INTRODUCTION TO CATALYSIS

CHE 323

BY

ADEWUYI Adewale

Chemical Sciences

Redeemer's University

CATALYSIS

- A catalyst is something that makes a reaction go faster, without being consumed in the process.
- Because the catalyst is not consumed in the process, each catalyst molecule can participate in many consecutive cycles, so we need only a small amount of catalyst relative to the substrate.
- The substrate/catalyst ratio reflects the catalyst's efficiency, which is measured as turnover number or turnover frequency.
- There are many different types of catalysts. They range from the proton, H^+, through Lewis acids, organometallic complexes, organic and inorganic polymers, all the way to enzymes
- To simplify things, we divide catalysis into three categories: homogeneous catalysis, heterogeneous catalysis, and biocatalysis
- Although the catalysts and the process conditions in each category can be very different, the principles of catalysis are the same. Once you understand these principles, you can apply them in all three categories
- The catalystturnover number (TON) and the turnover frequency (TOF) are two important quantities used for comparing catalyst efficiency
- In homogeneous catalysis, the TON is the number of cycles that a catalyst can run through before it deactivates
- The TOF is simply TON/time
- TON and TOF are often defined per active site, or per gram catalyst
- The main advantages of catalysis is that you get the desired product faster, using fewer resources and generating less waste.

# Homogeneous Catalysis, Heterogeneous Catalysis, and Biocatalysis

Homogeneous catalysis
the catalyst is in the same phase as the reactants and products. With emphasis being on liquid phase;

Production of biodiesel
In the classic case, the reactant (also called the substrate) molecules and the catalyst are reacted in a solvent. For example, the transesterification of fatty acid triglycerides with methanol (Figure 1.10) is catalyzed by hydroxide (OH^-) ions. This is an important process for making fatty acid methyl esters which are then used as biodiesel.

In Figure below the "OH^- is written" above the reaction arrow, rather than on the same line as the reactants and products. This notation reminds us that the catalyst, although it participates in the reaction, remains unchanged when the reaction is completed. This does not mean that the catalyst does not change during the reaction. A catalytic reaction is made up of several steps. These form a cyclic process, called a catalytic cycle. Although the catalyst can (and often does) change during the catalytic cycle, it returns to its original form at the "end" of the cycle. Typical TONs for this reaction are approximately 1000, so each OH^- anion catalyzes many consecutive cycles.
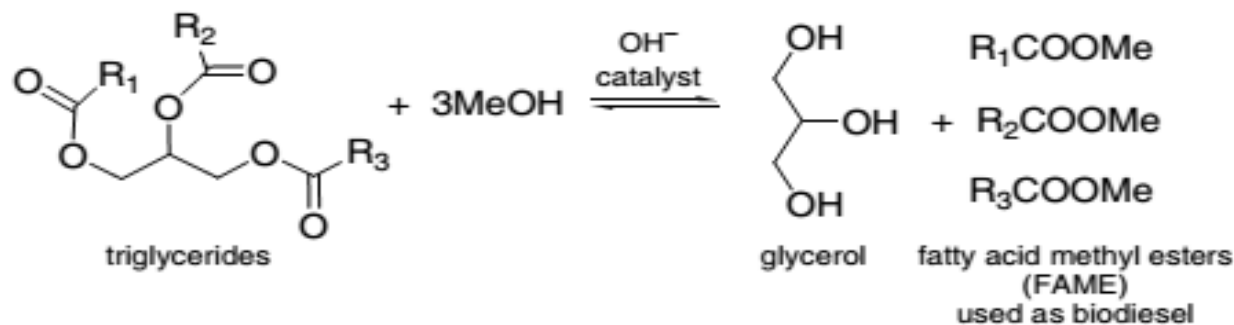
Base-catalyzed transesterification of triglycerides.

The easiest way to illustrate catalytic circle is using an example. Figure 1.11a shows the classic catalytic cycle for the Pd-catalyzed cross-coupling between an alkene and an aryl halide. This reaction, discovered independently by Heck and Mizoroki in 1968, is known as the Heck reaction. Since its discovery it has become ubiquitous in organic chemistry, and is used today in severalfine-chemical processes. We see that the catalyst goes through at least six different structures (these are called the catalytic intermediates). Each of these is "the catalyst"as much as any other. The point is, however, that at the end of the cycle the original catalyst is regenerated and is ready to catalyze the coupling reaction of two new substrate molecules. Figure 1.11b shows a "black box"version of the same catalytic cycle. This is what we actually observe: the substrates (aryl halide and alkene) enter the reactor and the products and by-products leave it. The catalyst remains in the reactor and, for all practical purposes, remains unchanged.

Many homogeneous catalysts are based on a (transition) metal atom that is stabilized by a ligand. The ligand is usually an organic molecule that attaches to the metal atom. By changing this ligand, one can change the catalyst's properties. Selecting the right metal and the right ligand can improve the catalyst's activity, selectivity, and stability.
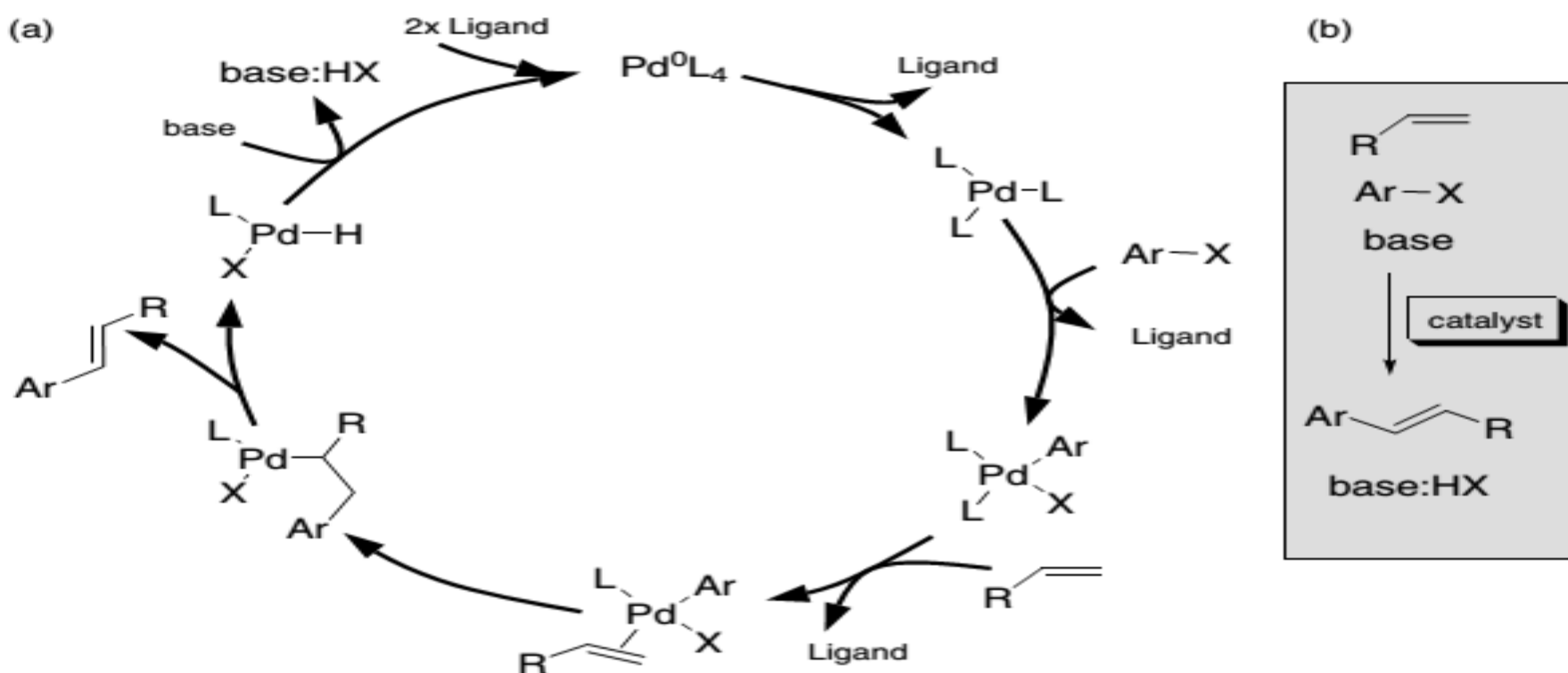
Figure 1.11 Proposed catalytic cycle for the Heck reaction, showing **a** the various catalytic intermediates and **b** the "black box" version. Some Pd catalysts exhibit TONs and TOFs of over 100 000 in this reaction.
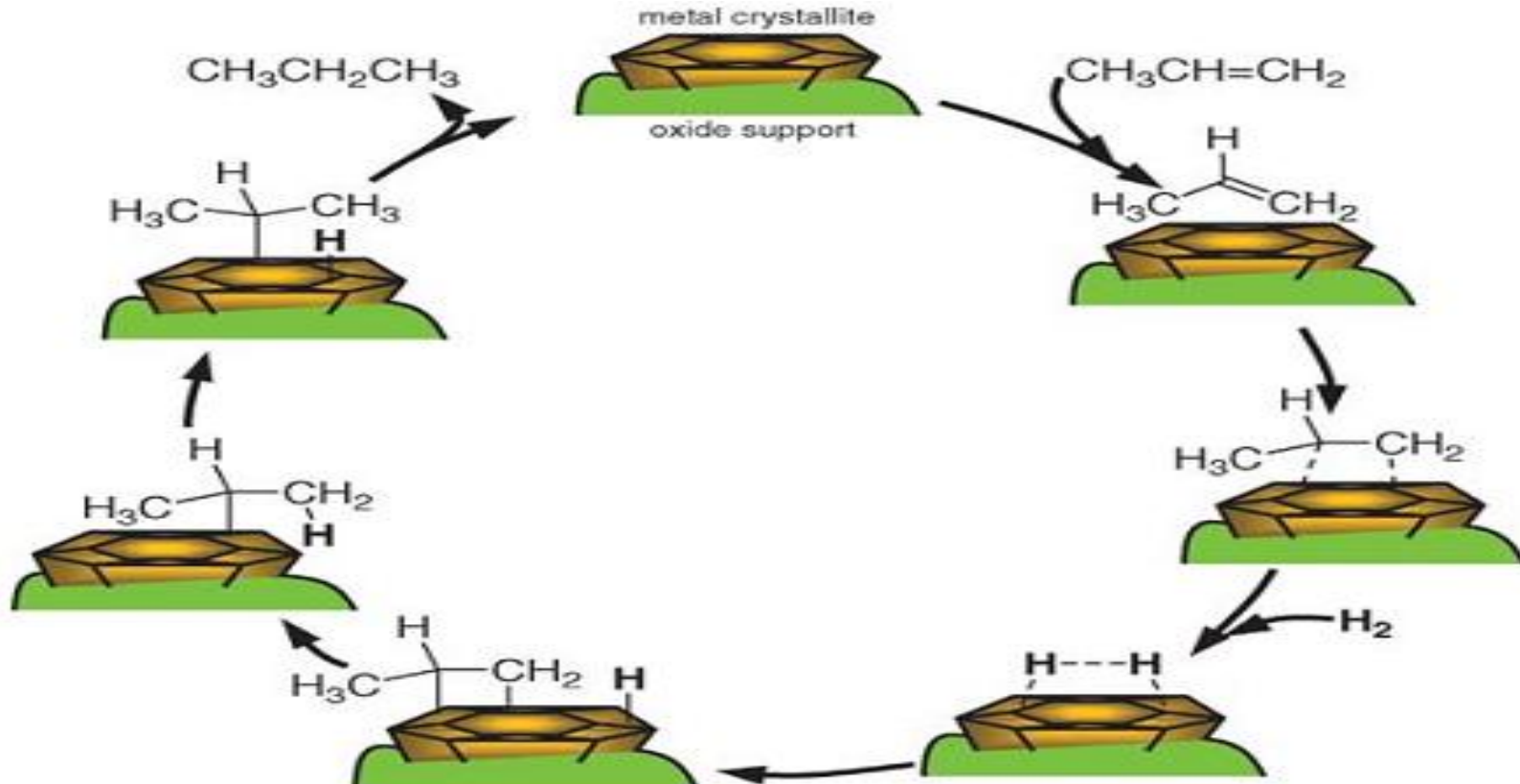
Heterogeneous catalysis

This covers all the cases where the catalyst and the substrate are in different phases. However, when chemists speak about heterogeneous catalysis, they usually refer to a system where the catalyst is a solid and the reactants are (most often) gases or liquids.

