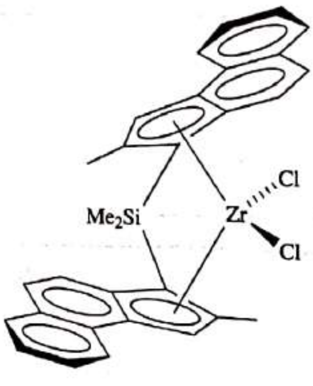


Fig. 25.16 A schematic representation of alkene polymerization on the surface of a Ziegler–Natta catalyst; the vacant coordination site must be *cis* to the coordinated alkyl group.

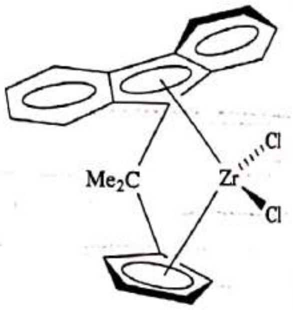
of the polymer chain. Heterogeneous $TiCl_3/Et_3Al$ or $MgCl_2/TiCl_4/Et_3Al$ catalysts are used industrially for the manufacture of isotactic polymers, e.g. polypropene. Only small quantities of syndiotactic polymers are produced by this route.

In addition to Ziegler–Natta catalysts, the modern polymer industry uses group 4 metallocene catalysts (see Box 24.6). Their development began in the 1970s with the observation that $(\eta^5\text{-}C_5H_5)_2MX_2$ (M = Ti, Zr, Hf) in the presence of methylaluminoxane $[MeAl(\mu\text{-}O)]_n$ catalysed the polymerization of propene. The stereospecificity of the catalysts was gradually improved (e.g. by changing the substituents on the cyclopentadienyl ring), and metallocene-based catalysts entered the commercial market in the 1990s. Although metallocenes can be used as homogeneous catalysts, for industrial purposes they are immobilized on SiO_2, Al_2O_3 or $MgCl_2$. Advantages of metallocenes over traditional Ziegler–Natta catalysts include the facts that, by changing the structure of the metallocene, the properties of the polymer may be tailored, narrow molar mass distributions can be obtained, and copolymers can be produced. Highly isotactic polypropene (e.g. using catalyst **25.27**) or syndiotactic polymers (e.g. using catalyst **25.28**) are manufactured, as well as block polymers with highly isotactic blocks or with purposely introduced irregularities (e.g. to lower the melting point). For example, isotactic polypropene with a melting point of 419 K and a molar mass of $\approx 33 \times 10^4$ g mol^{-1} can be produced using catalyst **25.27**, whereas the product using **25.29** as catalyst melts at 435 K and has a molar mass of $\approx 99 \times 10^4$ g mol^{-1}. Note that each of metallocenes **25.27–25.29** contains a bridging group (CMe_2 or $SiMe_2$) that ties the cyclopentadienyl rings together and holds them in an open conformation. Changing the tilt-angle between the rings is (in addition to the ring substitution pattern) a way of tuning catalytic behaviour.

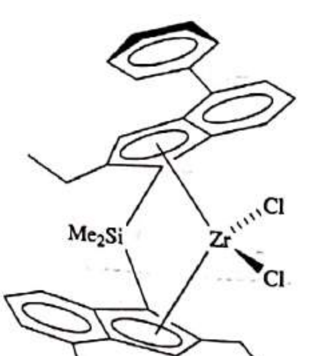
advanced Z N catalysts



(25.27)

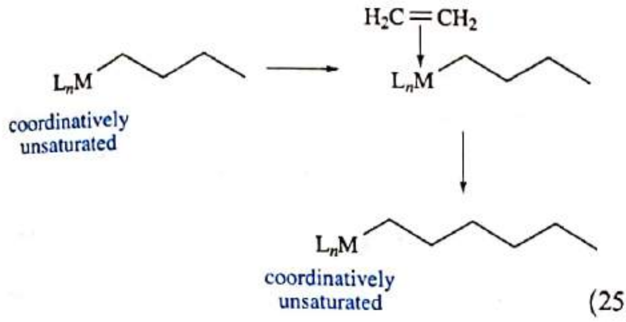


(25.28)



(25.29)

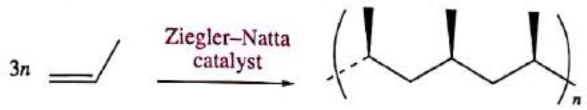
Most metallocene catalysts are active only in the presence of an $[MeAl(\mu\text{-}O)]_n$ cocatalyst. This alkylates the group 4 metal and also removes a chlorido-ligand, thereby creating a coordinatively unsaturated, cationic metal centre. The pathway for chain growth follows the Cossee–Arlman mechanism (Fig. 25.16 and eq. 25.31).



(25.31)

Self-study exercise

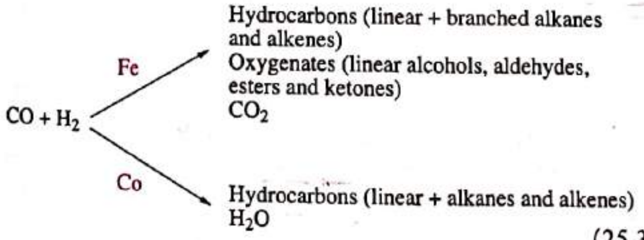
Propene polymerization by the Ziegler–Natta process can be summarized as follows.



Comment on the type of polymer produced and the need for selectivity for this form of polypropene.

Fischer–Tropsch carbon chain growth

Scheme 25.32 summarizes the Fischer–Tropsch (FT) reaction, i.e. the conversion of synthesis gas (see Section 10.4) into hydrocarbons. A range of catalysts can be used (e.g. Ru, Ni, Fe, Co) but Fe and Co are currently favoured.

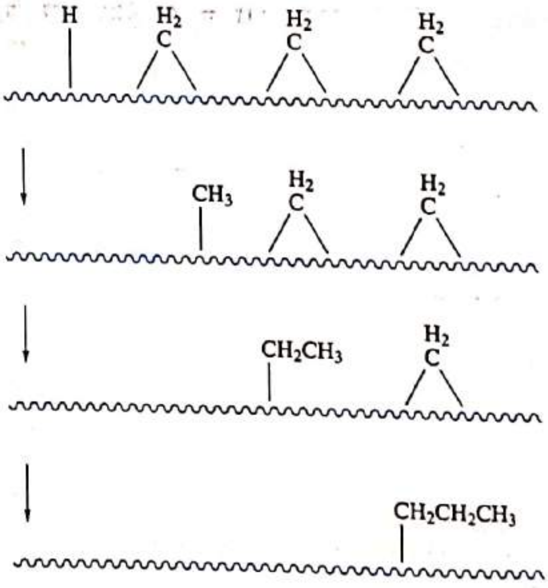


(25.32)

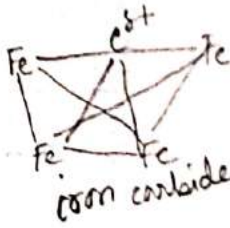
If petroleum is cheap and readily available, the FT process is not commercially viable and in the 1960s, many industrial plants were closed. In South Africa, the *Sasol process* continues to use H_2 and CO as feedstocks. Changes in the availability of oil reserves affect the views of industry as regards its feedstocks, and research interest in the FT reaction continues to be high. New initiatives in South Africa, Malaysia, New Zealand and the Netherlands are developing FT-based 'gas-to-liquid' fuels which use natural gas or biomass as the raw feedstock and convert it to liquid fuel.

