# Industrial Catalysis: A Practical Guide

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# Industrial Catalysis: A Practical Guide 6

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## Abstract

Every college student of chemistry, material science, and chemical engineering should be schooled in catalysis and catalytic reactions. The reason is quite simple; most products produced in the chemical and petroleum industries utilize catalysts to enhance the rate of reaction and selectivity to desired products. Catalysts are also extensively used to minimize harmful byproduct pollutants in environmental applications. Enhanced reaction rates translate to higher production volumes at lower temperatures with smaller reactors and less exotic materials of construction necessary. When a highly selective catalyst is used, large volumes of desired products are produced with virtually no undesirable byproducts. Gasoline, diesel, home heating oil, and aviation fuels owe their performance quality to catalytic processing used to upgrade crude oil. Intermediate chemicals in the production of pharmaceutical products utilize catalysts as well as the food industry in the production of every day edible products. Catalysts are playing a key role in developing new sources of energy and a variety of approaches in mitigating climate change and $CO_2$ upgrading.

This review describes the fundamentals of catalytic processes including the basic principles of catalysts and catalytic processes, general kinetics, selectivity, preparation, deactivation and characterization of catalysts. The application section describes petroleum processing, pollution abatement from vehicle exhausts, hydrogenation of vegetable oils for edible products, hydrogen generation technologies need in the production of ammonia, nitric acid production, pure hydrogen generation, low temperature (PEM) fuel cells, homogeneous catalysis and production of polyethylene and polypropylene polymers. Selected references are included for more in depth study.

## The Importance of Catalysis

A catalyst enhances the rate of reactions by lowering the activation energy towards desired products without itself being consumed. It is a kinetic effect that provides an alternative chemical path by which reactants are converted to products at moderate conditions. This permits lower temperatures to be utilized thereby conserving energy, materials of construction while lowering undesired product formation. What is a most desirable property is its ability to accelerate the desired reaction to a specific product referred to selectivity. Catalysts are composed of various chemical materials that participate by adsorbing reactants onto its active sites, producing products that rapidly desorb freeing the site for the next catalytic cycle. Enzymes (natures' catalysts) convert food to energy and perform thousands of metabolic functions in all living organisms.

Gasoline, diesel, home heating oil, and aviation fuels owe their performance quality to catalytic processing of crude oil. Margarine, cakes, chocolate, salad oils, and other everyday edible products are produced from natural oils via catalytic

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hydrogenation. Polyethylene and polypropylene plastics, commonly used in packaging of foods, films, fibers, liquid containers, etc., require catalysts for cost-effective high volume production. Because of highly active and selective catalysts, polyester fibers used in clothing can be produced at reasonable prices for the mass market. Catalysts allow the production of hydrogen and ammonia-based fertilizers that enrich the earth's nutrient deficient soils to enhance high volume food production. Catalytically produced ethylene oxide is a precursor to antifreeze and plastics. Formaldehyde is produced catalytically and used as a preservative and as a component in some polymer resins.

It is important to keep in mind the importance of catalysts in protecting the environment. They are frequently installed in the exhaust ducts of chemical operations to convert toxic volatile organic compounds (VOC) generated during manufacturing into benign products. Catalysts also provide the environmental benefit of clean air by abating pollutants generated from stationary and mobile combustion sources. In many locations around the industrialized world, coal- and gas-fired power plants have special catalysts installed in the ducts to eliminate pollutants dangerous to our health. Many gas-fired compressors that pump natural gas through millions of miles of pipelines are also equipped with exhaust catalysts to clean emissions at moderate conditions. Even fast food restaurants are equipped with catalysts to eliminate odors from the cooking process. The most widely used treatment of exhaust pollutants is that of the catalytic converter present in the exhaust manifold that cleans emissions from the internal combustion engines of gasoline- and diesel-fueled automobiles and trucks. As modern commercial passenger jets fly above 30,000 feet, there is a need to destroy the 2-4 ppm ozone that enters the airplane with make-up air to ensure passenger and crew comfort and safety. Radiators on select vehicles have a catalytic coating deposited on their surface that decomposes harmful ground-level ozone as the vehicle is driven.

All of this gives the consumer the benefits of readily available high-quality products at reasonable prices. From food to clothing to medicines to clean energy, to life in living organisms catalysts play a major role in products people use every day. For this reason every college student of chemistry, material science, and chemical engineering should be schooled in catalysis and catalytic reactions.

The forthcoming description of catalysts and catalytic processes should only serve as a primer towards understanding the basic principles with some examples of applications in the field of petroleum processing, alternative fuels, chemical production, and environmental air purification. Table 6.1 gives a list of some of the many commercial catalytic applications.

**Table 6.1** Some commercial catalytic reactions

| Reaction name | Example of chemical reaction | Major catalyst components | Commercial applications |
|---|---|---|---|
| *Petroleum processing* | | | |
| Cracking | $C_{16}H_{34}=C_8H_{18} + C_8H_{16}$ | Faujasite Zeolite | Naphtha, heating oil |
| Hydrodesulfurization | $RS + H_2=H_2S + RH$ | Co, Mo/$Al_2O_3$ (S) | Sulfur-free fuels |
| Naphtha reforming | $C_6H_{12}=C_6H_6 + 3\ H_2$ | Pt, Re/$Al_2O$(Cl) | High-octane gasoline |
| Alkylation | $C_3H_6 + C_4H_{10}=C_7H_{16}$ | Liquid acids | Gasoline |
| *Hydrogenation of functional groups* | | | |
| Double bonds | $H_2R=R'–R''H_3 + H_2=H_3R–R'HR''H_3$ | Ni or Pd or Ru on carriers | Air stable compounds, edible/non-edible oils |
| Aldehydes | $RCHO + H_2=RCH_2OH$ | Pd or Ru or Ni on carriers | Alcohols |
| *Selective oxidations* | | | |
| Nitrogen dioxide for nitric acid | $4NH_3 + 5O_2=4NO_2 + 6H_2O$ | Pt, Rh gauze | Fertilizer, explosives |
| Sulfuric acid | $SO_2 + 1/2O_2=SO_3$ | $V_2O_5$ on $TiO_2$ | Dissolving minerals |
| Ethylene oxide | $CH_2=CH_2 + 1/2O_2=C_2H_4O$ | Ag on alpha $Al_3O_3$ | Antifreeze, polyester, fibers, bottles |
| Formaldehyde | $CH_3OH + 1/2O_2=CH_2O + H_2O$ | Bi, Mo or Ag | Monomers, preservatives |
| *Synthesis gas/$H_2$* | | | |
| Synthesis gas | $CH_4 + H_2O=3\ H_2 + CO$ | $Ni/Al_2O_3$ | Production of chemicals |
| Water gas shift | $CO + H_2O=H_2 + CO_2$ | Fe, Cr and Cu, Zn, Al | High purity $H_2$ |
| *Pollution control* | | | |
| Automotive (TWC) | $CO, HC + O_2=CO_2 + H_2O$<br>$CO + NO=1/2N_2 + CO_2$ | Pt, Rh or Pd on $Al_2\ O_2$ on a Monolith | Clean emissions |
| Stationary reduction of $NO_x$ | $2NO_2 + 4NH_3 + O_2=3N_2 + 6H_2O$ | $V_2O_5/TiO_2$ on a monolith | Reduction of $NO_x$ from power plants |
| Polymerization | $nCH_2=CH_2=(–CH_2–)_{n+1}$ | $Cr/SiO_2$ or $TiCl_4$ + alkyl aluminum halide | Plastics |

## How Does a Catalyst Work?

A catalyst increases the reaction rate or activity relative to an un-catalyzed process by providing a less energetic pathway for conversion of reactants to products. In this regard the catalyst provides a chemical and energetic shortcut by lowering the energy barrier (i.e., activation energy) of reactants going to products. If no catalyst were present, a higher temperature would be required to initiate the reaction. Higher temperatures often lead to undesirable byproducts and sometimes decomposition of one of the reactants. Therefore, by initiating the reaction at a lower temperature, the process is better controlled and the desired product can be produced. Selectivity at moderate conditions is the most important advantage for catalytic processes that is exploited in many product applications.