One important advantage of heterogeneous catalysis is the ease of catalyst separation. In gas/solid systems the catalyst is easily separated and cleaned, and in liquid/solid systems it can be simply filtered.

Hydrogenation of propene to propane

In this reaction, a hydrogen molecule is added to the propene double bond in the presence of a group VIII metal catalyst (Ni, Pd, or Pt). The catalytic cycle is shown below. This involves several steps. First, a propene molecule is adsorbed on the catalyst surface. The carbon–carbon p-bond breaks and bonds with the surface are created. Meanwhile, H_2 molecules are also adsorbed on the catalyst. The H-H bond then breaks, and the H atoms move across the metal surface. Eventually, an H atom diffuses close to one of the bonded C atoms. The C–metal bond is then replaced by a C-H bond. When this happens at the other C atom also, the connection with the surface breaks and the new propane molecule diffuses back into the gas phase.

Note that each of these simple elementary reactions is reversible, and so the entire catalytic cycle is also reversible. This is known as the principle of microscopic reversibility. Consequently, if platinum is a good hydrogenation catalyst, then it must also be a good dehydrogenation catalyst. In fact, as we will see later, catalysts change only the reaction rate, not the equilibrium. Every catalyst catalyzes both the "forward" and the "reverse" reactions in the same proportions. In the above example, the reverse reaction is actually more interesting for industry, because propene is a valuable monomer for making poly(propylene) and other polymers.

Hydrogenation of propene to propane in the presence of a supported metal catalyst (the reverse arrows are omitted for clarity).

Not all heterogeneous catalysis occurs on metal surfaces. Zeolites, for example, are excellent solid acid catalysts. These are porous crystalline structures of metal oxides, often made from silicon, titanium, aluminum, and oxygen. By substituting cations in the zeolite framework, one can create Brønsted and/or Lewis acid sites. Zeolites are widely used in industry for enriching gasoline octane numbers via gas/solid catalysis.

Nevertheless, they can also catalyze liquid/solid reactions, as in the example of geraniol cyclization as shown in **Fig. below**.

Geraniol and its corresponding cyclic derivatives are important intermediates in the flavor and fragrance industry. The suggested reaction mechanism involves both carbocation formation, via protonation of the double bond at a Brønsted acid site, and complexation of the hydroxy group with a Lewis acid site.
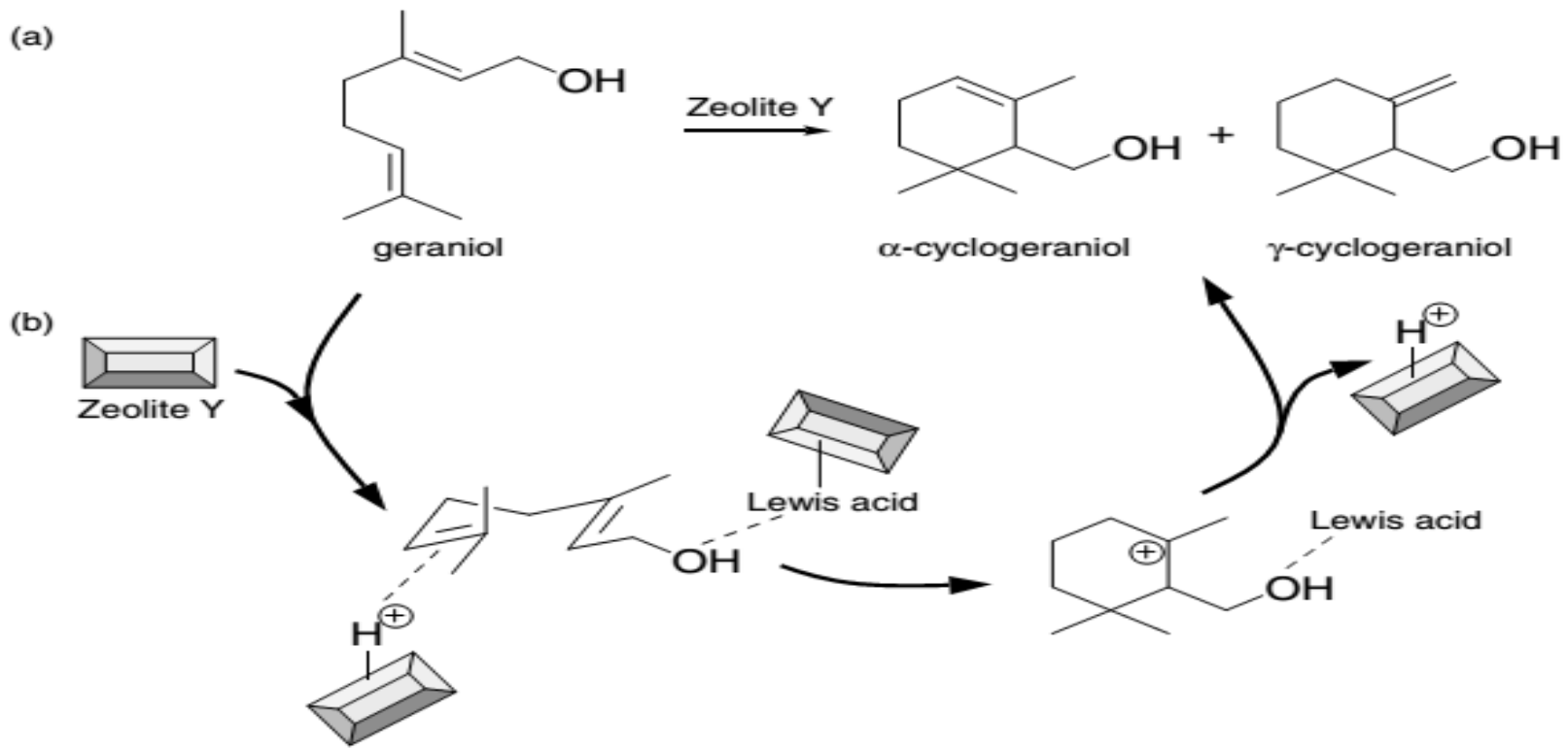
(a) Equation for the cyclization of geraniol, and (b) possible mechanism in the presence of zeolite Y, a solid acid catalyst that has both Brønsted and Lewis acid sites.

Biocatalysis

It is a rather special case, somewhere between homogeneous and heterogeneous catalysis. In most cases, the biocatalyst is an enzyme–a complex protein that catalyzes the reactions in living cells.

Enzymes are extremely efficient catalysts. An enzyme typically completes 1000 catalytic cycles in one second. Compared to this, conventional homogeneous and heterogeneous catalysts are slow and inefficient (100–10 000 cycles per hour). Speed, however, is not the only advantage: **enzymes specialize in converting one specific reactant into another specific product**. This specificity even includes chiral centres, so an enzyme will catalyze the reaction of one substrate enantiomer, but not of the other. Such enantiospecific reactions are extremely important in the pharmaceutical and food industries, because often only one enantiomer has the desired activity. *This is the case for many drugs, food additives,flavorings, and fragrances*.

Further advantages of biocatalysis over "chemical catalysis" include *shorter synthesis routes and milder reaction conditions*. Enzymatic reactions are not confined to *invivo* systems–many enzymes are also available as isolated compounds which catalyze reactions in water and even in organic solvents.

Although biocatalysis is the "new kid on the block," more and more companies are using enzymes for chemical manufacture. One reason for this is that biocatalysts give sustainable alternatives to chemical manufacture, and not just for making chiral products.

Synthesis of acrylamide via an enzyme-catalyzed water addition to acrylonitrile (2-propenenitrile)

It uses theRhodococcus enzyme nitrile hydratase. Commercialized in 1985 by Nitto Chemicals in Japan, this process replaced an acid-catalyzed process, and also avoided the acrylic acid by-product. Biocatalytic acrylamide processes are now running at 50 000 tpa worldwide

acrylonitrile + H₂O → (Rhodococcus, nitrile hydratase) → acrylamide
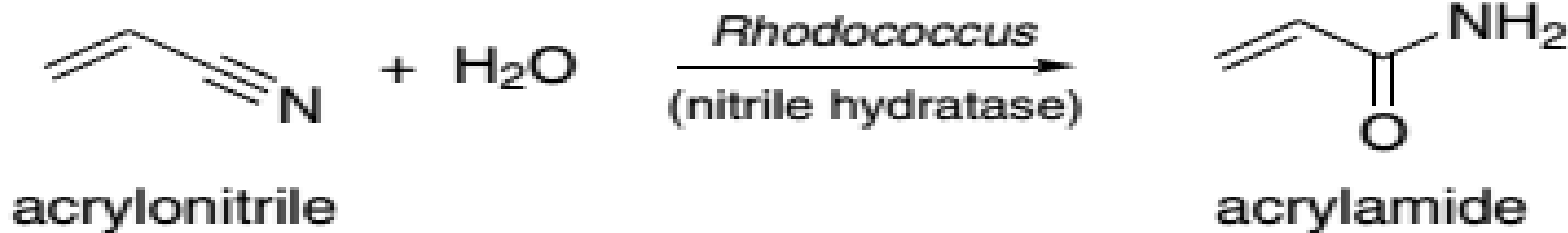
The biocatalytic synthesis of acrylamide from acrylonitrile is performed in Japan on a scale of 10 000 tons per year. The bacterial cells are immobilized in a poly(acrylamide) gel, and the process is run at pH 8.0–8.5 in semi-batch mode, keeping the substrate concentration below 3%.

Recent advances in genetic engineering are bringing forth new and exciting possibilities for biocatalysis. One example is the synthesis of important bulk industrial chemicals from renewable feedstocks. **Adipic acid**, for example, is a key monomer for making nylon 6.6. The world production of adipic acid is 2.2 million tons per annum. Practically all of this is produced from benzene, via cyclohexane and cyclohexanol/hexanone (**Figure below, left**). Although the process itself is quite efficient, it has three main drawbacks:

- First, it relies on petroleum, a nonrenewable fossil fuel, as a raw material.
- Second, it uses benzene, a known carcinogen.
- Third, it requires high pressures of hydrogen and oxygen, and uses concentrated HNO3 in the intermediate oxidation step, generating N_2O as a by-product.