The product distribution, including carbon chain length, of an FT reaction can be controlled by choice of catalyst, reactor design and reaction conditions. The addition of promoters such as group 1 or 2 metal salts (e.g. K_2CO_3) affects the selectivity of a catalyst. The exact mechanism by which the FT reaction occurs is not known, and many model studies have been carried out using discrete metal clusters (see Section 25.9). The original mechanism proposed by Fischer and Tropsch involved the adsorption of CO, C–O bond cleavage to give a surface carbide, and hydrogenation to produce CH_2 groups which then polymerized. Various mechanisms have been put forward, and the involvement of a surface-bound CH_3 group has been debated. Any mechanism (or series of pathways) must account for the formation of surface carbide, graphite and CH_4, and the distribution of organic products shown in scheme 25.32. Current opinion favours CO dissociation on the catalyst surface to give surface C and O and, in the presence of adsorbed H atoms (eq. 25.30), the formation of surface CH and CH_2 units and release of H_2O. If CO dissociation and subsequent formation of CH_x groups is efficient (as it is on Fe), the build-up of CH_x units leads to reaction between them and to the growth of carbon chains. The types of processes that might be envisaged on the metal surface are represented in scheme 25.33. Reaction of the surface-attached alkyl chain would release an alkane. If it undergoes β-elimination, an alkene is released.

mechanism no. 1

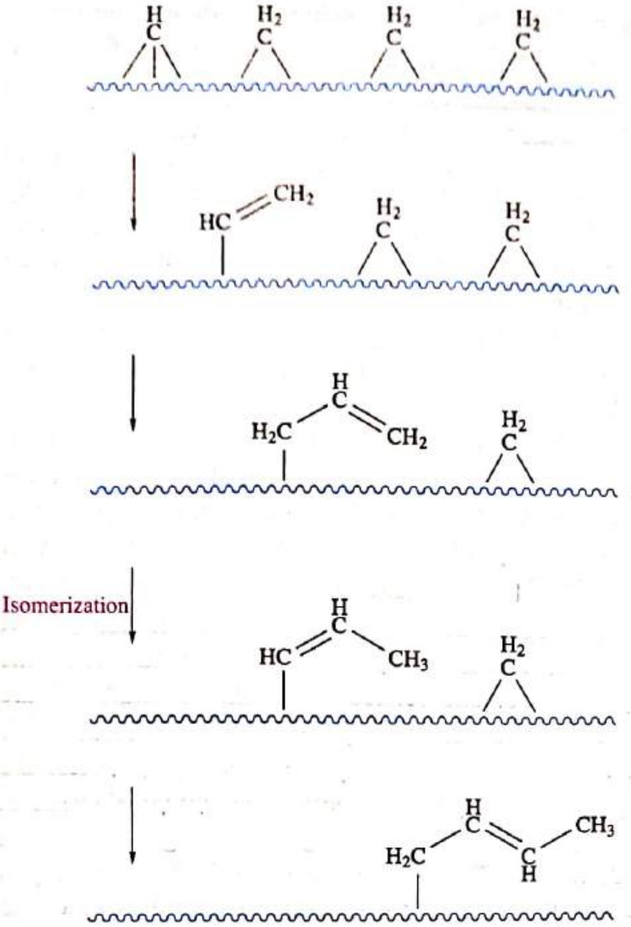


(25.33)



It has also been suggested that vinylic species are involved in FT chain growth, and that combination of surface-bound CH and CH_2 units to give $CH{=}CH_2$ may be followed by successive incorporation of CH_2 units alternating with alkene isomerization as shown in scheme 25.34. Release of a terminal alkene results if reaction of the adsorbate is with H instead of CH_2.

mechanism no. 2



(25.34)

15.21 → $N_2 + 3H_2 = 2NH_3$ $\Delta H_r(298K) = -92\,kJ\,mol^{-1}$

$\Delta G_r(298K) = -33\,kJ\,mol^{-1}$

Haber process

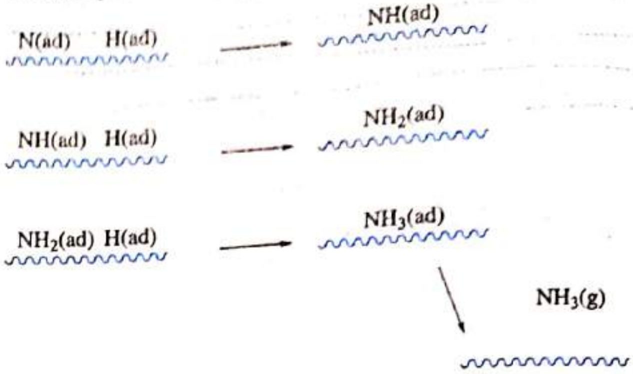
The vast scale on which the industrial production of NH_3 is carried out and its growth over the latter part of the 20th century was illustrated in Box 15.3. In eq. 15.21 and the accompanying discussion, we described the manufacture of NH_3 using a heterogeneous catalyst. Now we focus on the mechanism of the reaction and on catalyst performance.

mechanism

Without a catalyst, the reaction between N_2 and H_2 occurs only slowly, because the activation barrier for the dissociation of N_2 and H_2 in the gas phase is very high. In the presence of a suitable catalyst such as Fe, dissociation of N_2 and H_2 to give adsorbed atoms is facile, with the energy released by the formation of M–N and M–H bonds more than offsetting the energy required for N≡N and H–H fission. The adsorbates then readily combine to form NH_3 which desorbs from the surface. The rate-determining step is the dissociative adsorption of N_2 (eq. 25.35). The notation '(ad)' refers to an adsorbed atom.

(25.35)

Dihydrogen is similarly adsorbed (eq. 25.30), and the surface reaction continues as shown in scheme 25.36 with gaseous NH_3 finally being released. Activation barriers for each step are relatively low.



(25.36)

metal choice

catalyst preparation

impurities

tempt

Metals other than Fe catalyse the reaction between N_2 and H_2, but the rate of formation of NH_3 is metal-dependent. High rates are observed for Fe, Ru and Os. Since the rate-determining step is the chemisorption of N_2, a high activation energy for this step, as is observed for late *d*-block metals (e.g. Co, Rh, Ir, Ni and Pt), slows down the overall formation of NH_3. Early *d*-block metals such as Mo and Re chemisorb N_2 efficiently, but the M–N interaction is strong enough to favour retention of the adsorbed atoms. This blocks surface sites and inhibits further reaction. The catalyst used industrially is active α-Fe which is produced by reducing Fe_3O_4 mixed with K_2O (an *electronic promoter* which improves catalytic activity), SiO_2 and Al_2O_3 (*structural promoters* which stabilize the catalyst's structure). High-purity (often synthetic) magnetite and the catalyst promoters are melted electrically and then cooled. This stage distributes the promoters homogeneously within the catalyst. The catalyst is then ground to an optimum grain size. High-purity materials are essential since some impurities poison the catalyst. Dihydrogen for the Haber process is produced as synthesis gas (Section 10.4), and contaminants such as H_2O, CO, CO_2 and O_2 are *temporary catalyst poisons*. Reduction of the Haber process catalyst restores its activity, but over-exposure of the catalyst to oxygen-containing compounds decreases the efficiency of the catalyst irreversibly. A 5 ppm CO content in the H_2 supply (see eqs. 10.13 and 10.14) decreases catalyst activity by ≈5% per year. The performance of the catalyst depends critically on the operating temperature of the NH_3 converter, and a 770–790 K range is optimal.

Self-study exercises

1. Write equations to show how H_2 is manufactured for use in the Haber process. [*Ans.* See eqs. 10.13 and 10.14]
2. The catalytic activity of various metals with respect to the reaction of N_2 and H_2 to give NH_3 varies in the order Pt < Ni < Rh ≈ Re < Mo < Fe < Ru ≈ Os.

What factors contribute towards this trend?

[*Ans.* See text in this section]

3. In 2009, 130 Mt of NH_3 (the mass is in terms of nitrogen content) were manufactured worldwide. Production has increased dramatically over the last 40 years. Account for the scale of production in terms of the uses of NH_3.