The catalyst is not consumed in the process; it does undergo various chemical changes during the process by interacting with the reactants and products and finally returning to its original state prepared for the next cycle. Mechanistically some or all of the reactants adsorb onto active sites where bonds are rapidly made or broken. For a heterogeneous solid catalyst processing a liquid and/or gas, the adsorption of reactants is called chemisorption that has the kinetics and reaction energies equivalent to a chemical reaction. Frequently chemisorbed species decompose to an intermediate that is rapidly converted to other intermediates or the final product. After the reaction is complete, the catalyst returns to its original state. In this regard there is no net change of the catalyst. Therefore, a very small amount of catalyst can process many molecules.

## What Are the Catalytic Metals and Metal Oxides?

Most catalytic metals and metal oxides are derived from Group VIII of the periodic table. Of special importance are Fe, Co, Ni, Rh, Pd, and Pt, but also of importance are Cu and Ag in Group 1b, V in Group Vb, and Cr and Mo in Group V1b. Three of the precious metals Rh, Pd, and Pt are extensively used in many industries due to their extremely high activity and selectivity. They are rare in nature and therefore expensive and thus spent catalysts are routinely recycled, purified, and reused. However, the so-called base metals Fe, Co, Ni, Cu, V, Cr, and Mn but especially Ni and Cu, are used for specialty chemical applications. Base metal catalysts usually have modest activities, but are much less expensive and in certain cases more selective than the precious metals. Therefore, it is always desirable to search for less expensive base-metal catalysts whenever possible. This has been especially the case for replacing precious metal-containing automotive emission control catalysts, but because of lower activity and lack of stability in the severe environment of an automobile exhaust they are only used as promoters.

Examples of the efficient use of catalytic metals and metal oxides will be given in the applications section of this brief review.

## The Structure of Heterogeneous Catalysts

The process of chemisorption of reactants requires adsorption on the surface of the catalyst. Therefore, to maximize the rate, the catalytic surface area should also be maximized. This is achieved by dispersing the catalytic species, as nano size particles, onto a high surface area inorganic carrier. An ideal dispersion of Ni on $Al_2O_3$ is shown in Fig. 6.1.

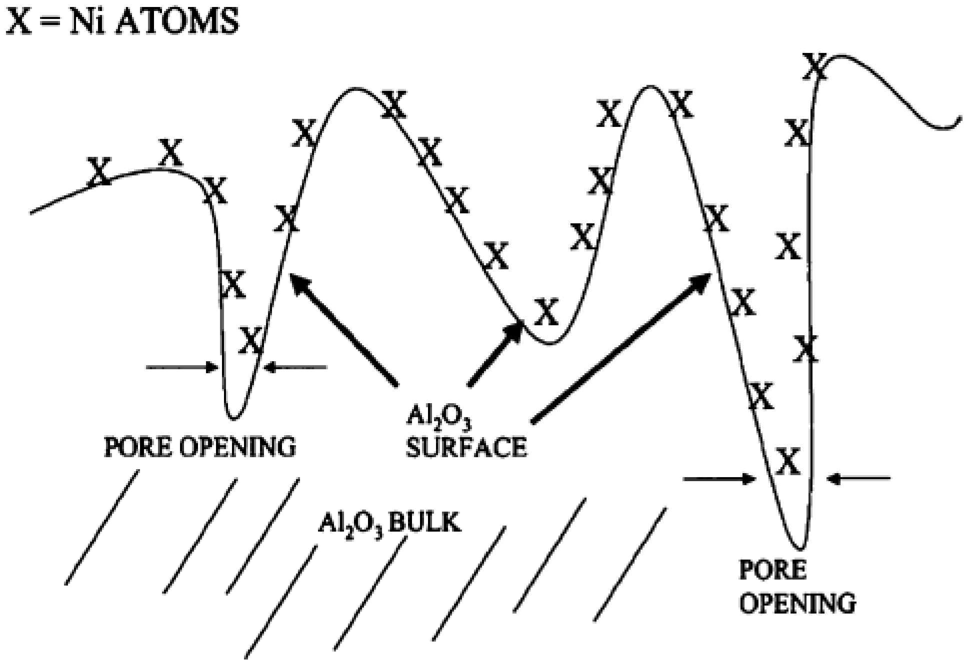


**Fig. 6.1** Ideal dispersion of an active catalyst species on a porous carrier. Example given is Ni on $Al_2O_3$

Ideally every Ni atom should be accessible to the reactants for maximum efficiency in the conversion process. Although this is possible when the catalyst is first prepared, the dynamics of the catalytic reactions lead to some agglomeration or loss of catalytic surface area. Catalyst scientists, however, have developed procedures and stabilizers to minimize the extent of agglomeration and therefore dispersed catalysts can be classified as nanomaterials (nm) with sizes only slightly greater than 1 nm or 10 Å.

The carrier can be thought of as a sponge with pores from 1 to 100 nm (10–1,000 Å) in diameter. Porous inorganic carriers such as $Al_2O_3$, $SiO_2$, $TiO_2$, $CeO_2$, $ZrO_2$, C, and combinations of these materials are commonly used. All have different surface properties and are used in applications dependent on the requirement for acidity, inertness to solubility, interactions with reactants, affinity for catalytically active components, and resistance to components in the gas phase. High surface area $Al_2O_3$ is not well suited for some environmental applications in which $SO_2/SO_3$ are present in la4rge amounts due to the formation of $Al_2(SO_4)_3$ which physically blocks reactant accessibility to the inner catalytic sites dispersed within the carrier. In such cases, high surface area $TiO_2$ and/or $ZrO_2$ are used because of their inertness. Carbons are mostly used for supporting precious metals in hydrogenation reactions. In addition to their chemical role, precious metal recovery is achieved simply by burning the carbon leaving the precious metals for re use.

The most common carrier used in heterogeneous catalysis is gamma alumina ($\gamma$-$Al_2O_3$). It has an internal area of >200–300 $m^2/g$. Its surface is highly hydroxylated (i.e., $Al\text{-}O^{-}H^{+}$). The $H^+$ sites provide acidity required for many reactions and exchange sites for catalytic metal cations.