In 2002, Frost and co-workers successfully constructed a mutated *Escherichia coli* bacterium that can convert D-glucose to cis, cis-muconic acid, which is then easily hydrogenated to adipic acid (**Figure below, right**). The biosynthetic route is certainly more complex than the conventional synthesis: it has nine steps, and uses eight different enzymes.
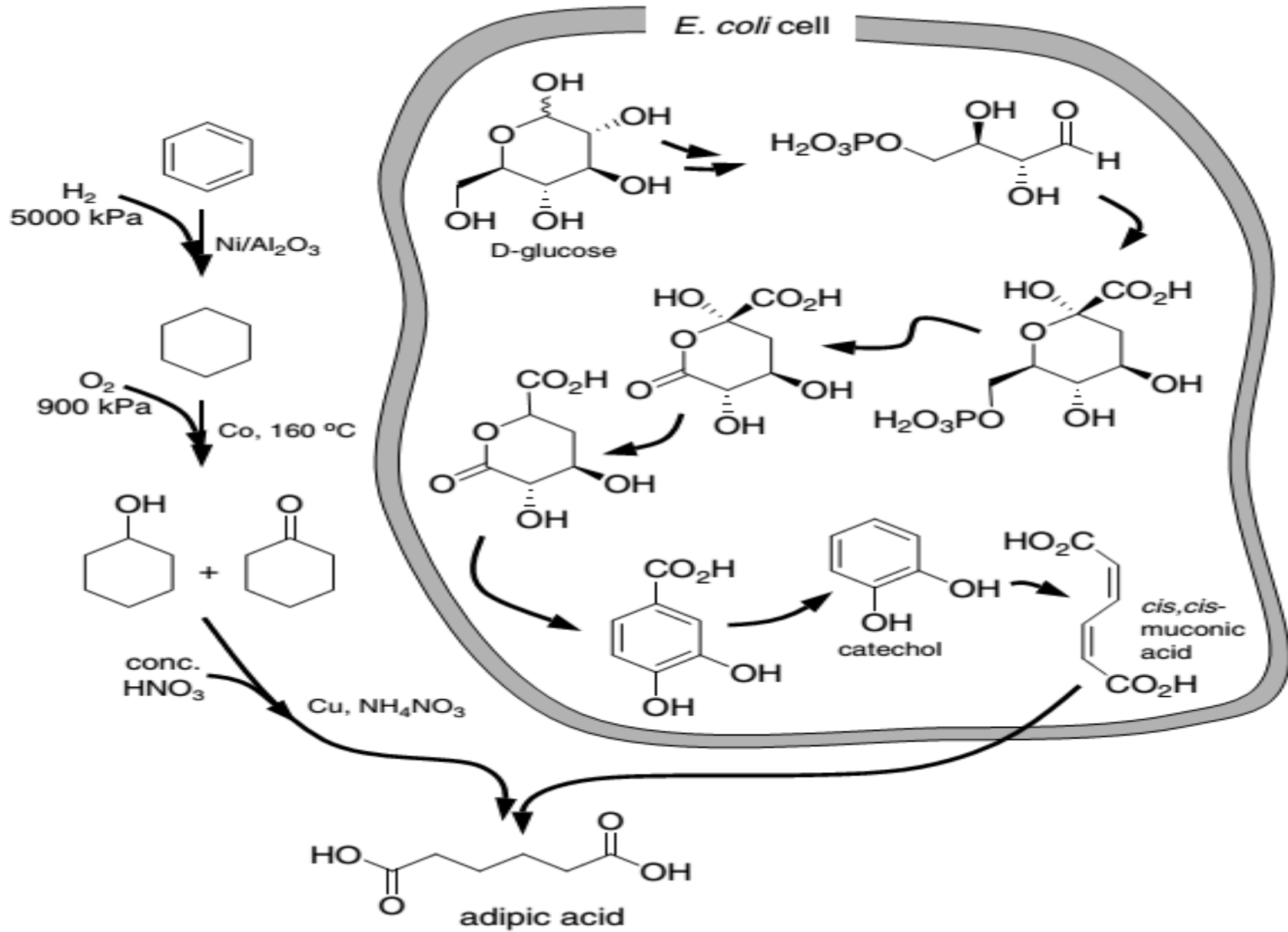
The classic Du Pont route to adipic acid (left) and Frost's biosynthetic route using a genetically modified E. Coli cell (right; the enzymes and the reagents are omitted for clarity).

Tools in Catalysis Research

Catalysis plays an integral role in many chemical reactions, all the way from petrochemistry to pharmaceutical chemistry. Because catalysis covers such a wide area, researchers use a variety of tools. These can be roughly divided into three groups: synthesis and testing tools, characterization tools, and modeling/mechanistic studies tools .
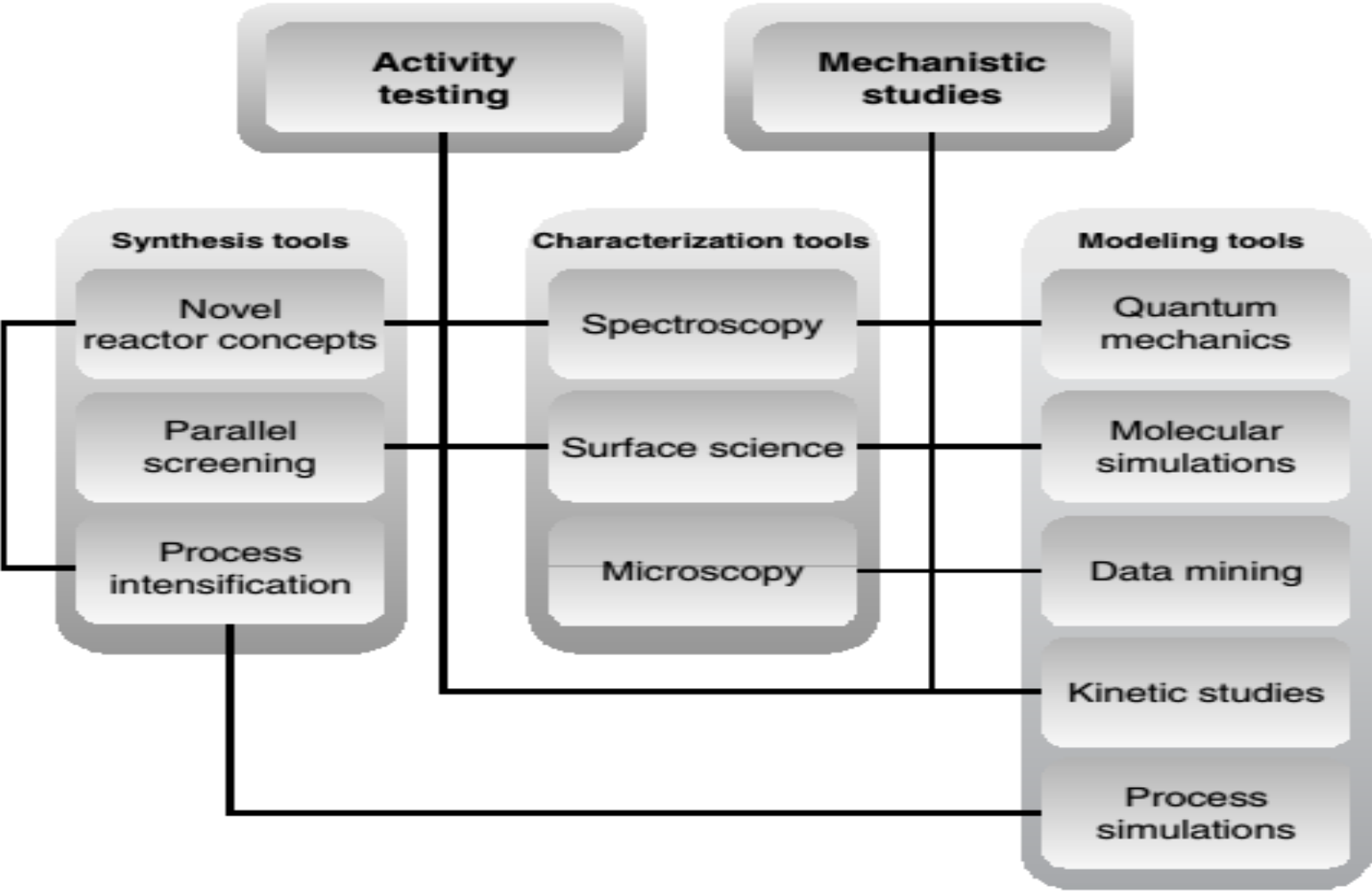
Heterogeneously Catalyzed Processes in Industry

Heterogeneous catalysts are used on a large scale in the following areas:

- ✓ Production of organic and inorganic chemicals
- ✓ Crude oil refining and petrochemistry
- ✓ Environmental protection
- ✓ Energy conversion processes

Production of Inorganic Chemicals

(1) Production of hydrogen and synthesis gas

Steam reforming of natural gas - sometimes referred to as steam methane reforming (SMR) - is the most common method of producing commercial bulk hydrogen at about 95% of the world production of 500 billion m^3 in 1998. Hydrogen is used in the industrial synthesis of ammonia and other chemicals. At high temperatures (700 – 1100 °C) and in the presence of a metal-based catalyst (nickel), steam reacts with methane to yield carbon monoxide and hydrogen.

$$CH_4 + H_2O \rightleftharpoons CO + 3\ H_2$$
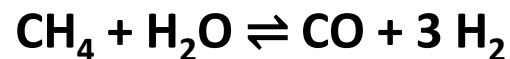
Catalysts with high surface area to volume ratio are preferred because of diffusion limitations due to high operating temperature. Examples of catalyst shapes used are spoked wheels, gear wheels, and rings with holes. Additionally, these shapes have a low pressure drop which is advantageous for this application.

Additional hydrogen can be recovered by a lower-temperature gas-shift reaction with the carbon monoxide produced, in the presence of a copper or iron catalyst. The reaction is summarized by:

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$
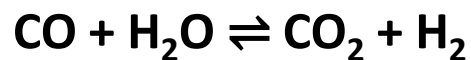
The first reaction is strongly endothermic (consumes heat, ΔH_r= 206 kJ/mol), the second reaction is mildly exothermic (produces heat, ΔH_r= -41 kJ/mol).

(2) Production of ammonia (The Haber process)

The Haber Process combines nitrogen from the air with hydrogen derived mainly from natural gas (methane) into ammonia. The reaction is reversible and the production of ammonia is exothermic.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \quad \Delta H = -92 \text{ kJ mol}^{-1}$$

A flow scheme for the Haber Process looks like this:
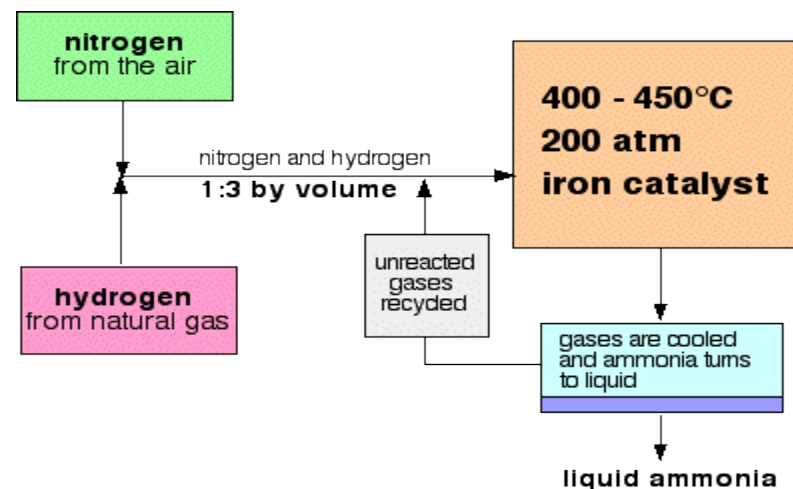
The catalyst
The catalyst is actually slightly more complicated than pure iron. It has potassium hydroxide added to it as a promoter - a substance that increases its efficiency.

The pressure
The pressure varies from one manufacturing plant to another, but is always high. You can't go far wrong in an exam quoting 200 atmospheres.

Recycling
At each pass of the gases through the reactor, only about 15% of the nitrogen and hydrogen converts to ammonia. (This figure also varies from plant to plant.) By continual recycling of the unreacted nitrogen and hydrogen, the overall conversion is about 98%

(3)   Oxidation of SO2 to SO3

Clean, dry sulfur dioxide is the feedstock for this stage. Electrostatic precipitators are used to remove any ash from the stream.

Relevant Equations: $SO_{2(g)} + {}^{1/2}O_{2(g)} <-> SO_{3(g)}$ Δ = -99 kJ/mol

The sulfur dioxide is mixed with air at pressure slightly higher than atmospheric, and is passed through a catalyst tower, called a converter. The tower contains 3 or 4 layers of *vanadium oxide* catalyst. Unreacted gases are recycled back into the gas stream
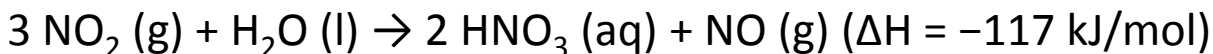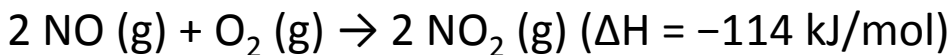
(4)   Ostwald process for nitric acid production

The **Ostwald process** is a chemical process for making nitric acid (HNO_3). Wilhelm Ostwald developed the process, and he patented it in 1902. The Ostwald process is a mainstay of the modern chemical industry, and it provides the main raw material for the most common type of fertilizer production. Historically and practically, the Ostwald process is closely associated with the Haber process, which provides the requisite raw material, ammonia (NH_3).