[*Ans.* See Box 15.3]

Production of SO_3 in the Contact process

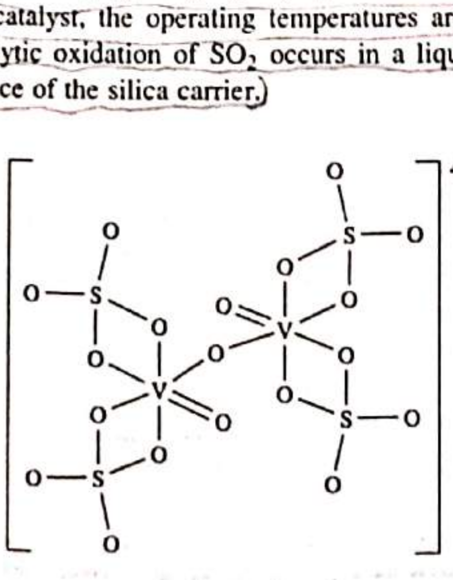
Production of sulfuric acid, ammonia and phosphate rock (see Section 15.2) heads the inorganic chemical and mineral industries in the US. The oxidation of SO_2 to SO_3 (equ. 25.37) is the first step in the Contact process, and in Section 16.8 we discussed how the yield of SO_3 depends on temperature and pressure. At ordinary temperatures, the reaction is too slow to be commercially viable, while at very high temperatures, equilibrium 25.37 shifts to the left, decreasing the yield of SO_3.

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 \qquad \Delta_r H^\circ = -96\,\text{kJ per mole of } SO_2 \qquad (25.37)$$

Catalyst choice

Use of a catalyst increases the rate of the forward reaction 25.37, and active catalysts are Pt, V(V) compounds and iron oxides. Modern manufacturing plants for SO_3 use a V_2O_5 catalyst on an SiO_2 carrier (which provides a large surface area) with a K_2SO_4 promoter. The catalyst system contains 4–9% by weight of V_2O_5. Passage of the reactants through a series of catalyst beds is required to obtain an efficient conversion of SO_2 to SO_3, and an operating temperature of 690–720 K is optimal. Since oxidation of SO_2 is exothermic and since temperatures >890 K degrade the catalyst, the $SO_2/SO_3/O_2$ mixture must be cooled between leaving one catalyst bed and entering the next. Although the $V_2O_5/SiO_2/K_2SO_4$ system is introduced as a solid catalyst, the operating temperatures are such that the catalytic oxidation of SO_2 occurs in a liquid melt on the surface of the silica carrier.

tempt



(25.30)

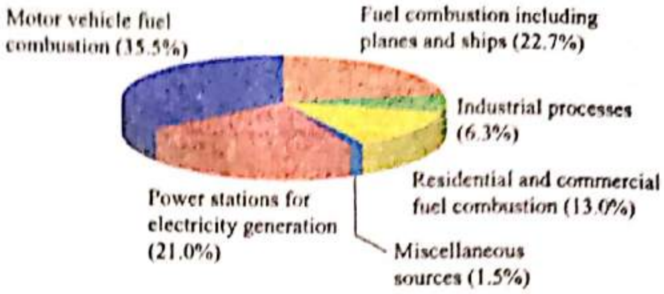


Fig. 25.17 Sources of NO_x emissions in the US. [Data: Environmental Protection Agency (2005).]

The mechanism of catalysis is complicated and has not been fully established. Initially, the liquid catalyst takes up large amounts of SO_2, and the accepted working model for the catalytic system is represented as $M_2S_2O_7$–M_2SO_4–V_2O_5/O_2–SO_2–SO_3–N_2 (M = Na, K, Rb, Cs). At normal operating temperatures, $[V(O)_2(SO_4)]^-$, the complex **25.30**, and related vanadium(V) oligomers are formed. Complex **25.30** in particular is considered to be catalytically active, while any V(III) or V(IV) species are thought to be catalytically inactive. One proposal suggests that complex **25.30** activates O_2, facilitating the oxidation of SO_2 to SO_3. The direct reaction of **25.30** with SO_2 to yield SO_3 results in reduction of V(V) to V(IV) and the formation of a catalytically inactive species. Much work remains to elucidate the details of the Contact process.

Mechanism

Catalytic converters

Environmental concerns have grown during the past few decades (see, for example, Box 10.2), and to the general public, the use of motor vehicle catalytic converters is well known. Regulated exhaust emissions[†] comprise CO, hydrocarbons and NO_x (see Section 15.8). The radical NO is one of several species that act as catalysts for the conversion of O_3 to O_2 and is considered to contribute to depletion of the ozone layer. Although industrial processes and the generation of electricity (see Box 12.2) contribute to NO_x emissions,[‡] the combustion of transport fuels is the major source (Fig. 25.17). A typical catalytic converter is ≥90% efficient in reducing emissions. In 2005, European regulations called for emission levels of CO, hydrocarbons and NO_x to be ≤ 1.0, 0.10 and 0.08 g km^{-1}, respectively, for passenger cars with petrol engines. The toughest regulations to meet are those laid down in California (the Super Ultra Low Emissions Vehicle, SULEV, standards). SULEV

[†] For reports on the current status of motor vehicle emission control, see: M.V. Twigg (2003) *Platinum Metals Rev.*, vol. 47, p. 157; M.V. Twigg and P.R. Phillips (2009) *Platinum Metals Rev.*, vol. 53, p. 27.

[‡] Shell and Bayer are among companies that have introduced processes to eliminate industrial NO_x emissions: *Chemistry & Industry* (1994) p. 415 – 'Environmental technology in the chemical industry'.

regulates emission levels of CO, hydrocarbons, NO_x and particulate matter to ≤ 0.62, 0.006, 0.012 and 0.006 g km^{-1}, respectively.

Structure

A catalytic converter consists of a honeycomb ceramic structure coated in finely divided Al_2O_3 (the *washcoat*). Fine particles of catalytically active Pt, Pd and Rh are dispersed within the cavities of the washcoat and the whole unit is contained in a stainless steel vessel placed in sequence in the vehicle's exhaust pipe. As the exhaust gases pass through the converter at high temperatures, redox reactions 25.38–25.42 occur (C_3H_8 is a representative hydrocarbon). Under legislation, the only acceptable emission products are CO_2, N_2 and H_2O.

function

$$2CO + O_2 \longrightarrow 2CO_2 \qquad (25.38)$$

$$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O \qquad (25.39)$$

$$2NO + 2CO \longrightarrow 2CO_2 + N_2 \qquad (25.40)$$

$$2NO + 2H_2 \longrightarrow N_2 + 2H_2O \qquad (25.41)$$

$$C_3H_8 + 10NO \longrightarrow 3CO_2 + 4H_2O + 5N_2 \qquad (25.42)$$

Whereas CO and hydrocarbons are oxidized, the destruction of NO_x involves its reduction. Modern catalytic converters have a 'three-way' system which promotes both oxidation and reduction. Pd and Pt catalyse reactions 25.38 and 25.39, while Rh catalyses reactions 25.40 and 25.41, and Pt catalyses reaction 25.42.)

efficiency of catalyst

(The efficiency of the catalyst depends, in part, on metal particle size, typically 1000–2000 pm diameter. Over a period of time, the high temperatures needed for the operation of a catalytic converter cause ageing of the metal particles with a loss of their optimal size and a decrease in the efficiency of the catalyst. Constant high-temperature running also transforms the γ-Al_2O_3 support into a phase with a lower surface area, again reducing catalytic activity. To counter degradation of the support, group 2 metal oxide stabilizers are added to the alumina. Catalytic converters operate only with unleaded fuels; lead additives bind to the alumina washcoat, deactivating the catalyst.)

air : fuel ratio

(In order to achieve the regulatory emission standards, it is crucial to control the air : fuel ratio as it enters the catalytic converter: the optimum ratio is 14.7 : 1. If the air : fuel ratio exceeds 14.7 : 1, extra O_2 competes with NO for H_2 and the efficiency of reaction 25.41 is lowered. If the ratio is less than 14.7 : 1, oxidizing agents are in short supply and CO, H_2 and hydrocarbons compete with each other for NO and O_2. The air : fuel ratio is monitored by a sensor fitted in the exhaust pipe; the sensor measures O_2 levels and sends an electronic signal to the fuel injection system or carburettor to adjust the air : fuel ratio as necessary.)