Zeolites are combinations of $Al_2O_3$ and $SiO_2$ that are crystalline structures with precisely defined pore structures in the molecular size range (0.4–1.5 nm or 4–15 Å). A related group of materials known as mesoporous silica–alumina extend the range of pore sizes attainable in ordered $SiO_2$–$Al_2O_3$ supports to 4 nm (40 Å). Zeolites are commonly used in the chemical and petroleum industry due to their surface acidity and ability to exclude molecules larger than the pore diameter. For this reason, they are often referred to as molecular sieves. Their surfaces contain Al–OH groups with acidic and exchangeable $H^+$. In the application section some of these materials will be more thoroughly discussed.

## Rate-Limiting Steps for a Supported Catalyst

Supporting a catalytic component introduces a physical size constraint dictated by the pore size of the carrier. Thus, a key consideration is the accessibility of the reactants to the active catalytic sites within the high surface area carrier. Consider a hydrogenation reaction in which Ni is located in extremely small pores (i.e., 1 nm or 10 Å). The $H_2$ molecule has easy access, but a large molecule, having a size comparable to the diameter of the pore, would experience great resistance moving towards the active sites. If large amounts of Ni are present in pores and are not accessible to the molecules to be hydrogenated, the reaction rate will not be enhanced to its fullest potential. Thus, the carrier with its geometric size pores and its pore size distribution must be carefully designed to permit the reagents and products to move in the pores with minimum resistance.

Following are the seven fundamental steps in converting a reagent molecule(s) to its product(s) using a supported heterogeneous catalyst.

1. Bulk diffusion of all reactants through a boundary layer of the reaction medium to the outer surface of the catalyzed carrier.

2. Diffusion through the porous network of the carrier to the active sites
3. Chemisorption onto the catalytic sites (or adjacent sites) by one or more of the reactants
4. Conversion and formation of the chemisorbed product
5. Desorption of the products from the active site
6. Diffusion of the products through the porous network to the outer surface of the catalyzed carrier
7. Bulk diffusion of the products to the external fluid medium

Steps 1, 2, 6, and 7 depend on the physical properties of the catalyzed carrier and are not activated processes (no intermediate chemical complex is formed). For this reason, we use the term apparent activation energy which is a term useful for comparing temperature dependence as described later. Steps 3–5 are chemically activated (with intermediate complexes formed during conversion to products) and depend on the chemical nature of the interaction of the reactants and products with the active sites [1–3]. Step 1 is referred to as bulk mass transfer. It describes the transfer of reactants from the bulk fluid to the surface of the catalyzed carrier through a stagnant layer produced by friction of the flowing media at the carrier surface. When this step is rate limiting, reactant molecules arriving at the external surface of the catalyst are converted instantaneously resulting in zero concentration of reactants at the surface. Thus, the internal surface of the catalyst is not used. Since a mass transfer controlled process is non-activated it has little temperature dependence and has an apparent activation energy of less than ~ 2 kcal/mol (~10 Kj/mol). Rates vary only slightly with temperature ($T^{3/2}$) which, as will be shown below, allows it to be distinguished from other rate-limiting steps. Step 7 is similar to Step 1 except that the products diffuse from the external surface of the catalyst particle into the bulk fluid also through the stagnant layer of reaction media at the external carrier surface. The temperature dependence of this phenomenon is relatively weak and has apparent activation energy similar to that observed in Step 1. When only the external surface of the catalyst particle is participating in the catalysis, it is said to have a low effectiveness factor. The effectiveness factor is defined as the actual rate divided by the maximum rate achievable when all catalytically active sites participate in the reaction. In the case of bulk mass transfer being rate limiting, the effectiveness factor approaches zero.

Steps 2 and 6 are pore diffusion processes with apparent activation energies between ~4 and 8 kcal/mol (~16-32 Kj/mol). The concentration of reactants decreases from the outer perimeter towards the center of the catalyst particle for pore diffusion (step 2). In this case some of the interior of the catalyst is being utilized but not fully. Therefore, the effectiveness factor is greater than zero but considerably less than one. These reactions are moderately influenced by temperature, but to a greater extent than bulk mass transfer. This apparent activation energy is stated to be about 1/2 that of the chemical rate activation energy but this varies with the pore size of the carrier and cross sectional area of reactants and/or products.

Steps 3, chemisorption of the reactant(s), 4, chemical reaction forming the adsorbed product, and 5, desorption of the product(s) from the active site(s) are dependent on the chemical nature of the molecule(s) and the nature of their interaction with the active site(s). Activation energies for reactions that are chemical kinetically controlled are greater than 10 kcal/mol (~40 Kj/mol). Chemical kinetic phenomena are controlling when all transport processes are fast relative to the reactions occurring at the surface of the active species so the effectiveness factor is one. All available sites are being utilized and the concentration of reactants and products is uniform throughout the particle. These reaction processes are affected by temperature more than either transport mechanisms. Figure 6.2 shows the conversion vs. temperature and concentration profiles of a reagent (R) for the three regimes of rate control.

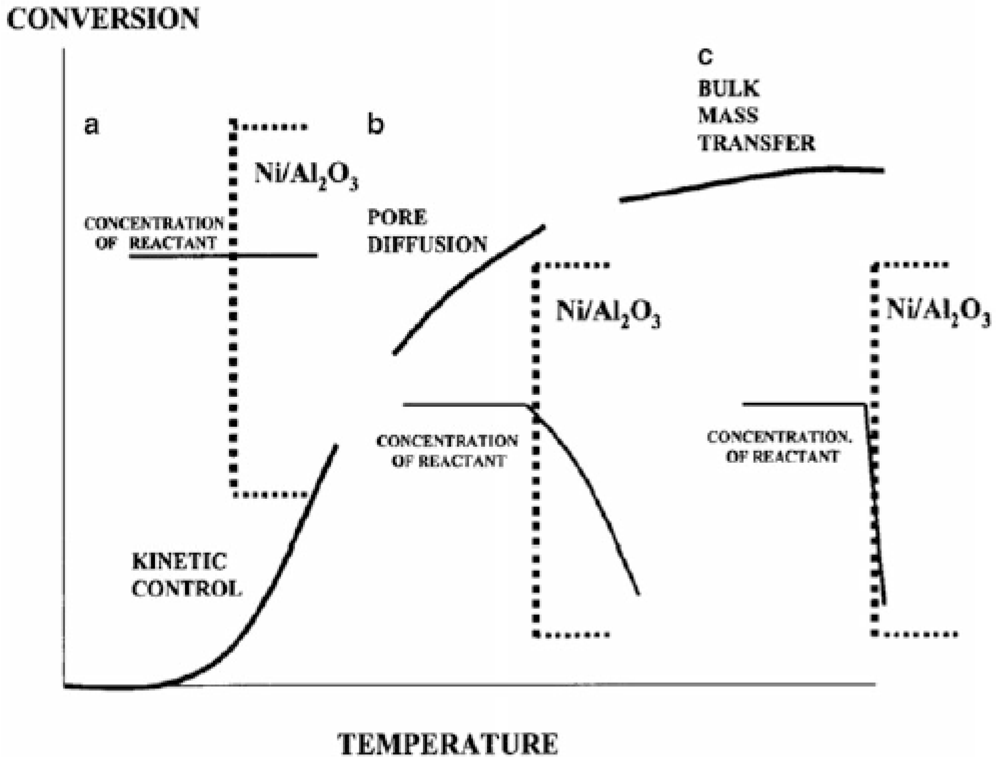


**Fig. 6.2** Conversion of a reactant vs. temperature. The concentration of reactants [*R*] within the porous catalyst structure. Concentration of *R* is (**a**) uniform for kinetic control, (**b**) decreasing within the catalyst for pore diffusion control, and (**c**) zero immediately at the surface of the catalyst for bulk mass transfer