Ammonia is converted to nitric acid in 2 stages. It is oxidized by heating with oxygen in the presence of a catalyst such as ***platinum with 10% rhodium***, to form nitric oxide /nitrogen(ii)oxide and water/steam. This reaction is strongly exothermic, making it a useful heat source once initiated.

$4\ NH_3\ (g) + 5\ O_2\ (g) \rightarrow 4\ NO\ (g) + 6\ H_2O\ (g)\ (\Delta H = -905.2\ kJ/mol)$
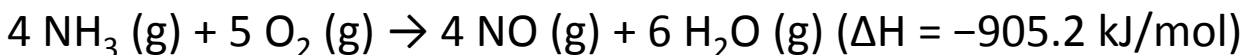
Stage two encompasses two reactions and is carried out in an absorption apparatus containing water. Initially nitric oxide is oxidized again to yield nitrogen dioxide/nitrogen(iv)oxide. This gas is then readily absorbed by the water, yielding the desired product (nitric acid, albeit in a dilute form), while reducing a portion of it back to nitric oxide:

$2\ NO\ (g) + O_2\ (g) \rightarrow 2\ NO_2\ (g)\ (\Delta H = -114\ kJ/mol)$
$3\ NO_2\ (g) + H_2O\ (l) \rightarrow 2\ HNO_3\ (aq) + NO\ (g)\ (\Delta H = -117\ kJ/mol)$

The NO is recycled, and the acid is concentrated to the required strength by distillation.

Alternatively, if the last step is carried out in air:

$$4 \; NO_2 \; (g) + O_2 \; (g) + 2 \; H_2O \; (l) \rightarrow 4 \; HNO_3 \; (aq)$$
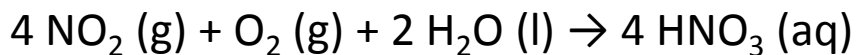
Typical conditions for the first stage, which contribute to an overall yield of about 98%, are:

- Pressure is between 4 and 10 standard atmospheres (410 and 1,000 kPa; 59 and 150 psi) and
- Temperature is about 500 K (230 °C; 440 °F).

A complication that needs to be taken into consideration involves a side-reaction in the first step that reverts the nitric oxide back to N_2:

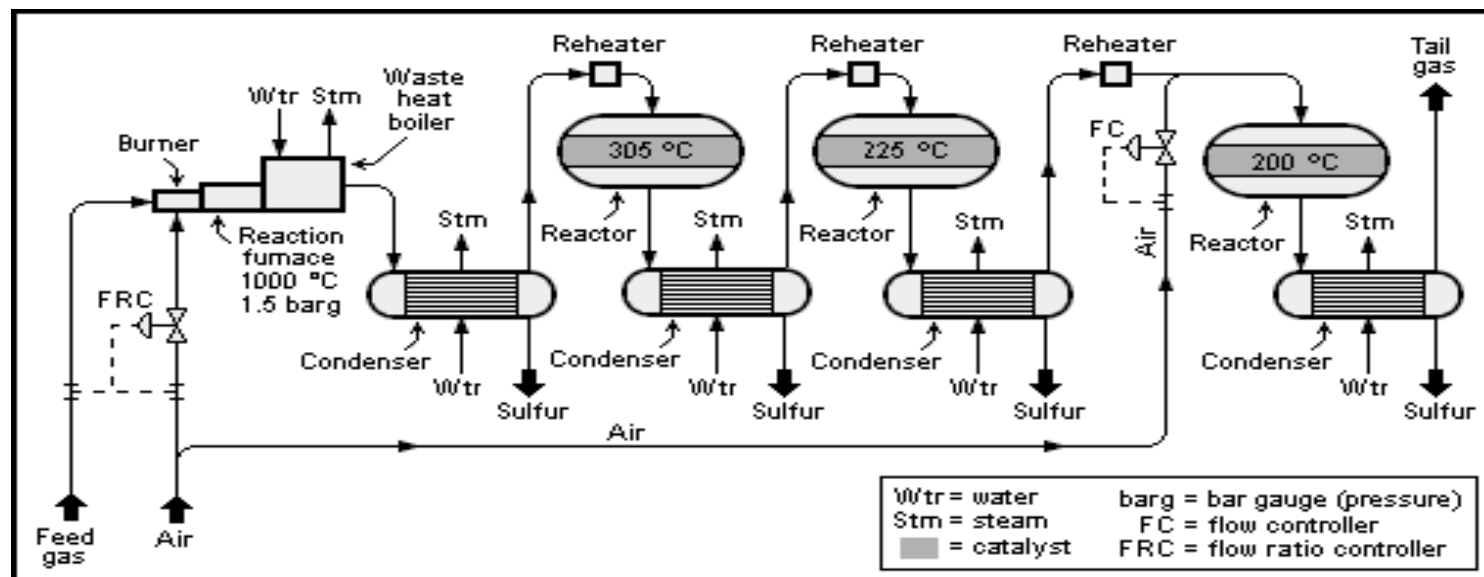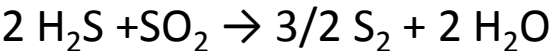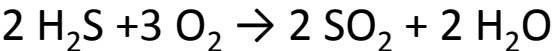$$4 \; NH_3 + 6 \; NO \rightarrow 5 \; N_2 + 6 \; H_2O$$
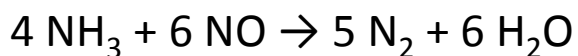
(5)   Claus process

The **Claus process** is the most significant gas desulfurizing process, recovering elemental sulfur from gaseous hydrogen sulfide.
The multi-step Claus process recovers sulfur from the gaseous hydrogen sulfide found in raw natural gas and from the by-product gases containing hydrogen sulfide derived from refining crude oil and other industrial processes.
Hydrogen sulfide produced, for example, in the hydro-desulfurization of refinery naphthas and other petroleum oils, is converted to sulfur in Claus plants. The reaction consists in two steps:

$$2 \text{ H}_2\text{S} + 3 \text{ O}_2 \rightarrow 2 \text{ SO}_2 + 2 \text{ H}_2\text{O}$$

$$2 \text{ H}_2\text{S} + \text{SO}_2 \rightarrow 3/2 \text{ S}_2 + 2 \text{ H}_2\text{O}$$

The Claus reaction continues in the catalytic step with activated aluminum(III) or titanium(IV) oxide, and serves to boost the sulfur yield. More hydrogen sulfide (H_2S) reacts with the SO_2 formed during combustion in the reaction furnace in the Claus reaction, and results in gaseous, elemental sulfur:

$$2 \text{ H}_2\text{S} + \text{SO}_2 \rightarrow 3 \text{ S} + 2 \text{ H}_2\text{O} \qquad (\Delta H = -1165.6 \text{ kJ mol}^{-1})$$

Table 8-1 Heterogeneous catalysis for the production of industrial gases and inorganic chemicals [T41]

Process or product	Catalyst (main components)	Conditions
Steam reforming of methane $H_2O + CH_4 \rightarrow 3H_2 + CO$	Ni/Al_2O_3	750–950 °C, 30–35 bar
CO conversion $CO + H_2O \rightleftharpoons H_2 + CO_2$	Fe/Cr oxides Cu/Zn oxides	350–450 °C 140–260 °C
Methanization (SNG) $CO + 3H_2 \rightarrow CH_4 + H_2O$	Ni/Al_2O_3	500–700 °C, 20–40 bar
Ammonia synthesis	Fe_3O_4 (K_2O, Al_2O_3)	450–500 °C, 250–400 bar
Oxidation of SO_2 to SO_3	V_2O_5/support	400–500 °C
Oxidation of NH_3 to NO (nitric acid)	Pt/Rh nets	ca. 900 °C
Claus process (sulfur) $2H_2S + SO_2 \rightarrow 3S + 2H_2O$	bauxite, Al_2O_3	300–350 °C

Production of Organic Chemicals

The processes can be classified according to reaction type.

(1)   Hydrogenation

Hydrogenation – to treat with hydrogen – is a chemical reaction between molecular hydrogen (H_2) and another compound or element, usually in the presence of a catalyst such as nickel, palladium or platinum. The process is commonly employed to reduce or saturate organic compounds. Hydrogenation typically constitutes the addition of pairs of hydrogen atoms to a molecule, often an alkene. Catalysts are required for the reaction to be usable; non-catalytic hydrogenation takes place only at very high temperatures. Hydrogenation reduces double and triple bonds in hydrocarbon.


linoleic

linoleic

oleic

H_2, Ni

stearic

oleic

oleic

margarine
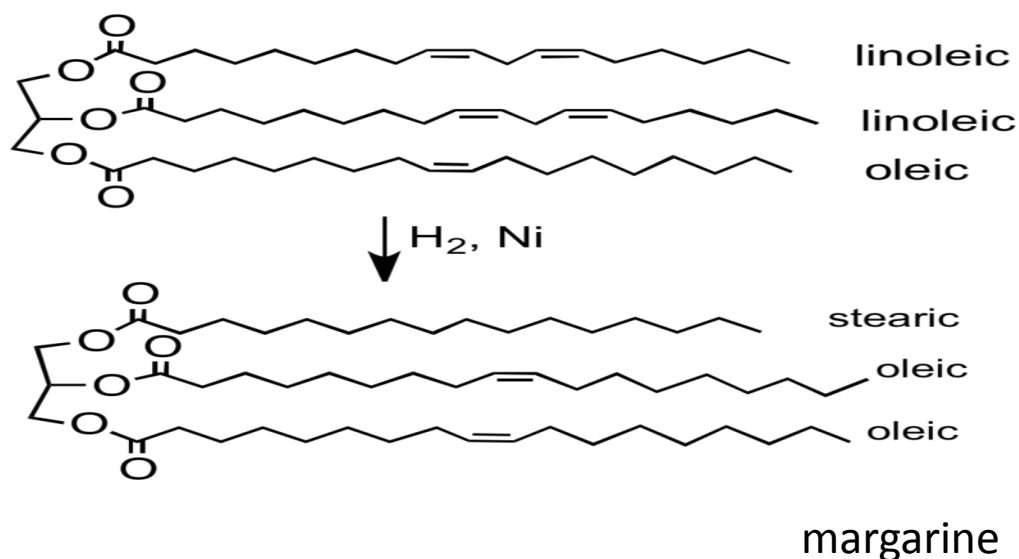
(2)   Methanol synthesis (from synthesis gas)

Carbon monoxide and hydrogen react over a catalyst to produce methanol. Today, the most widely used catalyst is a mixture of *copper and zinc oxides, supported on alumina*, as first used by ICI (**Imperial Chemical Industries**) in 1966. At 5–10 MPa (50–100 atm) and 250 °C (482 °F), the reaction is characterized by high selectivity (>99.8%):

$$CO + 2\ H_2 \rightarrow CH_3OH$$
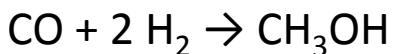
Since the production of synthesis gas from methane produces three moles of hydrogen for every mole of carbon monoxide, whereas the synthesis consumes only two moles of hydrogen gas per mole of carbon monoxide. One way of dealing with the excess hydrogen is to inject carbon dioxide into the methanol synthesis reactor, where it, too, reacts to form methanol according to the equation:
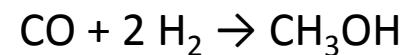
$$CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O$$
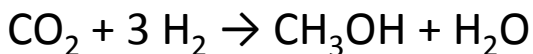
In terms of mechanism, the process occurs via initial conversion of CO into CO_2, which is then hydrogenated.

$$CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O$$
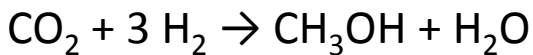
where the H_2O byproduct is recycled via the water-gas shift reaction.
$$CO + H_2O \rightarrow CO_2 + H_2$$
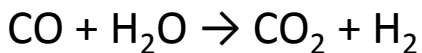
This gives an overall reaction, which is the same as listed above.

$$CO + 2 H_2 \rightarrow CH_3OH$$

(3)   Selective Oxidation of Propene

The heterogeneously catalyzed gas-phase oxidations of unsaturated hydrocarbons are large-scale industrial processes. The best known processes are:

– Oxidation of ethylene to ethylene oxide
– Oxidation of propene to acrolein and ammoxidation to acrylonitrile
– Oxidation of n-butane, butenes, or benzene to maleic anhydride
– Oxidation of o-xylene to phthalic anhydride

Economic operation of these processes requires a selectivity of at least 60 %. In the last few decades the industrial oxidation catalysts have been so much improved that selectivities of over 90 % are achieved in some cases. Thus the space–time yields of the processes could be improved and better use made of the raw materials.