CeO_2/Ce_2O_3

(Catalytic converter design also includes a CeO_2/Ce_2O_3 system to store oxygen. During 'lean' periods of vehicle running, O_2 can be 'stored' by reaction 25.43. During 'rich' periods when extra oxygen is needed for hydrocarbon and CO oxidation, CeO_2 is reduced (eq. 25.44 shows oxidation of CO).

$$2Ce_2O_3 + O_2 \longrightarrow 4CeO_2 \qquad (25.43)$$

$$2CeO_2 + CO \longrightarrow Ce_2O_3 + CO_2 \qquad (25.44)$$)

[illegible]

A catalytic converter cannot function immediately after the 'cold start' of an engine. At its 'light-off' temperature (typically 620 K), the catalyst operates at 50% efficiency but during the 90–120 s lead time, exhaust emissions are not controlled. Several methods have been developed to counter this problem, e.g. electrical heating of the catalyst using power from the vehicle's battery.

Cu-ZSM-5

(The development of catalytic converters has recently encompassed the use of zeolites, e.g. Cu-ZSM-5 (a copper-modified ZSM-5 system), but at the present time, and despite some advantages such as low light-off temperatures, zeolite-based catalysts have not shown themselves to be sufficiently durable for their use in catalytic converters to be commercially viable.)

Zeolites as catalysts for organic transformations: uses of ZSM-5

For an introduction to zeolites, see Fig. 14.27 and the accompanying discussion. (Many natural and synthetic zeolites are known, and it is the presence of well-defined cavities and/or channels, the dimensions of which are comparable with those of small molecules, that makes them invaluable as catalysts and molecular sieves.) Zeolites are environmentally 'friendly' and the development of industrial processes in which they can replace less acceptable acid catalysts is advantageous. In this section, we focus on catalytic applications of synthetic zeolites such as ZSM-5 (structure-type code MFI, Fig. 25.18); the latter is silicon-rich with composition $Na_n[Al_nSi_{96-n}O_{192}]\cdot\approx 16H_2O$ ($n < 27$).[†] When H^+ replaces Na^+, the zeolite is referred to as HZSM-5 and this is highly catalytically active (see below). Within the aluminosilicate framework of ZSM-5 lies a system of interlinked channels. One set can be seen in Fig. 25.18, but the channels can be represented in the form of a structure such as **25.31**. In ZSM-5, for example, there are two sets of channels running through the structure, one of cross-section $\approx 540 \times 560$ pm and the other of cross-section $\approx 510 \times 540$ pm. The *effective pore size* is comparable to the *kinetic molecular diameter* of a molecule such as 2-methylpropane or benzene, leading to the *shape-selective* properties of zeolite catalysts. The effective pore size differs from that determined crystallographically because it takes into account the flexibility of the zeolite framework as a function of temperature. Similarly,

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[†] Structures of zeolites can be viewed and manipulated using the website: http://www.iza-structure.org/databases/

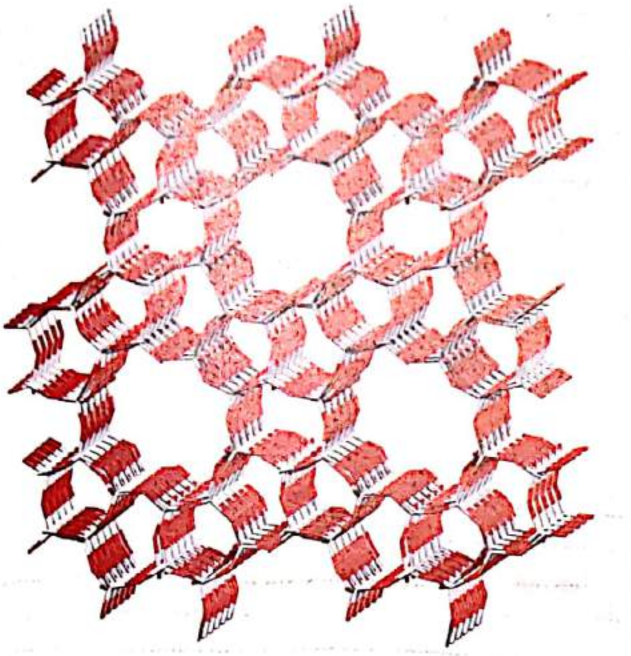
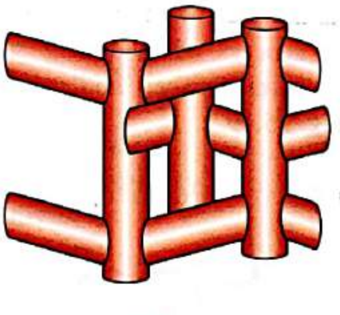


Fig. 25.18 Part of the aluminosilicate framework of synthetic zeolite ZSM-5 (structure-type MFI). Colour code: Si/Al, pale grey; O, red.

the kinetic molecular diameter allows for the molecular motions of species entering the zeolite channels or cavities.



(25.31)

The high catalytic activity of zeolites arises from the Brønsted acidity of Al sites, represented in resonance pair 25.32. The Si : Al ratio affects the number of such sites and acid strength of the zeolite.

Zeolite catalysts are important in the catalytic cracking of heavy petroleum distillates. Their high selectivities and high rates of reactions, coupled with reduced coking effects, are major advantages over the activities of the alumina/silica catalysts that zeolites have replaced. Ultrastable Y (USY) zeolites are usually chosen for catalytic cracking because their use leads to an increase in the gasoline (motor fuels) octane number. It is essential that the catalyst is robust enough to withstand the conditions of the cracking process. Both USY and ZSM-5 (used as a co-catalyst because of its shape-selective properties) meet this requirement. The shape-selectivity of ZSM-5 is also crucial to its activity as a catalyst in the conversion of methanol to hydrocarbon fuels. The growth of carbon chains is restricted by the size of the zeolite channels and this gives a selective distribution of hydrocarbon products. In the 1970s, Mobil developed the MTG (methanol-to-gasoline) process in which ZSM-5 catalysed the conversion of MeOH to a mixture of higher ($>C_5$) alkanes, cycloalkanes and aromatics. Equations 25.45–25.47 show the initial dehydration of methanol (in the gas phase) to give dimethyl ether, followed by representative dehydrations leading to hydrocarbons. Such processes are commercially viable only when petroleum prices are high. This was the case in the 1970s and 1980s, and the MTG process was run by Mobil during the 1980s in New Zealand.

MTG process

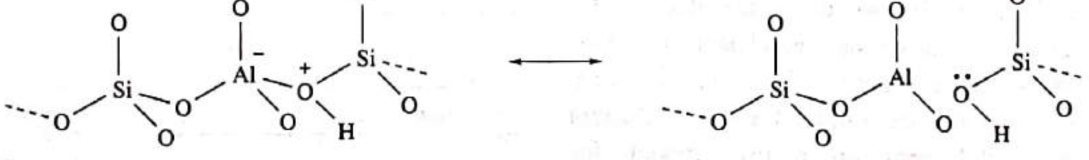
$$2CH_3OH \xrightarrow{\text{ZSM-5 catalyst}} CH_3OCH_3 + H_2O \qquad (25.45)$$

$$2CH_3OCH_3 + 2CH_3OH \xrightarrow{\text{ZSM-5 catalyst}} C_6H_{12} + 4H_2O \qquad (25.46)$$

$$3CH_3OCH_3 \xrightarrow{\text{ZSM-5 catalyst}} C_6H_{12} + 3H_2O \qquad (25.47)$$

Recent advances have shown zeolites are effective in catalysing the direct conversion of synthesis gas to motor fuels. The MTO (methanol-to-olefins) process converts MeOH to C_2–C_4 alkenes and is also catalysed by ZSM-5. The development of a gallium-modified ZSM-5 catalyst (Ga-ZSM-5) has provided an efficient catalyst for the production of aromatic compounds from mixtures of C_3 and C_4 alkanes (commonly labelled LPG).