Because of the significant differences in temperature dependence the kinetically limited reactions can be distinguished from pore diffusion which in turn can be differentiated from bulk mass transfer. This is shown in Fig. 6.2 in which conversion of reactants is measured against temperature. The first evidence of conversion is the sharply increasing slope that indicates kinetic control, whereas pore diffusion shows a lower change in slope as the temperature increases. The bulk mass transfer process shows little change in conversion with increasing temperature. Thus, at low temperature the reaction is controlled by chemical reactions (3, 4, or 5) and strongly dependent on temperature. Pore diffusion limited reactions exist when the supply of reactants to the active sites within the particle is limiting the rate (2 or 6) usually at moderate temperatures. Finally, at the highest temperature, chemical reactions and pore diffusion rates are so fast the reaction is considered limited by bulk mass transfer (1-7).

The corresponding concentration of reactant R is also shown for each regime. The concentration of R is constant within the catalyst for kinetically limited reactions. The concentration of reactant gradually decreases within the catalyst particle for the pore diffusion limited case because the rate is limited by transport through the porous network. For bulk mass transfer limited cases, the concentration of R is approximately zero at the gas/solid interface.

*Activation Energies and Rate-Limiting Steps*. The heterogeneous catalyzed $NH_3$ synthesis from $N_2$ and $H_2$ will be used to illustrate the relationship between rate and activation energy. This reaction is catalyzed by moderately high surface area metallic Fe and thus no carrier is needed.

The process steps within the pore structure of the catalyst are

1. Diffusion of $N_2$ and $H_2$ to the active Fe site within the catalyst pore structure
2. Chemisorption of $H_2$ on the active Fe surface
3. Dissociation of chemisorbed $H_2$ to H atoms on the Fe site
4. Chemisorption of $N_2$ on the Fe site
5. Dissociation of $N_2$ to N atoms on the Fe surface
6. Multiple surface reactions between adsorbed N and H atoms forming chemisorbed $NH_3$
7. Desorption of $NH_3$ from the surface
8. Diffusion of the $NH_3$ into the bulk gas

Dissociation of chemisorbed $N_2$ (Step 5) is the slowest and thus is rate limiting.

$$N_2 \text{-----Fe} \rightarrow 2(\text{N----Fe})$$

The rate constant $k$ (and the overall rate of reaction) is related to the activation energy ($E$) by the equation below.

$$k = k_o \exp(-E/RT)$$

Here $R$ = the universal gas constant, $T$ = the absolute temperature and $k_o$ is the pre exponential term related to the activated species during the energy peak transition from the reactants to products. The overall rate of reaction is determined by the slowest of these steps with the overall reaction never faster than the slowest step. The slow step for the rate of ammonia synthesis is characterized by the activation energy for the $N_2$ dissociation reaction on Fe.

An important detail is that an individual rate-limiting step may be endothermic, whereas the overall reaction is exothermic as in this case. This is illustrated in Fig. 6.3. The chemisorption of $N_2$ is exothermic and its dissociation is endothermic (1A). However, the overall reaction of $N_2$ + $H_2$ to $NH_3$ is exothermic (1B). The overall activation energy and kinetics are dictated by the slow step. The reaction heat liberated ($\Delta H_{25}$°C) = −11 kcal/mole (~ 44 Kj/mol) is the thermodynamic value associated with the overall reaction.

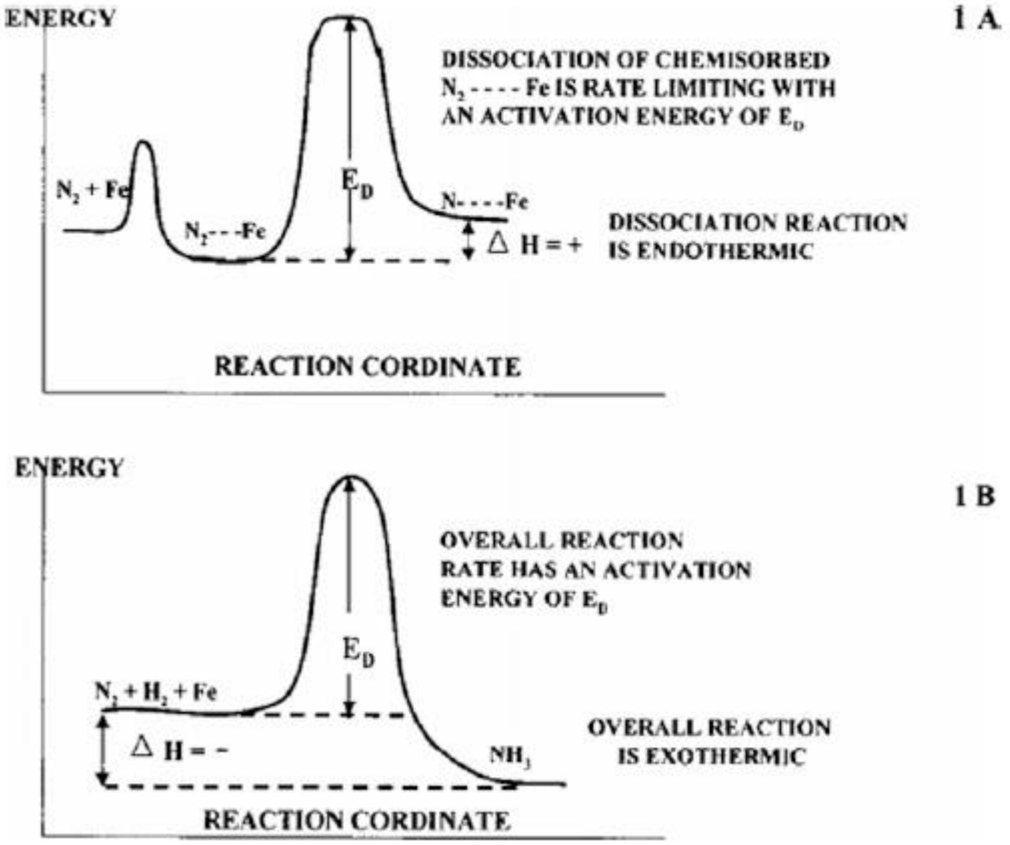


**Fig. 6.3** Activation energy diagram for $NH_3$ synthesis: (1A) chemisorbed $N_2$ dissociation (rate-limiting step); (1B) overall reaction for $NH_3$ synthesis

It is very important to understand that the catalyst only promotes the rate of a reaction and cannot change the equilibrium concentrations of reactants and products. It cannot make a thermodynamically unfavorable reaction occur. It increases the rate at which equilibrium is achieved while always respecting the thermodynamics of the equilibrium constant and the enthalpy ($\Delta H$) and free energy ($\Delta G$) of the overall reaction. Process conditions (*T&P*) are changed to give more favorable thermodynamics and rates.