Selective oxidation still offers interesting development possibilities for the chemical engineer. Here we shall consider the oxidation and ammoxidation of propene, which both proceed by a similar mechanism, in more detail. In the selective oxidation of propene, metal oxides are mainly used as catalysts, and many different products are obtained (Scheme 8-5), depending on the catalyst used.
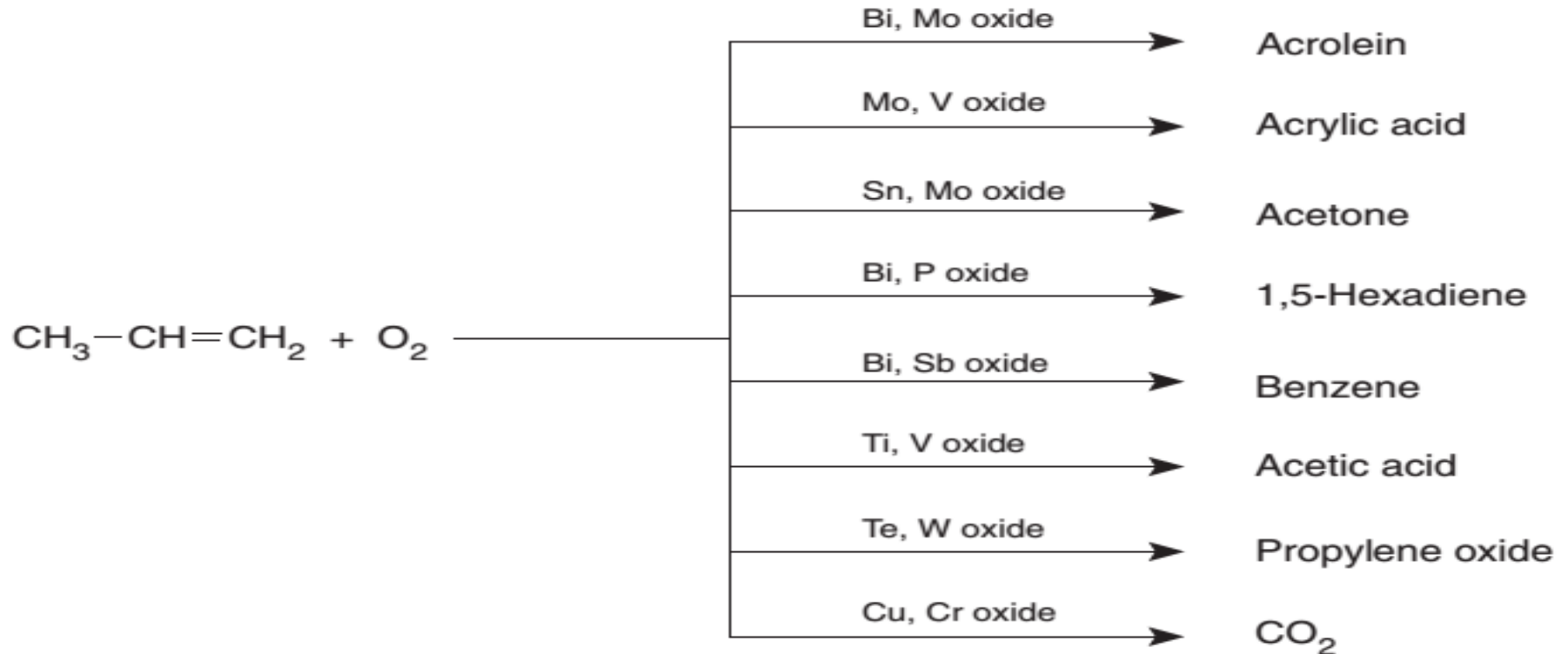
**Scheme 8-5** Oxidation of propene on various metal oxide catalysts

The catalytic oxidation of propene leads preferentially to formation of acrolein.

$$H_2C=CH-CH_3 + O_2 \longrightarrow H_2C=CH-CHO + H_2O$$
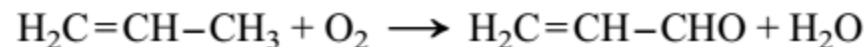
$$\Delta H_R = -368 \text{ kJ/mol}$$

Carbon dioxide, acetaldehyde, and acrylic acid are formed as side products. A technical breakthrough was achieved by Standard Oil of Ohio (SOHIO) with the discovery of the bimetallic bismuth molybdate and bismuth phosphomolybdate catalysts. Propene is oxidized with air on a Bi_2O_3/MoO_3 catalyst at 300–400C and 1–2 bar in a fixed-bed tubular reactor, which allows effective removal of heat from the exothermic reaction

The mechanism of the allyl oxidation of propene is explained in terms of a reaction cycle. As shown in Scheme 8-6, propene and air do not react directly with one another. Instead, the propene initially forms a π complex **A** with an Mo center of the bismuth molybdate catalyst. Hydrogen abstraction by an oxo oxygen atom on bismuth leads to formation of a hydroxyl group and a π-allyl complex at Mo **B**, whereby one
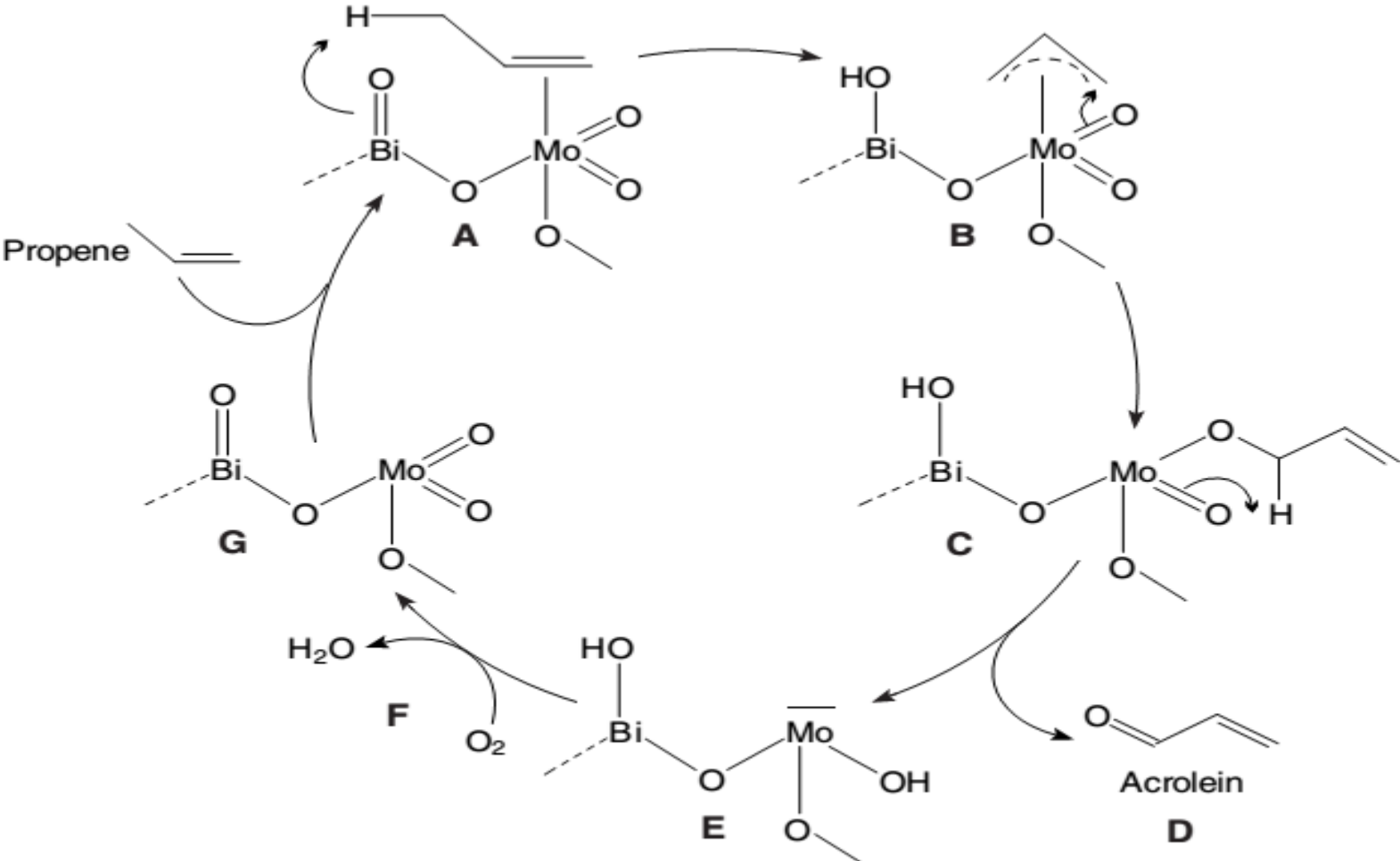
Scheme 8-6 Oxidation of propene to acrolein on Bi/Mo catalysts [19]

electron flows into the lattice. Transfer of oxygen to the allyl group forms an Mo–alkylate bond, and a further hydrogen abstraction (**C**) on the same Mo center leads to formation of acrolein, which is desorbed from the catalyst surface (**D**). In these steps, three electrons flow into the lattice, and what remains is an oxygen-deficient bismuth molybdate with OH groups (**E**). This reacts with atmospheric oxygen with cleavage of water (**F**) and re-formation of the original catalyst (**G**). In the reoxidation of the catalyst, an O_2 molecule is reduced to O^{2-} ions by four electrons, available in the lattice. The oxide ions then diffuse to the lattice vacancies.

How can the side products of the oxidation reaction be explained? It can be assumed that the allylmolybdenum complex (**B**) is cleaved into C_1 and C_2 fragments, which result in acetaldehyde and CO_2, the latter presumably via formaldehyde as intermediate. Carbon dioxide can, however, also be formed by total oxidation of propene.

(4)   Olefin Polymerization

The polymerization of olefins has been carried out industrially for decades and can be performed by various mechanisms. The high-pressure radical polymerization of ethylene leads to low-density polyethylene (LDPE, ρ= 0.92–0.93 g/cm³). In the mid-1950s Ziegler achieved the low-pressure polymerization of ethylene and propylene (up to 10 bar, 50–150°C) by using organometallic catalysts based on TiCl4/Al$(C_2H_5)_3$. The Ziegler catalysts give less branched, linear high-molecular polyethylene (high-density polyethylene, HDPE; ρ= 0.94–0.97 g/cm³).