Zeolites are replacing acid catalysts in a number of manufacturing processes. One of the most important is the alkylation of aromatics. The Mobil–Badger process for producing C_6H_5Et from C_6H_6 and C_2H_4 provides the



(25.32)

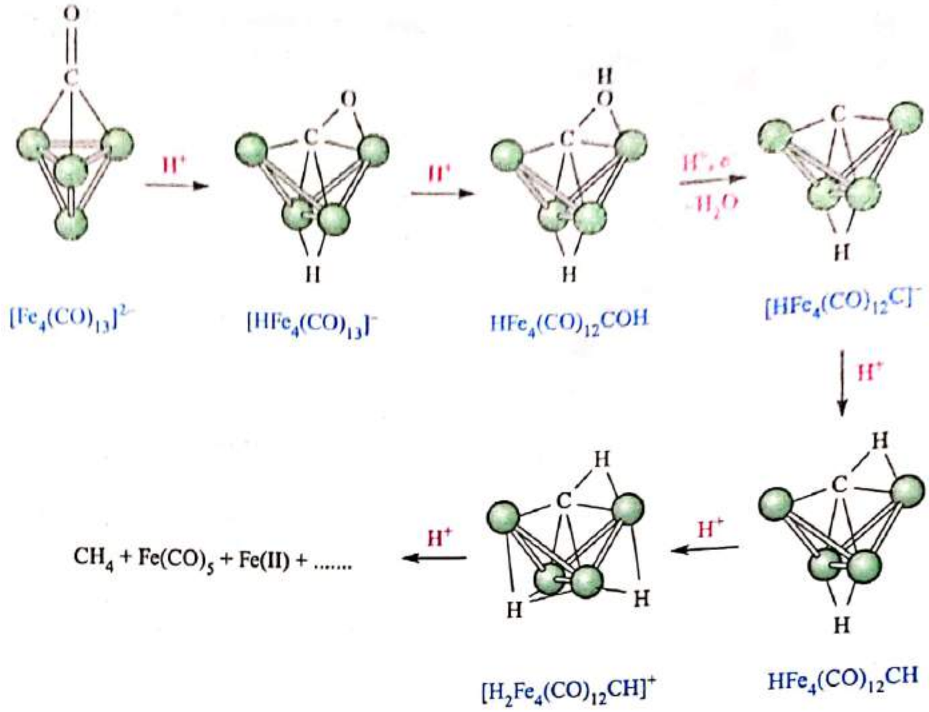


Fig. 25.19 The proton-induced conversion of a cluster-bound CO ligand to CH_4: a cluster model for catalysed hydrogenation of CO on an Fe surface. Each green sphere represents an $Fe(CO)_3$ unit.

precursor for styrene (and hence polystyrene) manufacture. The isomerization of 1,3- to 1,4-dimethylbenzene (xylenes) is also catalysed on the acidic surface of ZSM-5, presumably with channel shape and size playing an important role in the observed selectivity.)

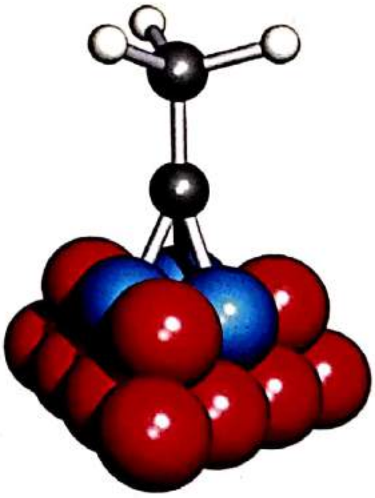
Self-study exercises

1. What are the similarities and differences between the structures of a feldspar mineral and a zeolite?
2. How does a zeolite function as a Lewis acid catalyst?
3. Give two examples of the commercial application of ZSM-5 as a catalyst.

[*Answers*: See Sections 14.9 and 25.8]

25.9 Heterogeneous catalysis: organometallic cluster models

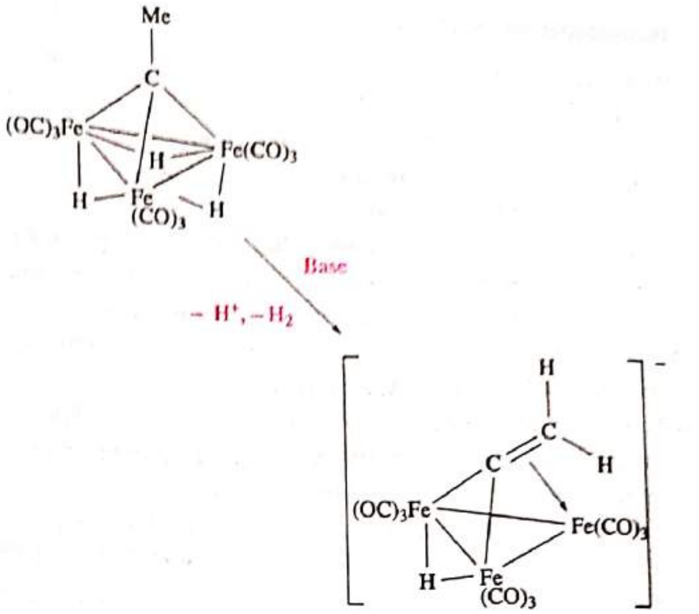
One of the driving forces behind organometallic cluster research is to model metal-surface catalysed processes such as the Fischer–Tropsch reaction. The *cluster-surface analogy* assumes that discrete organometallic clusters containing *d*-block metal atoms are realistic models for the bulk metal. In many small clusters, the arrangements of the metal atoms mimic units from close-packed arrays, e.g. the M_3-triangle and M_4-butterfly in structures **25.25** and **25.26**. The success of modelling studies has been limited, but a well-established and much-cited result is that shown in Fig. 25.19.[†]



(25.33)

[†] For further details, see M.A. Drezdon, K.H. Whitmire, A.A. Bhattacharyya, W.-L. Hsu, C.C. Nagel, S.G. Shore and D.F. Shriver (1982) *J. Am. Chem. Soc.*, vol. 104, p. 5630 – 'Proton induced reduction of CO to CH_4 in homonuclear and heteronuclear metal carbonyls'.

Model studies involve transformations of organic fragments which are proposed as surface intermediates, but do not necessarily address a complete sequence of reactions as is the case in Fig. 25.19. For example, metal-supported ethylidyne units (**25.33**) are proposed as intermediates in the Rh- or Pt-catalysed hydrogenation of ethene, and there has been much interest in the chemistry of M_3-clusters such as $H_3Fe_3(CO)_9CR$, $H_3Ru_3(CO)_9CR$ and $Co_3(CO)_9CR$ which contain ethylidyne or other alkylidyne units. In the presence of base, $H_3Fe_3(CO)_9CMe$ undergoes reversible deprotonation and loss of H_2 (eq. 25.48), perhaps providing a model for an organic fragment transformation on a metal surface.



(25.48)

KEY TERMS

The following terms have been used in this chapter. Do you know what they mean?