## Selectivity

In many processes, multiple reaction pathways are possible and it is the role of the optimum catalyst and reaction conditions to maximize the rate along the desired path. Selectivity is defined as the amount of desired product produced divided by reactant converted. A practical example of the catalyst directing reactants to a selective product is shown by the oxidation of ammonia to nitric oxide, which is used in the production of nitric acid and ultimately fertilizers.

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

$$\Delta H^o = -54 \text{ Kcal/mol } (\sim - 220 \text{ Kj/mol}) \text{ of } NH_3$$

The operating temperature of the process is 900°C and both the standard free energy of $\Delta G_{25} = -57.2$ kcal/mol of $NH_3$ (~ -240 Kj/mol) and the equilibrium constant of $K_{NO} = 10^{10}$ are very favorable.

However, the decomposition pathway to $N_2$ is even more thermodynamically favorable with $\Delta G_{25} = -77.9$ kcal/mol of $NH_3$ (~ -320 Kj/mol) and an equilibrium constant of $K_{N2} = 10^{15}$ at 900°C.

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$$

$$\Delta H^o = -75 \text{ Kcal/mol } (\sim -300 \text{ Kj/mol}) \text{ of } NH_3$$

The presence of a PtRh gauze catalyst catalyzes the reactants along the NO pathway with a selectivity of 98%. Therefore, although the free energy is more favorable and the equilibrium constant for the $N_2$ reaction is $10^5$ times greater, the highly selective PtRh catalyst promotes the $NH_3$ oxidation reaction to NO. In contrast, the presence of Pd favors the $N_2$ product. In each case the catalyst respects the equilibrium constant, but directs the reactants to specific products.

A second reaction that is currently receiving a great amount of attention because of low-temperature fuel cells is the purification of traces of CO present in a $H_2$ stream. The fuel cell will be discussed later. Traces of CO exiting the reformer must be removed from the $H_2$ because it poisons the anode of the low-temperature fuel cell. The $H_2$ content of the gas is about 75%, and the CO is about 0.1% (balance is $H_2O$ and $CO_2$). Although both standard state free energies are similar, a highly selective Pt-containing catalyst promotes the oxidation of the CO with minimum oxidation of the $H_2$ purifying the latter for a low-temperature fuel cell.

$$CO + 1/2O_2 \rightarrow CO_2; \quad \Delta G^o = -61 \text{ Kcal/mol } (\sim -250 \text{ Kj/mol})$$

$$H_2 + 1/2O_2 \rightarrow H_2O; \quad \Delta G^o = -57 \text{ Kcal/mol } (\sim -240 \text{ Kj/mol})$$

A small amount of air is injected into the reactor containing an inlet $H_2$/CO ratio of 750. The exit ratio must be 75,000 for fuel cell quality $H_2$. Thus, the free energy for CO oxidation is becoming less favorable (more positive) as CO is reduced below 10 ppm. An effective catalyst [4] currently in use commercially is Pt on $Al_2O_3$ promoted with a small amount of Fe. It operates at an inlet of 90°C and reduces the CO to less than 0.001% with a selectivity of well over 50% depending on management of the exothermic heat of reaction. This is quite remarkable selectivity given the increasingly large excess of $H_2$ as the reaction approaches completion. The same catalyst, but without the Fe, requires 170°C to achieve the same conversion of CO but with a selectivity less than 25%.

## Catalyst Preparation

In the example given above, a small amount of Fe is added to a Pt on $Al_2O_3$ catalyst. The catalyst is prepared by a very unique procedure that must be strictly adhered to in order to achieve the desired results. The Pt and Fe must be in such close proximity that the CO chemisorbs on the Pt and the $O_2$ on the Fe after which they react to form $CO_2$ [4]. Simply reproducing the general composition will not give acceptable performance. The specific details of catalyst preparation may be confidential and are most often covered by patents and trade secrets.

Some general guidelines for supported catalyst preparations are presented below; however, the reader should consult the many references and patents available on the subject [5]. Even by doing so the precise details used by industry to optimize the catalyst will often not be found.

Known amounts of salt(s) of catalytic metals are dissolved in aqueous solutions and impregnated into carrier materials. The wet mass is dried at 110°C and calcined in air at 300–500°C, releasing the decomposable salt components and depositing the metal oxide on the surface within the depths of the porous carrier. For many oxidation reactions, the catalyst is now ready for use, but for hydrogenation it is necessary to reduce the impregnated metal oxide to the active metallic state. Usually this is accomplished by flowing $H_2$, under conditions consistent with the maximum temperature of use for the reaction of interest.

The carrier can be in the form of a powder used for slurry reactions or a particulate such as a sphere, cylinder, or tablet (typically a few mm in diameter) used in fixed bed reactors. The size and shape depend very much on what is anticipated to be the rate-limiting step. For example, for a reaction limited by pore diffusion, it is customary to use a smaller particle in the shape of a star, trilobe, or wagon wheel to decrease the diffusion path while increasing the external geometric surface area.

Mechanical strength and solubility under reaction conditions must be considered in the selection. Although it is often stated that the carrier is inert, there are many cases where this is not the case. Some carriers provide acid or basic sites that act as co-catalysts with the metal or metal oxides performing other functions. Naphtha (petroleum) reforming (discussed later) requires a hydrogenation function, provided by the metal, to dissociate $H_2$ and the carrier provides the acid site to enhance isomerization reactions.

Multi-channel ceramic monoliths (Fig. 6.4) are now the primary choice as support structures to carry the active catalytic species for cleaning emissions from various sources of pollution [6]. Figure 6.4 shows the shapes used for both automotive and stationary pollution abatement applications.