Homogeneous catalysis

1)   The Wacker Oxidation Process

The **Wacker process** or the **Hoechst-Wacker process** (named after the chemical companies of the same name) refers to the oxidation of ethylene to acetaldehyde in the presence of palladium(II) chloride as the catalyst. This chemical reaction was one of the first homogeneous catalysis with organopalladium chemistry applied on an industrial scale.
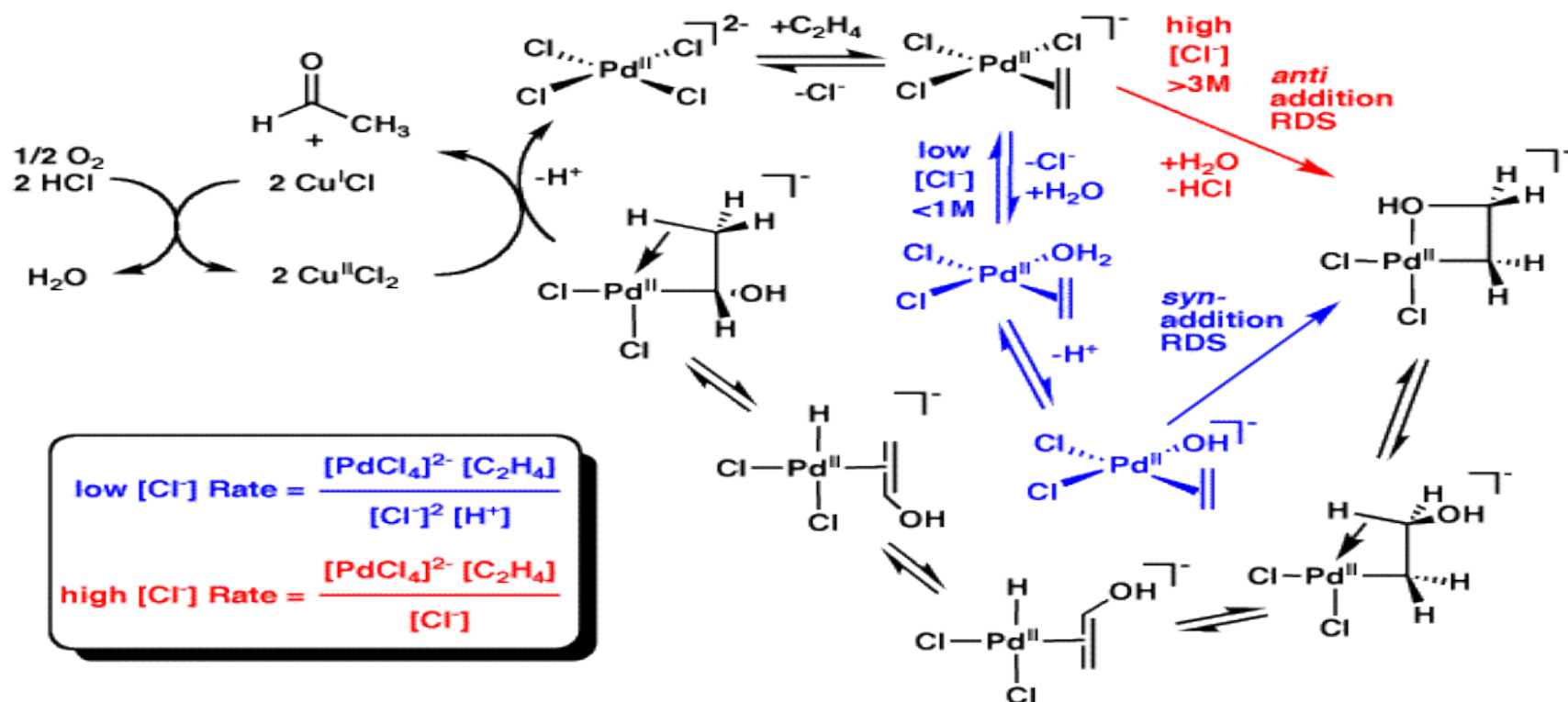
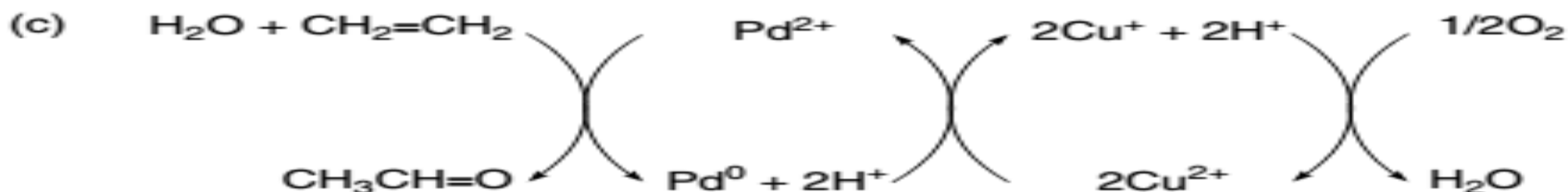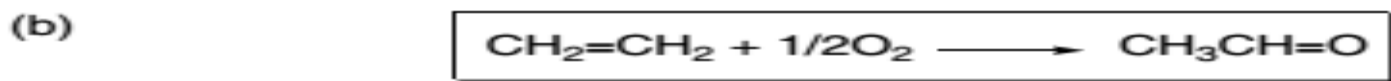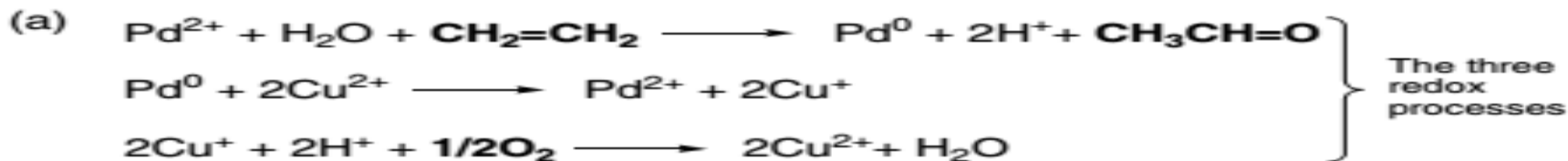The net reaction can also be described as follows:

$[PdCl_4]^{2-} + C_2H_4 + H_2O \rightarrow CH_3CHO + Pd + 2\ HCl + 2\ Cl^-$
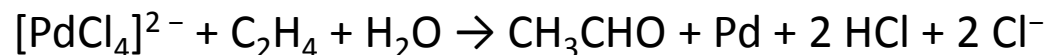
This conversion is followed by reactions that regenerate the Pd catalyst:

$$Pd + 2\ CuCl_2 + 2\ Cl^- \rightarrow [PdCl_4]^{2-} + 2\ CuCl$$

$$2\ CuCl + \tfrac{1}{2}\ O_2 + 2\ HCl \rightarrow 2\ CuCl_2 + H_2O$$
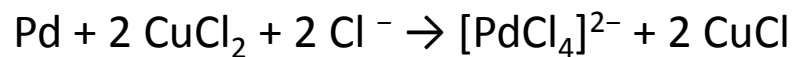
Note that all catalysts are regenerated and only the alkene and oxygen are consumed. Without copper(II) chloride as an oxidizing agent Pd(0) metal (resulting from reductive elimination of Pd(II) in the final step) would precipitate, stopping the reaction after one cycle. This stoichiometric reaction was discovered in 1894. Air, pure oxygen, or a number of other oxidizers can then oxidise the resultant CuCl back to $CuCl_2$, allowing the cycle to continue.

The Wacker process has three main steps. In the first step, ethene reacts with a Pd^{II} salt and water to give acetaldehyde, Pd^0, and two protons. In the second step, Pd^0 is re-oxidized by two equivalents of Cu^{II}, giving Pd^{II} and two equivalents of Cu^I. Finally, the Cu^I is re-oxidized by oxygen under acidic conditions, giving one equivalent of water and the regenerated Cu^{II} salt. As Figure 3.30 shows, all three steps are stoichiometric reactions, but taken together they form a dual-catalytic cycle. Note that although the net reaction is indeed the oxidation of ethene with oxygen to acetaldehyde, the oxygen atom in the acetaldehyde molecule does not come from the dioxygen molecule, but rather from the water!

The catalytic cycle for the Pd part is shown in Figure 3.31, which also demonstrates several of the elementary steps covered in Section 3.1. We start with $[Pd^{II}Cl_4]^{2-}$ as the catalyst precursor. Exchange of two of the chloride ligands for ethene and water is

(a)

$$Pd^{2+} + H_2O + CH_2=CH_2 \longrightarrow Pd^0 + 2H^+ + CH_3CH=O$$

$$Pd^0 + 2Cu^{2+} \longrightarrow Pd^{2+} + 2Cu^+$$

$$2Cu^+ + 2H^+ + 1/2O_2 \longrightarrow 2Cu^{2+} + H_2O$$

The three redox processes

(b)

$$CH_2=CH_2 + 1/2O_2 \longrightarrow CH_3CH=O$$

(c)

$H_2O + CH_2=CH_2$ Pd^{2+} $2Cu^+ + 2H^+$ $1/2O_2$

$CH_3CH=O$ $Pd^0 + 2H^+$ $2Cu^{2+}$ H_2O

Figure 3.30 a The three stoichiometric redox reactions and **b** the net reaction of the Wacker oxidation system; **c** a simplified representation of the Pd and the Cu catalytic cycles (the "reverse reaction" arrows are omitted, for clarity).
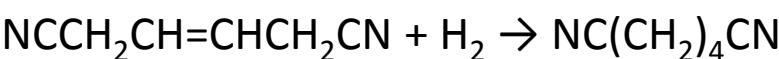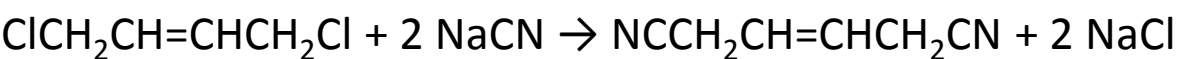
Wacker–Tsuji oxidation

The so-called **Wacker–Tsuji oxidation** is the laboratory scale version of the above reaction, for example the conversion of 1-decene to 2-decanone with palladium(II) chloride and copper(I) chloride in a water / dimethylformamide solvent mixture in the presence of air:

$$n\text{-}C_8H_{17}\text{-CH=CH}_2 \xrightarrow[\text{DMF, } H_2O]{\text{PdCl}_2,\ \text{CuCl},\ O_2} n\text{-}C_8H_{17}\text{-C(=O)-CH}_3$$
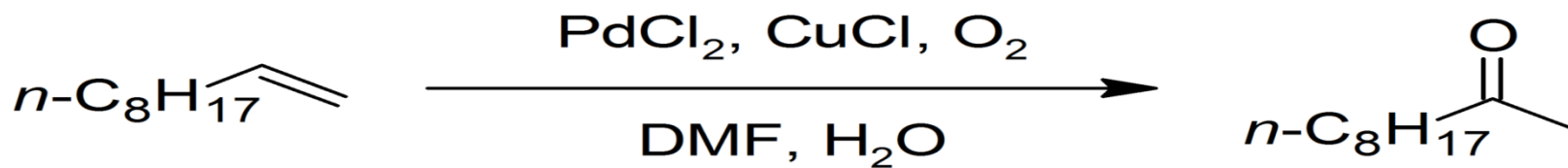
(2)   Synthesis of Adiponitrile

Adiponitrile is the organic compound with the formula $(CH_2)_4(CN)_2$. This dinitrile, a viscous, colourless liquid, is an important precursor to the polymer nylon-6,6.

Due to the industrial value of adiponitrile, many methods have been developed for its synthesis. Early industrial routes started from furfural and later by the chlorination of butadiene to give 1,4-dichloro-2-butene, which with sodium cyanide, converts to 3-hexenedinitrile, which in turn can be hydrogenated to adiponitrile:

$$ClCH_2CH=CHCH_2Cl + 2\ NaCN \rightarrow NCCH_2CH=CHCH_2CN + 2\ NaCl$$

$$NCCH_2CH=CHCH_2CN + H_2 \rightarrow NC(CH_2)_4CN$$

Modern routes

The majority of adiponitrile is prepared by the nickel-catalysed hydrocyanation of butadiene, as discovered at DuPont, pioneered by Drinkard. The net reaction is:

$$CH_2=CHCH=CH_2 + 2\ HCN \rightarrow NCCH_2CH_2CH_2CH_2CN$$
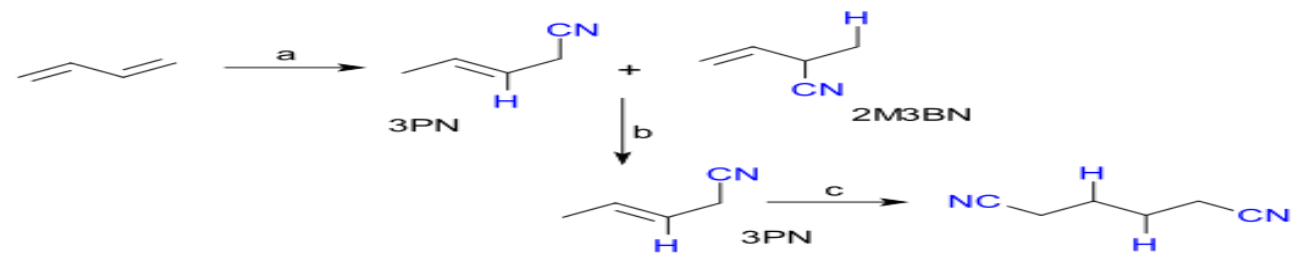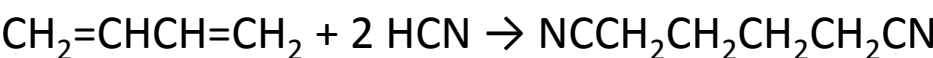
(3) The Ciba–Geigy Metolachlor Process

The asymmetric synthesis of (S)-metolachlor, commercialized by Ciba–Geigy in 1996, is atour de forceof homogeneous catalysis.