- ☐ catalyst
- ☐ catalyst precursor
- ☐ autocatalytic
- ☐ homogeneous catalyst
- ☐ heterogeneous catalyst
- ☐ catalytic cycle
- ☐ catalytic turnover number
- ☐ catalytic turnover frequency
- ☐ alkene metathesis
- ☐ alkyne metathesis
- ☐ Grubbs' catalyst
- ☐ Schrock-type catalysts
- ☐ Chauvin mechanism
- ☐ catenand
- ☐ catenate
- ☐ coordinatively unsaturated
- ☐ Wilkinson's catalyst
- ☐ asymmetric hydrogenation
- ☐ prochiral
- ☐ enantiomeric excess
- ☐ Monsanto acetic acid process
- ☐ Cativa acetic acid process
- ☐ Tennessee–Eastman acetic anhydride process
- ☐ hydroformylation (Oxo-process)
- ☐ chemoselectivity and regioselectivity (with respect to hydroformylation)
- ☐ biphasic catalysis
- ☐ physisorption
- ☐ chemisorption
- ☐ adsorbate
- ☐ alkene polymerization
- ☐ Ziegler–Natta catalysis
- ☐ Cossee–Arlman mechanism
- ☐ Fischer–Tropsch reaction
- ☐ Haber process
- ☐ Contact process
- ☐ catalytic converter
- ☐ zeolite

FURTHER READING

General texts

G.P. Chiusoli and P.M. Maitlis (eds) (2008) *Metal-catalysis in Industrial Organic Processes*, Royal Society of Chemistry, Cambridge – A detailed book that covers C–O and C–C bond formation, hydrogenation, syntheses involving CO, alkene metathesis, and polymerization as well as general aspects of catalysis.

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F.A. Cotton, G. Wilkinson, M. Bochmann and C. Murillo (1999) *Advanced Inorganic Chemistry*, 6th edn, Wiley Interscience, New York – Chapter 22 gives a full account of the homogeneous catalysis of organic reactions by *d*-block metal compounds.

Homogeneous catalysis

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A. Fürstner (2000) *Angew. Chem. Int. Ed.*, vol. 39, p. 3012 – 'Olefin metathesis and beyond': a review that considers catalyst design and applications in alkene metathesis.

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W.E. Piers and S. Collins (2007) in *Comprehensive Organometallic Chemistry III*, eds R.H. Crabtree and D.M.P. Mingos, Elsevier, Oxford, vol. 1, p. 141 – 'Mechanistic aspects of olefin-polymerization catalysis': Detailed mechanistic review that includes homogeneous group 4 metallocene catalysts.

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Heterogeneous catalysis including specific industrial processes

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O.B. Lapina, B.S. Bal'zhinimaev, S. Boghosian, K.M. Eriksen and R. Fehrmann (1999) *Catal. Today*, vol. 51, p. 469 – 'Progress on the mechanistic understanding of SO_2 oxidation catalysts'.

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R. Schlögl (2003) *Angew. Chem. Int. Ed.*, vol. 42, p. 2004 – 'Catalytic synthesis of ammonia – A "never-ending story"?'

G.A. Somorjai, A.M. Contreras, M. Montano and R.M. Rioux (2006) *Proc. Natl. Acad. Sci.*, vol. 103, p. 10577 – 'Clusters, surfaces, and catalysis'.

G. Wilke (2003) *Angew. Chem. Int. Ed.*, vol. 42, p. 5000 – 'Fifty years of Ziegler catalysts: Consequences and development of an invention'.

Industrial processes: general

J. Hagen (2006) *Industrial Catalysis*, 2nd edn., Wiley-VCH, Weinheim – Covers both homogeneous and heterogeneous catalysis, including catalyst production, testing and development.

Ullmann's Encyclopedia of Industrial Inorganic Chemicals and Products (1998) Wiley-VCH, Weinheim – Six volumes with detailed accounts of industrial processes involving inorganic chemicals.

R.I. Wijngaarden and K.R. Westerterp (1998) *Industrial Catalysts*, Wiley-VCH, Weinheim – A book that focuses on practical aspects of applying catalysts in industry.

Biphasic catalysis

L.P. Barthel-Rosa and J.A. Gladysz (1999) *Coord. Chem. Rev.*, vol. 190–192, p. 587 – 'Chemistry in fluorous media: a user's guide to practical considerations in the application of fluorous catalysts and reagents'.

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D.M. Roundhill (1995) *Adv. Organomet. Chem.*, vol. 38, p. 155 – 'Organotransition-metal chemistry and homogeneous catalysis in aqueous solution'.

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Polymer-supported catalysts

B. Clapham, T.S. Reger and K.D. Janda (2001) *Tetrahedron*, vol. 57, p. 4637 – 'Polymer-supported catalysis in synthetic organic chemistry'.

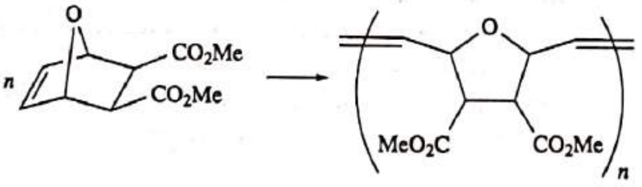
PROBLEMS

25.1 (a) Analyse the catalytic cycle shown in Fig. 25.20, identifying the types of reactions occurring. (b) Why does this process work best for R′ = vinyl, benzyl or aryl groups?

25.2 Give equations that illustrate each of the following processes. Define any abbreviations used.

(a) Cross-metathesis between two alkenes.
(b) Alkyne metathesis catalysed by a high oxidation state metal alkylidyne complex $L_nM{\equiv}CR$.
(c) ROMP.

25.3 Suggest a suitable catalyst for the following reaction, and outline the initial steps in the mechanism of the reaction:



25.4 The isomerization of alkenes is catalysed by $HCo(CO)_3$ and Fig. 25.21 shows the relevant catalytic cycle. (a) $HCo(CO)_4$ is a catalyst precursor; explain what this means. (b) Give a fuller description of what is happening in each of the steps shown in Fig. 25.21.

25.5 Outline the catalytic processes involved in the manufacture of acetic acid (Monsanto process) and acetic anhydride (Tennessee–Eastman process), and compare the catalytic pathways.

25.6 (a) Of the following alkenes, which are prochiral: $PhHC{=}CHPh$, $PhMeC{=}CHPh$, $H_2C{=}CHPh$, $H_2C{=}C(CO_2H)(NHC(O)Me)$?
(b) If an asymmetric hydrogenation proceeds with 85% ee favouring the *R*-enantiomer, what is the percentage of each enantiomer formed?

25.7 (a) Assuming some similarity between the mechanism of hydroformylation using $HCo(CO)_4$ and $HRh(CO)(PPh_3)_3$ as catalysts, propose a mechanism for the conversion of $RCH{=}CH_2$ to RCH_2CH_2CHO and explain what is happening in each step.
(b) 'The regioselectivity of the hydroformylation of $RCH{=}CH_2$ catalysed by $HRh(CO)(PPh_3)_3$ drops when the temperature is increased'. Explain what is meant by this statement.

25.8 The hydroformylation of pent-2-ene using $Co_2(CO)_8$ as the catalyst was found to give rise to three aldehydes in a ratio 35:12:5. Show how the three products arose, and suggest which was formed in the most and which in the least amount.

25.9 (a) The hydrogenation of propene is catalysed by $RhCl(PPh_3)_3$ or $HRh(CO)(PPh_3)_3$. Outline the mechanisms by which these reactions occur,

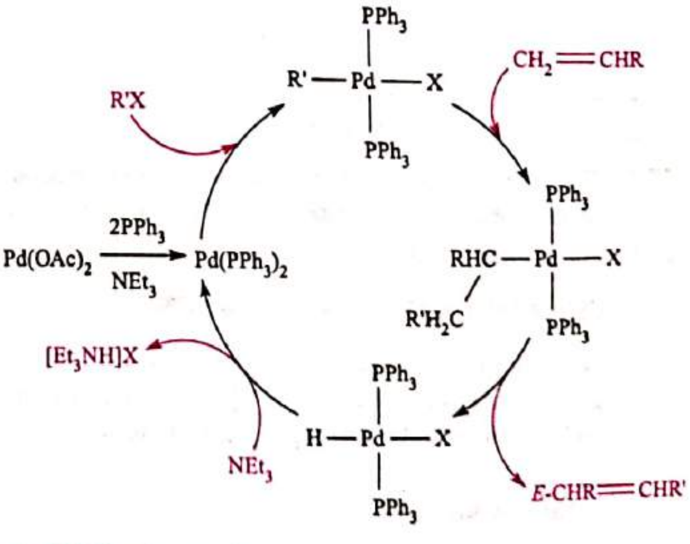


Fig. 25.20 Catalytic cycle for use in problem 25.1.