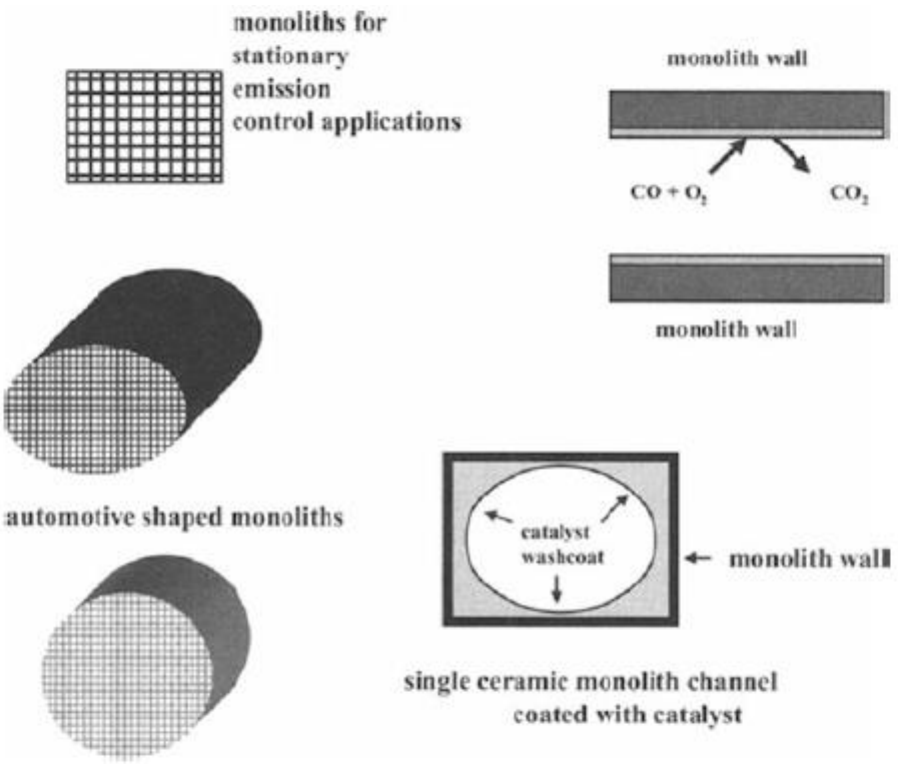


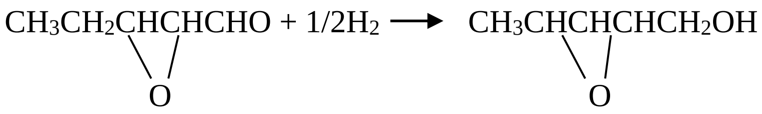
**Fig. 6.4** Typical ceramic monolith geometries used for environmental emission control for vehicle and stationary applications

The largest application for monoliths or structured reactors is the automotive catalytic converter that converts carbon monoxide (CO), hydrocarbons (HC), and nitric oxides ($NO_x$) to nontoxic compounds. The monolith structure offers high cell densities and thus geometric surface area upon which the catalyst is deposited permitting smaller reactor sizes, high mechanical strength, excellent thermal shock resistance, and low-pressure drop [6]. A powdered carrier, usually stabilized $Al_2O_3$, is impregnated with catalyst precursor salts. An aqueous slurry of the impregnated carrier is prepared and milled to some desirable particle size. The monolith is dipped into the slurry and "washcoated" onto the channel walls (see Fig. 6.4). Air is blown through the channels to remove excess slurry. It is then dried and calcined in air at about 500°C. The finished structure now contains the proper amount of catalyst deposited throughout the channel length. The washcoat thickness is greatest at the corners or fillets of the cell due to its sharp angle. The pollutants (or reactants) flow through the channels and catalysis occurs on the washcoated walls. There are many other variations of preparing monolith catalysts with different carriers and compositions. There are monoliths made of metal, some of which have parallel channels and others with nonparallel channels designed for tortuous flow to enhance bulk mass transfer.

### A Heterogeneous Catalytic Reaction: An Example

There is a great desire to use naturally occurring and renewable biomass for producing useful products. Furfural is extracted from cornhusks and contains an aldehyde functional group. If this group is selectively hydrogenated to the corresponding alcohol, the product furfuryl alcohol can be used to make corrosion-resistant resins for preparing polymers to make molds for shaping products. This reaction is selectively carried out with a Cu,

$Cr_2O_3$ catalyst (copper chromite powder) in a slurry phase stirred batch reactor (see “Reactor Types” below) at 3,000 psig and 150°C.



$$CH_3CH_2\underset{\setminus\,O\,/}{CHCH}CHO + 1/2H_2 \longrightarrow CH_3\underset{\setminus\,O\,/}{CHCH}CHCH_2OH$$

Hydrogen gas dissociates when chemisorbed onto the surface of the Cu-containing catalyst producing highly active adsorbed hydrogen atoms. High pressure is needed to ensure adequate solubility of the $H_2$ in the furfural liquid. The $H_2$ is dissociated at an active site within the catalyst. The aldehyde functional group forms a weak bond with other active sites reacts with adsorbed H atoms to the finished product. In the absence of the catalyst, the diatomic hydrogen molecule would have to be dissociated in the gas phase at a much higher temperature leading to the decomposition of the aldehyde group.

### Active Catalytic Sites

Not all catalytic sites are equal. Ideally each catalytic site is an atom or molecule having equal activity. This is never the case for supported heterogeneous catalysts. One of the great mysteries in catalysis is the exact nature of the active site. Some catalytic species may be so well dispersed that they have no defined structure or are amorphous (no long-range structural order), whereas others may be highly crystalline as is the case for zeolites. Amorphous catalytic components have greater catalytic surface area because fewer atoms are buried within a large crystal and are accessible to the reactants. However, the nature of the carrier and the method used to deposit the catalytic component on it gives rise to a very heterogeneous surface with different sites having different sizes, surface energies and hence different activities. For example, it is believed that defects in the crystal structure produce highly energetic and active sites for catalytic reactions. This may be true but the more crystalline the catalytic site, the lower the number of surface atoms and the lower its catalytic surface area. There are reactions that favor certain catalyst crystalline sizes and are said to be structure sensitive. The above discussion points to the mystery of catalysis. The goal of finding a universal model describing the nature of the active catalytic site still eludes us today and will undoubtedly be the subject of fundamental research for years to come. What is remarkable is that industry can utilize catalysts effectively without having a precise knowledge of the catalytic site nor the chemical mechanism of the reaction.

### Reactor Types

There are many different reactor designs, but the two most commonly used for heterogeneous reactions are fixed bed and batch slurry phase. For a fixed bed reactor, a given volume of solid particulate or monolith supported catalyst is fixed in a reactor located within a furnace and liquid and/or gaseous reactants flow through the bed. This type of process is commonly used for large scale continuous-volume production where the reactor is dedicated to making only one product such as a bulk chemical or petroleum product.

Monolithic reactors are also classified as fixed bed and are almost exclusively used for environmental applications. They will be discussed in more detail later [6].

Batch reactors are used mostly for small-scale production such as the hydrogenation of intermediates in the production of medicines in the pharmaceutical industry. The catalyst powder is mixed in a precise amount of reactant in a pressurized-stirred autoclave. A gaseous reactant, usually $H_2$, is introduced at elevated pressures and the reaction proceeds with continuous monitoring of the $H_2$ consumed. The catalyst is separated from the product via filtration and is often used again depending on its retained activity and selectivity.

For the production of gasoline and other fuels by catalytic cracking of oils, a fluid bed reactor is used. This is a hybrid of a fixed bed and slurry phase reactor. The catalyst is fluidized as it interacts with the feed to be processed. This application is so important that it will be highlighted in the application section of this review.

## Kinetics

The overall kinetics of a heterogeneous catalytic reaction can be controlled by any of the seven steps listed above [7–10]. We can distinguish that which rate is controlling by determining the temperature dependence of the reaction. Once we know this we can design the catalyst to enhance the rate of the slowest step.

For example, bulk mass transfer (Steps 1 and 7) can be enhanced by increasing the turbulence of the reactants by increased stirring for a batch process. Increasing the geometric surface area of the catalyst also favors a reaction limited by bulk mass transfer. This is accomplished by decreasing the particle size of a particulate or by increasing the number of channels in a monolithic structure. Turbulence can be introduced in a monolith channel by modifying the surface from smooth to rough and/or for any type of particle by increasing the linear velocity of the reactants (see below). Because kinetically controlled reactions have larger temperature dependence than transport controlled reactions, they are affected the most by increasing temperature. Pore diffusion resistance is decreased by increasing the pore size of the carrier or by using a smaller diameter carrier. One may also deposit the active catalytic species nearer the surface of the carrier to decrease the diffusion path length. The rate of a reaction limited by pore diffusion is moderately enhanced with temperature.