Metolachlor (2-chloro-N-(6-ethyl-o-tolyl)-N-(2-methoxy-1-methylethyl)acetamide, or N-chloroacetyl-N-alkoxyalkyl-2-ethyl-6-methylaniline) is the active ingredient of the herbicide Dual Magnum used for protecting corn and other crops. It has two chiral elements: an asymmetric carbon atom, and a chiral axis (similarly to BINAP). This means that there are four possible stereoisomers, but only the (S) isomers are active herbicides (Figure below).
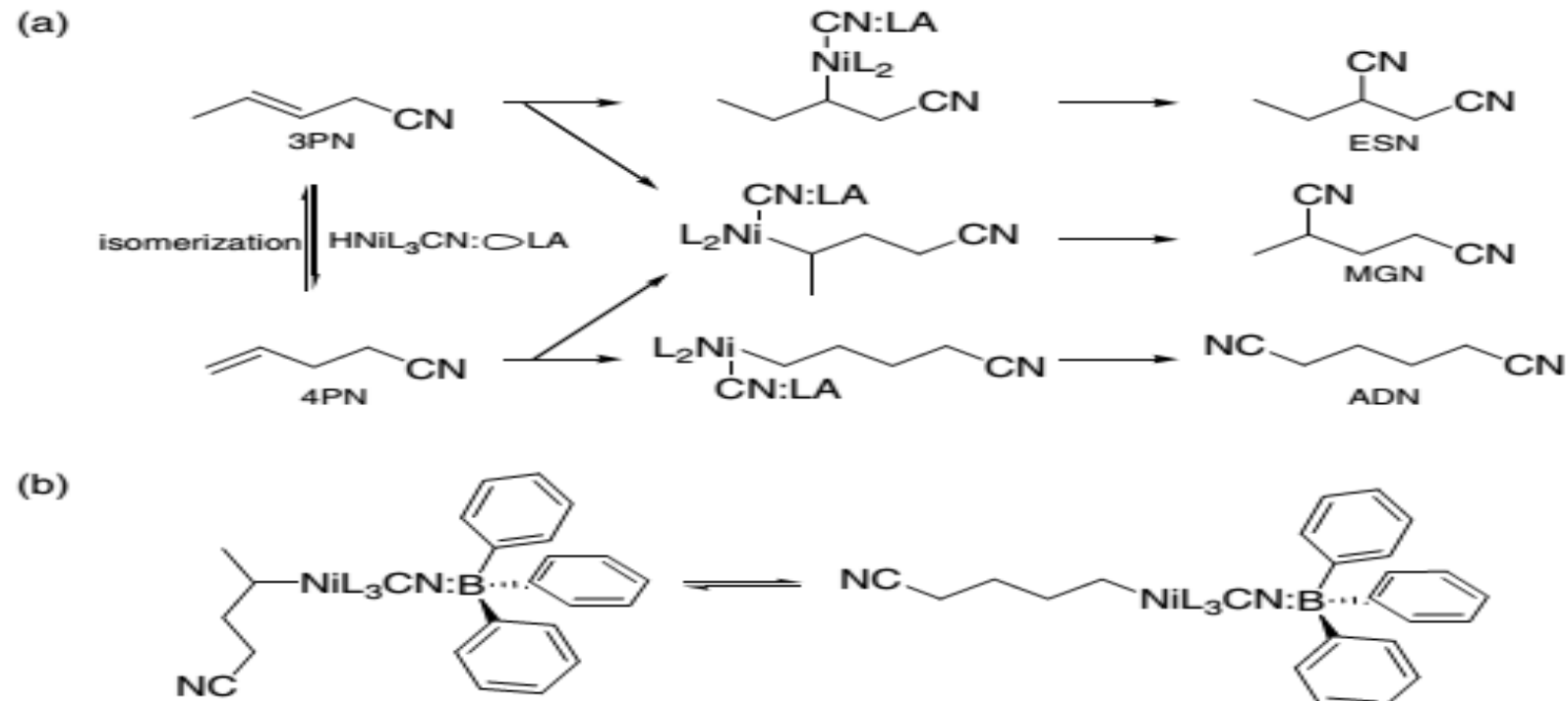
Formation of the various products in the second hydrocyanation step, co-catalyzed by Lewis acids (LA);bbulky Lewis acids such as BPh3shift the linear/branched product equilibrium toward the desired linear product.
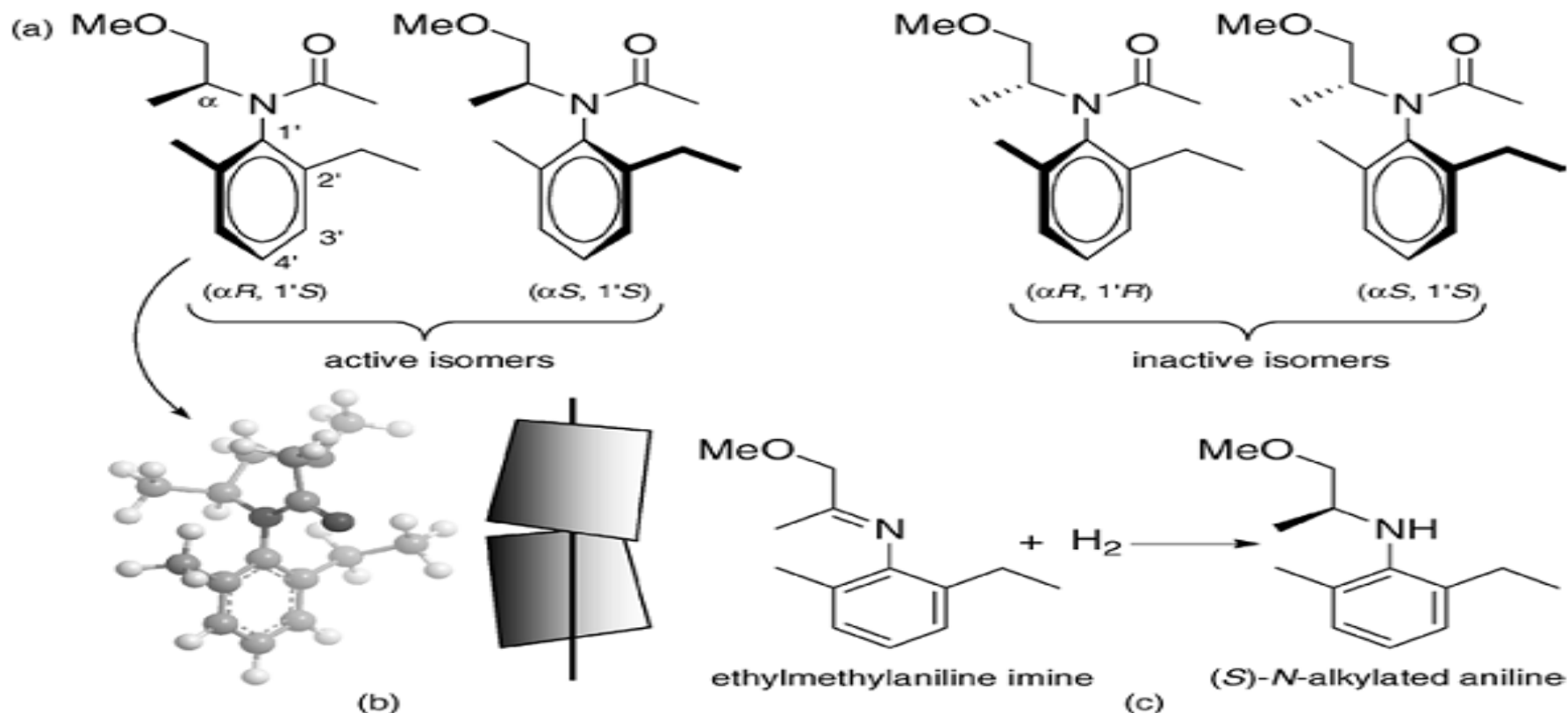
(a)   Chemical structures of the four stereoisomers of metolachlor; (b) 3D representation of the (αR,1'S) isomer, showing the chiral axis and (c) the asymmetric imine hydrogenation step.

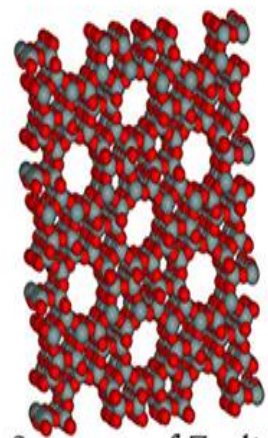## COMMERCIAL CATALYSTS

Zeolites

Zeolites are crystalline solids structures made of silicon, aluminum and oxygen that form a framework with cavities and channels inside where cations, water and/or small molecules may reside. They are often also referred to as molecular sieves.

Many of them occur naturally as minerals, and are extensively mined in many parts of the world finding applications in industry and medicine. However, most of zeolites have been made synthetically some of them made for commercial use while others created by scientists to study their chemistry. At present, there are 191 unique zeolite frameworks identified, and over 40 naturally occurring zeolite frameworks are known.
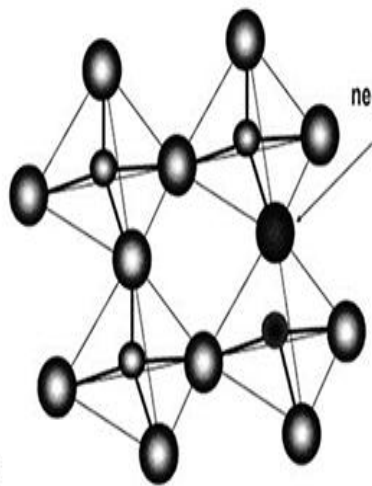
Zeolites were introduced in 1954 as adsorbents for industrial separations and purifications. Because of their unique porous properties, zeolites are used now in a variety of applications with world production estimated to be in the range of 2.5 million to 3 million metric tons (Mt) in 2008 year. They are used in petrochemical cracking, water softening and purification, in the separation and removal of gases and solvents, agriculture, animal husbandry and construction.