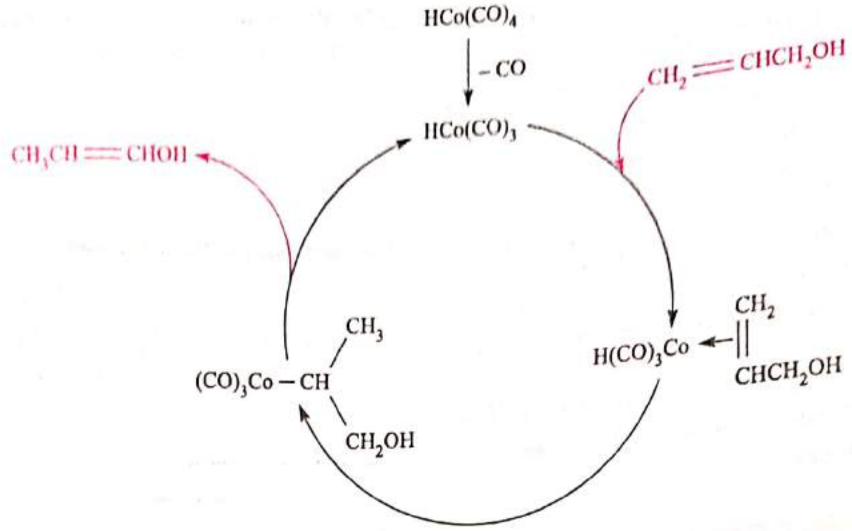


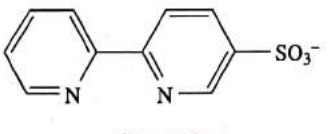
Fig. 25.21 Catalytic cycle for use in problem 25.4.

indicating clearly what the active catalyst is in each case.

(b) $HRuCl(PPh_3)_3$ is a very active catalyst for the hydrogenation of alkenes. However, at high catalyst concentrations and in the absence of sufficient H_2, orthometallation of the catalyst may accompany alkene hydrogenation. Write a reaction scheme to illustrate this process, and comment on its effect on the activity of the catalyst.

25.10 (a) Ligand **25.19** is used in biphasic catalysis. The IR spectrum of $Fe(CO)_4(PPh_3)$ shows strong absorptions at 2049, 1975 and 1935 cm^{-1}, while that of $[Fe(CO)_4(\mathbf{25.19})]^+$ exhibits bands at 2054, 1983 and 1945 cm^{-1}. What can you deduce from these data?

(b) Which of the complexes $[X][Ru(\mathbf{25.34})_3]$ in which $X^+ = Na^+$, $[^nBu_4N]^+$ or $[Ph_4P]^+$ might be suitable candidates for testing in biphasic catalysis using aqueous medium for the catalyst?



(25.34)

25.11 Give a brief discussion of the use of homogeneous catalysis in selected industrial manufacturing processes.

25.12 For the catalysed hydrocyanation of buta-1,3-diene:

$$CH_2{=}CHCH{=}CH_2 \xrightarrow{HCN} NC(CH_2)_4CN$$

(a step in the manufacture of nylon-6,6), the catalyst precursor is NiL_4 where $L = P(OR)_3$. Consider the addition of only the first equivalent of HCN.

(a) Some values of K for:

$$NiL_4 \rightleftharpoons NiL_3 + L$$

are 6×10^{-10} for $R = 4\text{-}MeC_6H_4$, 3×10^{-5} for $R = {}^iPr$ and 4×10^{-2} for $R = 2\text{-}MeC_6H_4$. Comment on the trend in values and on the relevance of these data to the catalytic process.

(b) The first three steps in the proposed catalytic cycle are the addition of HCN to the active catalyst, loss of L, and the addition of buta-1,3-diene with concomitant H migration. Draw out this part of the catalytic cycle.

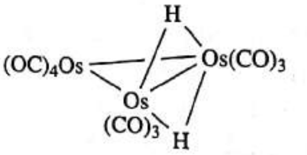
(c) Suggest the next step in the cycle, and discuss any complications.

25.13 $H_2Os_3(CO)_{10}$ (**25.35**) catalyses the isomerization of alkenes:

$$RCH_2CH{=}CH_2 \longrightarrow E\text{-}RCH{=}CHMe + Z\text{-}RCH{=}CHMe$$

(a) By determining the cluster valence electron count for $H_2Os_3(CO)_{10}$ deduce what makes this cluster an effective catalyst.

(b) Propose a catalytic cycle that accounts for the formation of the products shown.



(25.35)

25.14 Describe briefly why a clean nickel surface (fcc structure) should not be regarded as comprising a perfect close-packed array of atoms. Indicate the arrangements of atoms that an adsorbate might encounter on the surface, and suggest possible modes of attachment for CO.

25.15 (a) What advantages are there to using Rh supported on γ-Al_2O_3 as a catalyst rather than the bulk metal?

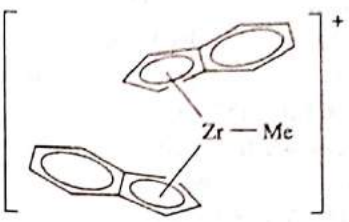
(b) In a catalytic converter, why is a combination of platinum-group metals used?

25.16 The forward reaction in eq. 25.37 is exothermic. What are the effects of (a) increased pressure and (b) increased temperature on the yield of SO_3? (c) In trying to optimize both the yield and rate of formation of SO_3, what problem does the Contact process encounter and how is it overcome?

25.17 (a) Outline how the gaseous reaction between N_2 and H_2 proceeds in the presence of a heterogeneous catalyst, and state why a catalyst is needed for the commercial production of NH_3.
(b) Suggest why V and Pt are poor catalysts for the reaction between N_2 and H_2, and give a possible reason why Os (although it is a good catalyst) is not used commercially.

25.18 (a) Summarize the structural features of importance in a Ziegler–Natta catalyst comprising $TiCl_4$ supported on $MgCl_2$.
(b) What is the role of the ethyl aluminium compounds which are added to the catalyst?
(c) Explain how a Ziegler–Natta catalyst facilitates the conversion of ethene to a representative oligomer.

25.19 (a) Why is it easier to investigate the Cossee–Arlman mechanism using metallocene alkene polymerization catalysts rather than Ziegler–Natta catalysts?
(b) The zirconium complex shown below is an active catalyst for the polymerization of $RCH{=}CH_2$. Draw a scheme to illustrate the mechanism of this reaction, assuming that it follows the Cossee–Arlman pathway.



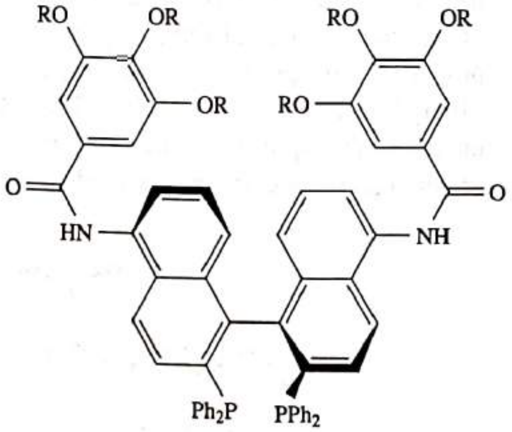
25.20 Give a brief discussion of the use of heterogeneous catalysis in selected industrial manufacturing processes.