For chemically controlled reactions, one must modify the catalyst itself by increasing the number of active sites (increasing the catalytic surface area) or finding a crystal size that is more active for a given reaction. Often the activity is increased by the addition of promoters to the catalyst (i.e., Fe addition to Pt described under “Selectivity”) that enhance the activity. Having the highest activation energy, it is affected more than the transport regimes by increasing the temperature. Many examples of this will be given in the example section of this chapter.

*General Kinetic Rate Equations.* The rate of a bi-molecular reaction is given by

For the general reaction

$$A + B \rightarrow C + D$$

$$\text{Rate} = -\,d[A]/dt = k_F\,[A]^a\,[B]^b\;-\;k_{REV}\,[C]^c\,[D]^d$$

Rate is defined here as the disappearance of a particular reactant i.e. $[A]$ expressed as the derivative $-d[A]/d(t)$ with reactant $[B]$ and $[C]$ and $[D]$ the concentration of the products. The exponents $a$, $b$, $c$, and d are the reaction orders for each compound. The rate constants are $k_F$ for the forward and $k_{REV}$ for the reverse reaction. For those cases where the reaction is far away from equilibrium, the reverse rate is negligible and this term is dropped from the rate expression.

To determine the rate constant and the reaction order at a specific temperature, it is often convenient to increase the concentration of one reactant at least 20 times that of the other to maintain it relatively constant during the reaction. Thus, with a high concentration of reactant $B$ one my write $k_F\ [B]^b = k_F^*$

$$\text{Rate} = d[A]/\text{d}t = -\ k_F^*(A)^a$$

If the reaction order is to be determined, one may take the natural log of the rate equation and obtain

$$\text{Ln(Rate)} = -\ \ln(d[A]/\text{d}t) = \ln k_F^* + a\ln[A]$$

A plot of the Rate (-ln($d[A]/dt$) vs. ln[$A$] will produce a straight line with a slope equal to $a$ and intercept ln $k_{F.}^*$

If one assumes $a = 1$ (first order reaction) and integrates the rate expression from the initial concentration $A_o$ to $A$ at anytime and from $t = 0$ to $t$

$$\ln([A_o]/[A]) = k_F^* t$$

$$[A] = [A_o - xA_o] \quad \text{where } x \text{ is the fraction converted}$$

Plotting ln $[1/(1-x)]$ vs. $t$ will give a straight line with a slope equal to $k_{F.}^*$

The activation energy for a general reaction can be estimated experimentally by varying the temperature while operating at low reactant conversions ($A$ and $B$ conversions < ~ 5%). Since both [A] and [B] are essentially constant they will not significantly influence the rate of reaction.

$$\text{Ln (Rate)} = \text{Ln } k_F + \text{CONSTANT}$$

$$\text{Since } k_F = k_o \exp(-E/RT)$$

$$\text{Ln (Rate)} = \text{Ln } k_F - (E/R)\ (1/T)$$

The variation of the Ln (Rate) with the inverse of absolute temperature gives a slope equal to $-E/R$. This allows one to access the rate limited step in the reaction by knowing the approximate activation energy.

*Kinetics for Fixed Bed Continuous Reactions*. For continuous flow reactors, we use the term space velocity (*SV*) defined as the volumetric flow rate at *STP* divided by the volume of catalyst. That ratio yields the reciprocal of the residence or space-time ($t$)

$$\text{SV(h}^{-1}) = \frac{\text{flow rate cm}^3/\text{h(STP)}}{\text{catalyst volume(cm}^3)}$$

$$\frac{1}{\text{SV}} = \text{residence time or space-time}$$

For the reaction $A + B$ going to products far from equilibrium, the rate equation for continuous flow reactions is

$$\ln([A_o]/[A]) = k_F^*t = k_F^*/\mathrm{SV}$$

Here we have assumed reactant [*B*] is in large excess of [*A*] that only the latter significantly affects the rate. Thus the term $k_F^* = k_F[B]$. Monitoring changes in [*A*] at various space velocities (SV) at a specific temperature with give a rate constant.

The linear velocity (*LV*) or superficial velocity is an important engineering term because it relates to pressure drop and turbulence. This parameter is often increased in fixed bed reactors to enhance bulk mass and heat transfer.

$$\mathrm{LV(cm/h)} = \frac{\text{flow rate cm}^3\text{/h(STP)}}{\text{frontal area of catalyst(cm}^2)}$$

*Kinetics of a Slurry Phase Reaction in a Batch Process*. The example below for the hydrogenation of nitrobenzene to aniline is carried out in the liquid phase using a powdered e.g. $Pd/Al_2O_3$ catalyst. These reactions typically are controlled by the supply of $H_2$ to the active sites.

$$3H_2 + C_6H_5NO_2 \longrightarrow C_6H_5NH_2 + 2H_2O$$

1. $H_2$ must be transported from the bulk gas phase and dissolved in the liquid nitrobenzene
2. Dissolved H2 must diffuse to the outside of the catalyst particle and into the interior of the catalyst
3. $H_2$ and nitrobenzene will react at the catalytic sites to form the product aniline and $H_2O$.
4. The aniline diffuses through the pores and into the bulk liquid

Steps 1, 2, and 4 are mass transfer phenomena while step 3 is kinetic. Steps 1 (related to $k_M$) and 3 (related to $k_R$) are usually rate limiting while 2 and 4 occur rapidly due to the small catalyst particle and adequate mixing. At steady state the rate of mass transfer of reactants $(Rate)_M$ is equal to the kinetic rate $(\mathrm{Rate})_R$.

$$(\mathrm{Rate})_{\mathrm{net}} = (\mathrm{Rate})_{\mathrm{MT}} = (\mathrm{Rate})_{\mathrm{R}}$$

$$(\mathrm{Rate})_{\mathrm{MT}} = k_{\mathrm{m}}(\mathrm{H}_{2g} - \mathrm{H}_{2s})/\mathrm{H}_{2g}$$

$$= 1 - (\mathrm{H}_{2s}/\mathrm{H}_{2g})$$

where $H_2g$ = $H_2$ concentration in the gas
$H_2s$ = $H_2$ concentration at catalyst surface
$k_m$ = Mass transfer rate constant

$$(\mathrm{Rate})_{\mathrm{R}} = k_{\mathrm{R}}(\mathrm{H}_{2s}Q)/H_{2g}$$

where $k_R$ = kinetic rate constant
$Q$ = the amount of catalyst

Equating $(\mathrm{Rate})_M$ and $(\mathrm{Rate})_R$ and rearranging one obtains

$$(\mathrm{Rate})_{\mathrm{net}} = \frac{k_{\mathrm{R}}k_{\mathrm{m}}Q}{k_{\mathrm{R}}Q + k_{\mathrm{m}}}$$

Plotting rate vs $Q$ yields Figure 6.5 A.

Taking the inverse for the general rate equation and dividing both sides by $k_R$ $k_m$ $Q$, one obtains

$$(\text{Rate})_{\text{net}}^{-1} = k_M^{-1} + (k_R Q)^{-1}$$

Figure 6.5 B is a plot of the inverse $(\text{Rate})_{\text{net}}$ vs. the inverse of $Q$ yielding a straight line with the slope equal to the inverse of $k_R$ and the intercept the inverse of $k_m$.