Zeolites are crystalline aluminosilicates with open 3D framework structures built of SiO_4 and AlO_4 tetrahedra linked to each other by sharing all the oxygen atoms to form regular intra-crystalline cavities and channels of molecular dimensions. A defining feature of zeolites is that their frameworks are made up of 4-coordinated atoms forming tetrahedra. These tetrahedra are linked together by their corners and make a rich variety of beautiful structures. The framework structure may contain linked cages, cavities or channels, which are big enough to allow small molecules to enter. The system of large voids explains the consistent low specific density of these compounds. In zeolites used for various applications, the voids are interconnected and form long wide channels of various sizes depending on the compound. These channels allow the easy drift of the resident ions and molecules into and out of the structure. The aluminosilicate framework is negatively charged and attracts the positive cations that reside in cages to compensate negative charge of the framework. Unlike most other tectosilicates, zeolites have largeer cages in their structures.
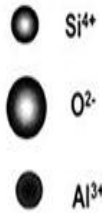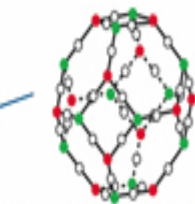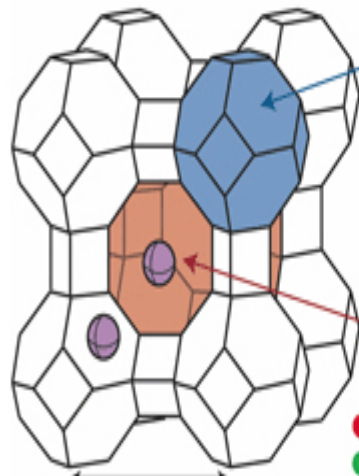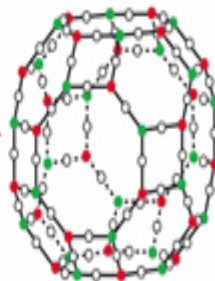
Structure of Zeolite

negative charge

Si^{4+}
O^{2-}
Al^{3+}

Zeolite A (LTA-type structure)

β-cage (sodalite cage)

1.23 nm

α-cage (supercage)

Si
Al
O
Cation site

(image from http://www.sssj.org/ejssnt/duan-small.jpg)
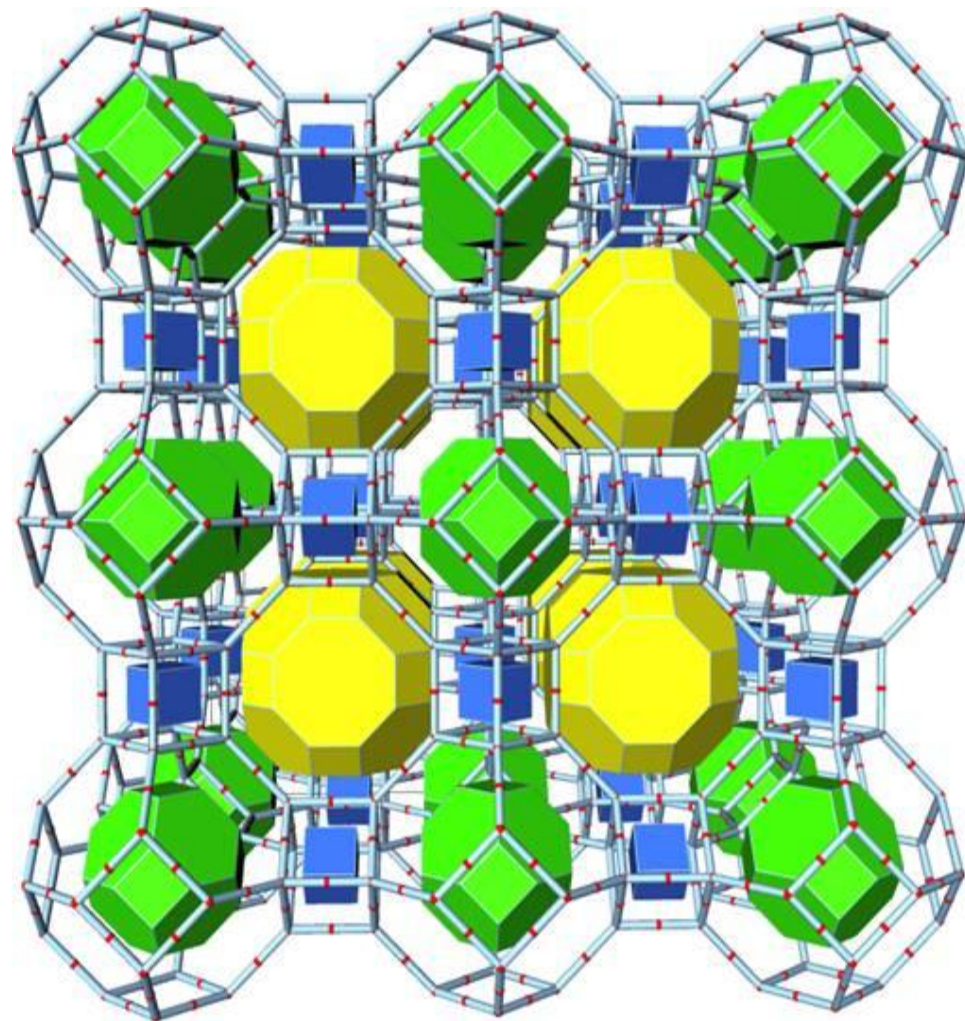
Related materials and discovery of new zeotypes

Zeolite-like materials have structures similar to zeolites but elements other than Si, Al and O can be present in them. For example, the isoelectronic substitution of $2Si \rightarrow Al + P$ has led to the discovery of a wide range of AlPO structures and related phosphate materials. Considerable success have been done recently on making tetrahedral frameworks with the congeners of Al and Si in the next row of the periodic table, namely, Ga and Ge, and only recently the first chiral germanosilicate ITQ-37 has the been discovered with a zeolite-like framework consisting entirely of tetrahedrally coordinated positions occupied by germanium and silicon. Although hundreds of laboratories are trying to synthesize new materials with novel zeolite framework structures, only 191 zeolite framework types have been approved by the International Zeolite Association (IZA) Structure Commission (IZA-SC).

The Atlas of Zeolite Structure Types published by the IZA Structure Commision assigns a three letter code to be used for a known framework topology irrespective of composition. The codes are normally derived from the name of the zeolite or "type material", e. g. LTA for Linde zeolites A, FAU for molecular sieves with a faujasite topology, e.g. zeolites X and Y, MOR for the mordenite topology, MFI for the ZSM-5 and silicate topologies. The more detailed information on topology of zeolites and related germanates compound is included in the Reticular Chemistry Structure Resource and the Database of Periodic Porous Structures

Applications

The properties of the porous materials depend both on the pore structures and the chemistry of the framework. The continuously increasing demands for materials with highly specific chemical and physical properties as zeolites have inspired scientists to make new porous materials with unique structures.
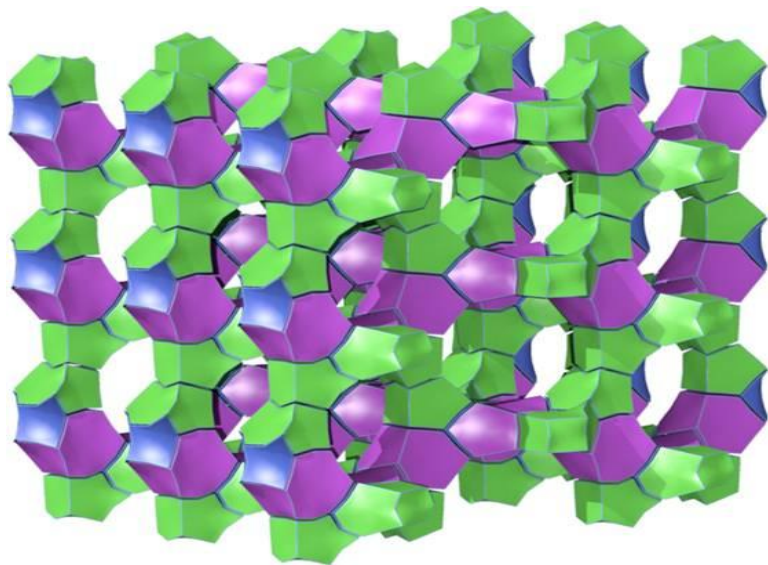
(1) Ion Exchange

Cation exchange properties of traditional aluminosilicate zeolites arise from the isomorphous positioning of aluminium in tetrahedral coordination within their Si/Al frameworks. This imposes a net negative charge of the framework ($Si^{+4} \rightarrow Al^{3+}$) counterbalanced by cations held within the cavities and channels. Ionic character of bonding between interstitial cations and the framework provide facile cation exchange for zeolites with open frameworks, where cations often readily exchanged for other cations in aqueous solution, though in some of the narrow-pored frameworks, such as natrolite, cation replacement is slow and difficult. Cation exchange is exploited in water softening, where alkali metals such as Na^+ or K^+ in zeolite framework are replaced by Ca^{2+} and Mg^{2+} ions from water. Many commercial washing powders thus contain substantial amounts of zeolites that enhance washing efficiency. LTA have the largest scale production of synthetic zeolites for use as "builders" in domestic and commercial detergents to remove the calcium and magnesium "hardness".

The unique ion exchange properties of zeolites can also be used for cleaning up of commercial waste water containing heavy metals and nuclear effluents containing radioactive isotopes. In a similar way zeolites can absorb ions and molecules and thus act as a filter for odor control and toxin removal.

Interstitial cations in zeolites can be exchanged to fine-tune the pore size of zeolites. For example, the sodium form of zeolite A has a pore opening of approximately 4 Å(4A molecular sieve). If Na^+ is exchanged with the larger K^+, the pore opening is reduced to approximately 3 Å; Ca^{2+} replaces 2 Na^+, thus, the pore opening increases to approximately 5 Å. Ion exchange with other cations is sometimes used for particular separation purposes.

Another potential application of zeolites is a drug delivery, when water in the structure is substituted by other liquid compound. Such treated zeolites act as a delivery system for the new fluid.

(2) **Adsorption and Separation**

Adsorption and separation are based on chromatographic processes which happen on the surface of zeolite crystals and are determined both by different migration speed of various compounds along the surface of adsorbent due to diversity in the intensity of their interactions with the surface and due to steric effects.

The shape-selective properties of zeolites are the basis for their use in molecular adsorption. The ability preferentially to adsorb certain molecules, while excluding others, has opened up a wide range of molecular sieving applications.

Sometimes it depends merely on the size and shape of pores controlling access into the zeolites; in other cases different types of molecule enter the zeolite, but some diffuse through the channels more quickly, leaving others stuck behind, as in the purification of para-xylene by the zeolites X or Y.

Cation-containing zeolites are extensively used as desiccants due to their high affinity for water, and also find applications in gas separation, where molecules are differentiated on the basis of their electrostatic interactions with the metal ions. Conversely, hydrophobic silica zeolites preferentially absorb organic solvents. Zeolites can thus separate molecules based on differences of size, shape and polarity.

(3) **Catalysis**

Zeolites have the ability to act as catalysts for chemical reactions which take place within the internal cavities. Essentially, zeolites have two properties which make them particularly suitable as starting materials for the preparation of catalysts.

(a)   They are cation exchangers, hence it is possible to introduce a large variety of cations with different catalytic properties into their intracrystalline pore system, which in turn offers the opportunity to create different catalytic properties, e. g. in acid- or metal-catalyzed reactions;

(b)   Zeolites are crystalline porous materials with pore dimensions in the same order as the dimensions of simple molecules; hence they possess molecular sieving properties when the shape and size of a particular pore system exert a steric influence on the reaction, controlling the access of reactants and products.

In the case of shape-selective catalysis in zeolites, the combination of both properties exploited to control the selectivity of catalytically conducted reactions.

Using zeolites as catalysts have many advantages since can be recovered and recycled with greater ease and low cost, leading to less waste and fewer byproducts, often function with higher activity, may combine several catalytic steps, reduce environment pollution by substitution of homogeneous catalysts used in the traditional chemical industry (mineral acids, salts, heavy metals).

Hydrogen-exchanged zeolites, whose framework-bound protons give rise to very high acidity are exploited in many organic reactions, including crude oil cracking, isomerisation and fuel synthesis. Because of high selectivity of zeolites, they are often the most efficient and cost-effective method for a number of refinery conversions.

Metal-exchanged zeolites can serve as oxidation or reduction catalysts, e. g. Ti-ZSM-5 in the production of caprolactam, and Cu-zeolites in NO_x decomposition. They have been employed on diesel vehicles as a less costly and more effective option for NO_x removal than the three-way catalytic converter.

Zeolites find and increasing application in production of petrochemicals, often replacing environmentally unfriendly catalysts. Zeolite catalysts typically yield fewer impurities, have higher capacity, give greater unit efficiency, and afford higher selectivity. Unlike the more hazardous acid catalysts that have been used in the past, e.g., solid phosphoric acid, hydrofluoric acid, etc., zeolites are non-hazardous and regenerable.

References

https://en.wikipedia.org/wiki/Catalysis

Jens Hagen. Industrial Catalysis. A Practical Approach. Second, Completely Revised and Extended Edition. Wiley.

Roth, Wieslaw J.; Nachtigall, Petr; Morris, Russell E.; Wheatley, Paul S.; Seymour, Valerie R.; Ashbrook, Sharon E.; Chlubná, Pavla; Grajciar, Lukáš; Položij, Miroslav. "A family of zeolites with controlled pore size prepared using a top-down method". Nature Chemistry. 5 (7): 628– 633.

https://en.wikipedia.org/wiki/Zeolite

Laidler, K.J. (1978) *Physical Chemistry with Biological Applications*, Benjamin/Cummings.

Nelson, D. L. and Cox, M. M. (2000) *Lehninger, Principles of Biochemistry* 3rd Ed. Worth Publishing: New York.