25.21 Comment on each of the following:
(a) Zeolite 5A (effective pore size 430 pm) is used to separate a range of *n*- and *iso*-alkanes.
(b) Zeolite ZSM-5 catalyses the isomerization of 1,3- to 1,4-$Me_2C_6H_4$ (i.e. *m*- to *p*-xylene), and the conversion of C_6H_6 to EtC_6H_5.

25.22 Summarize the operation of a three-way catalytic converter, including comments on (a) the addition of cerium oxides, (b) the light-off temperature, (c) optimum air–fuel ratios and (d) catalyst ageing.

OVERVIEW PROBLEMS

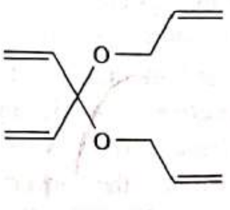
25.23 Ligand **25.36** has been designed for use in Ru-based catalysts for hydrogenation reactions in an EtOH/hexane solvent system. These solvents separate into two phases upon the addition of a small amount of water.
(a) For what types of hydrogenations would this catalyst be especially useful? Rationalize your answer.
(b) Ligand **25.36** is related to BINAP (**25.14**) but has been functionalized. Suggest a reason for this functionalization.



R = $CH_2C_6H_2$-3,4,5-$(OC_{10}H_{21})_3$

(25.36)

25.24 (a) One proposed method for removing NO from motor vehicle emissions is by catalytic reduction using NH_3 as the reducing agent. Bearing in mind the regulated, allowed emissions, write a balanced equation for the redox reaction and show that the oxidation state changes balance.
(b) In the presence of Grubbs' catalyst, compound **25.37** undergoes a selective ring-closure metathesis to give a bicyclic product **A**. Draw the structure of a 'first generation' Grubbs' catalyst. Suggest the identity of **A**, giving reasons for your choice. Write a balanced equation for the conversion of **25.37** to **A**.



(25.37)

25.25 The catalyst $[Rh(Ph_2PCH_2CH_2PPh_2)]^+$ can be prepared by the reaction of $[Rh(nbd)(Ph_2PCH_2CH_2PPh_2)]^+$ (nbd = **25.38**) with two equivalents of H_2. In coordinating solvents, $[Rh(Ph_2PCH_2CH_2PPh_2)]^+$, in the form of a solvated complex $[Rh(Ph_2PCH_2CH_2PPh_2)(solv)_2]^+$, catalyses the hydrogenation of $RCH{=}CH_2$.

(a) Draw the structure of $[Rh(nbd)(Ph_2PCH_2CH_2PPh_2)]^+$ and suggest what happens when this complex reacts with H_2.

(b) Draw the structure of $[Rh(Ph_2PCH_2CH_2PPh_2)(solv)_2]^+$, paying attention to the expected coordination environment of the Rh atom.

(c) Given that the first step in the mechanism is the substitution of one solvent molecule for the alkene, draw a catalytic cycle that accounts for the conversion of $RCH{=}CH_2$ to RCH_2CH_3. Include a structure for each intermediate complex and give the electron count at the Rh centre in each complex.

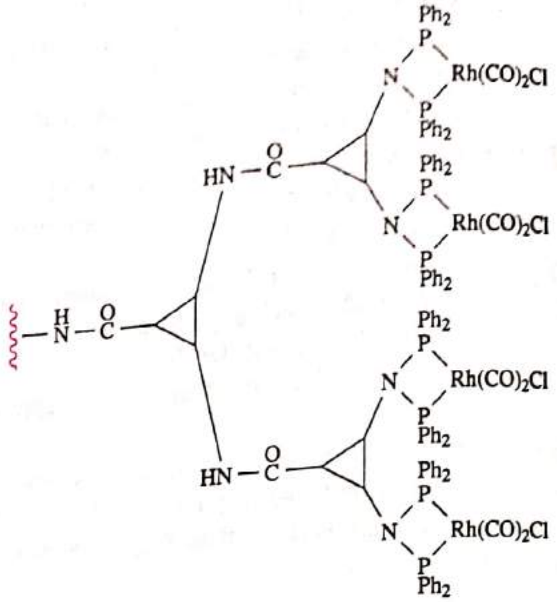
(25.38)

25.26 There is much current interest in 'dendritic' molecules, i.e. those with 'branched arms' that diverge from a central core. The supported dendritic catalyst **25.39** can be used in hydroformylation reactions, and shows high selectivity for branched over linear aldehyde products.

(a) Is **25.39** likely to be the active catalytic species? Rationalize your answer.

(b) What advantages does **25.39** have over a mononuclear hydroformylation catalyst such as $HRh(CO)_2(PPh_3)_2$?

(c) Give a general scheme for the hydroformylation of pent-1-ene (ignoring intermediates in the catalytic cycle) and explain what is meant by 'selectivity for branched over linear aldehyde products'.

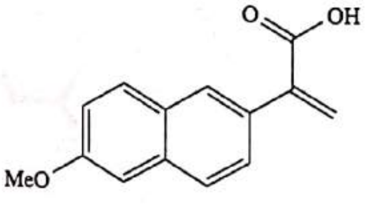


(25.39)

INORGANIC CHEMISTRY MATTERS

25.27 The first step in the Cativa process is the reaction between MeI and *cis*-$[Ir(CO)_2I_2]^-$. However, the catalyst may also react with HI and this step initiates a water gas shift reaction that competes with the main catalytic cycle. (a) What chemical is manufactured in the Cativa process? Why is this product of industrial importance? (b) Why is HI present in the system? (c) Give an equation for the water gas shift reaction, and state conditions typically used in industry. (d) Figure 25.22 shows the competitive catalytic cycle described above. Suggest identities for species **A**, **B**, **C** and **D**. What type of reaction is the conversion of *cis*-$[Ir(CO)_2I_2]^-$ to **A**? What changes in iridium oxidation state occur on going around the catalytic cycle, and what is the electron count in each iridium complex?

25.28 What roles do inorganic catalysts play in the following manufacturing processes: (a) production of aldehydes from alkenes, (b) polymerization of propene, (c) production of acetic anhydride, (d) hydrogenation of compound **25.40** to produce the drug (*S*)-Naproxen? State whether homogeneous or heterogeneous catalysts are used.



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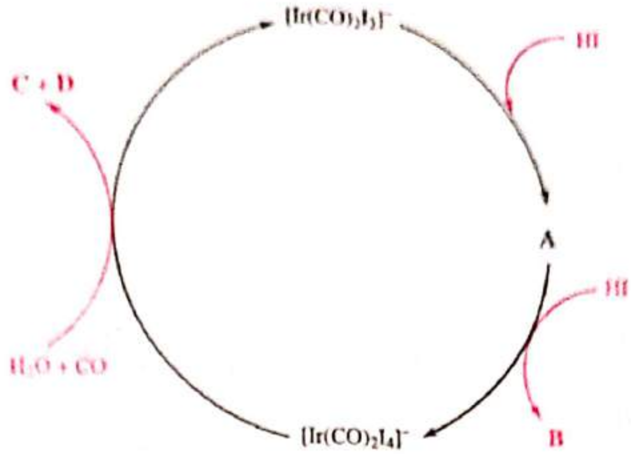

Fig. 25.22 Proposed catalytic cycle for the water gas shift reaction that is a competitive route in the Cativa process.

25.29 Measures taken to control atmospheric pollution include (a) scrubbing industrial waste gases to remove SO_2, and (b) reduction of NO in motor vehicle emissions. Explain how these are achieved and write balanced equations for relevant reactions. Are they catalytic processes?

25.30 In 2008, the US manufactured 32.4 Mt of sulfuric acid. The importance of H_2SO_4 is reflected in the fact that its consumption in a given country is a direct indicator of that country's industrial growth. (a) Give examples of commercial uses of H_2SO_4. (b) Starting from relevant feedstocks, outline how sulfuric acid is produced on an industrial scale, paying attention to reaction conditions. (c) How does the manufacture of 'by-product sulfuric acid' differ from the process you have described in part (b)?