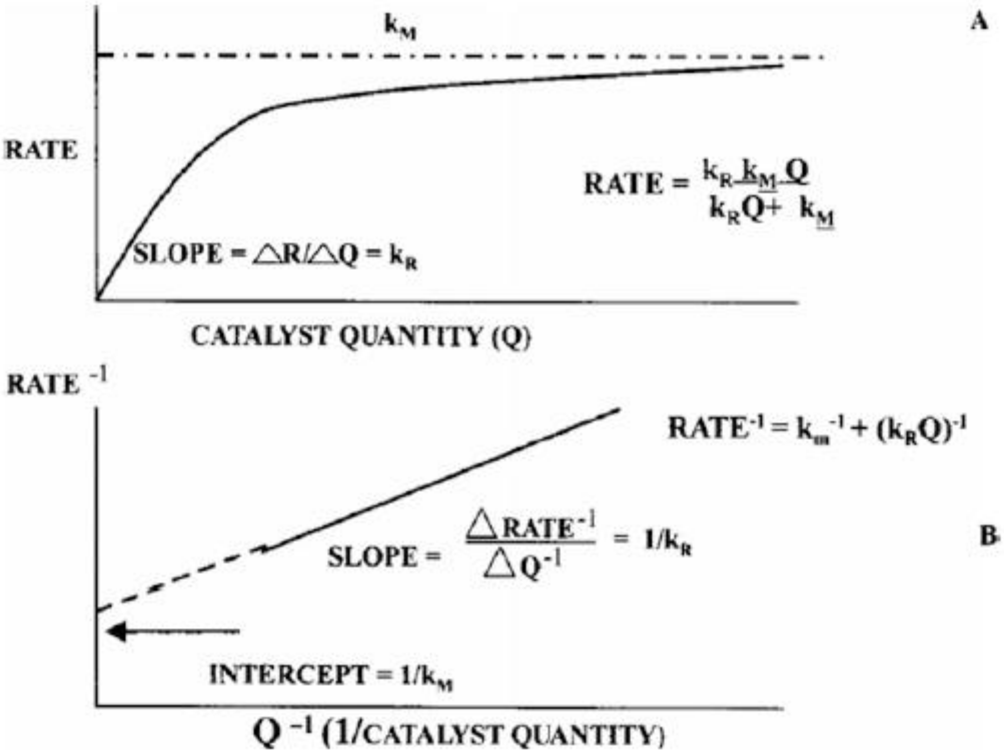


**Fig. 6.5** Kinetics for slurry phase/batch reaction: (**a**) rate vs. quantity of catalyst; (**b**) line plot of the rate expression

When the amount of catalyst $Q$ is large

$$(\text{Rate})_{\text{net}} = k_m$$

The rate is limited by mass transfer because the reactants are consumed immediately at the outer surface of the catalyst. For small amounts of catalysts

$$(\text{Rate})_{\text{net}} = k_R Q$$

The reaction is kinetically controlled limited by the amount of catalyst.

*Arrhenius Equation*. The general rate constant ($k$) is an exponential function of temperature as described by the Arrhenius equation (previously described).

$$k = k_o \exp^{(-E/RT)}$$

Taking the natural log of the equation gives

$$\ln(k) = \ln(k_o) - E/RT$$

The plot of ln ($k$) vs. $T^{-1}$ gives a straight line with a slope equal to $-E/R$ and intercept the absolute rate constant $k_o$ as shown in Fig. 6.6. The lowest slope represents reactions controlled by bulk mass transfer, and the largest for chemical or kinetic control. This method allows for the comparison of different rate-limiting steps, but it must be clearly understood that diffusion processes are not activated and thus we use the term apparent activation energy for them only to allow comparisons to activated processes such as chemically controlled processes.

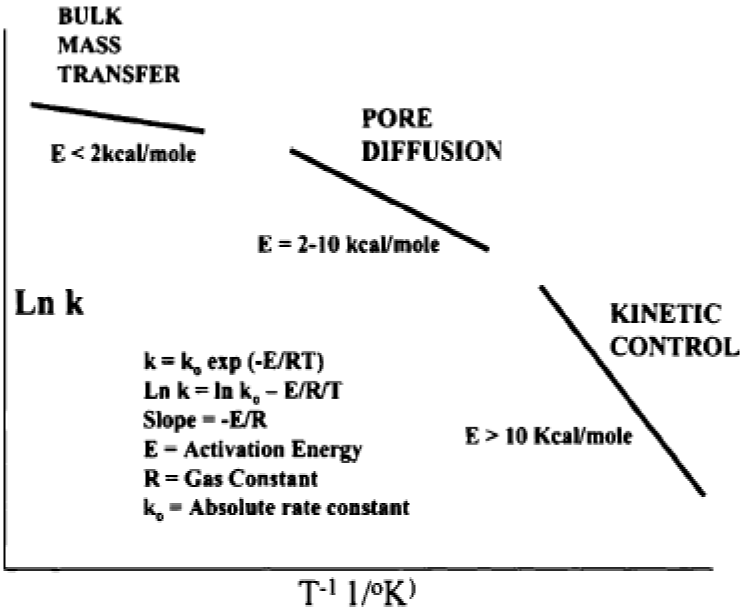


**Fig. 6.6** Arrhenius profile for three regimes of rate control with activation energies ($E$)

## Rate Models

The Langmuir-Hinshelwood kinetic model describes a reaction in which the rate-limiting step is reaction between two adsorbed species such as chemisorbed CO and O reacting to form $CO_2$ over a Pt catalyst. The Mars-van Krevelen model for an oxidation reaction is a mechanism in a reactant reduces an active site and an O from the carrier or another component in the catalyst re-oxidizes the active site. The oxygen deficiency is then satisfied by gas phase $O_2$. The dehydrogenation of ethyl benzene to styrene over $Fe_2O_3$ is another example of this model. Ethyl benzene reduces the $Fe^{+3}$ to $Fe^{+2}$, whereas the steam present re-oxidizes it, completing the oxidation-reduction (redox) cycle. This mechanism is prevalent for many reducible base metal oxide catalysts. There is also an Eley-Rideal mechanism where the chemisorbed species reacts with a gas phase molecule and the combination rapidly converts to the final product. There are many kinetic models that describe different mechanisms and the reader is directed to some outside references [7–10].

## Catalyst Deactivation

We have stated that the catalyst is not consumed while it enhances the rate of the desired reaction. This definition is applicable for an ideal process but the catalyst life can be influenced by the environment in which it is operating. This most often leads to catalyst deactivation due to a number of process conditions that can reduce its effectiveness. It is a goal of the catalytic scientist and engineer to sustain its life by identifying the major sources of deactivation and addressing them by modifying the catalyst or the process conditions.

The first indication of catalyst deactivation is a significant change in the activity/selectivity of the process. Catalyst deactivation occurs in all processes, but it often can be controlled if its causes are understood. This subject is very extensive and the reader is encouraged to seek additional information in references given here [11, 12]. In the following we will present some of the most common deactivation modes especially for heterogeneous catalysts. These are pictorially shown in cartoon form in Fig. 6.7.

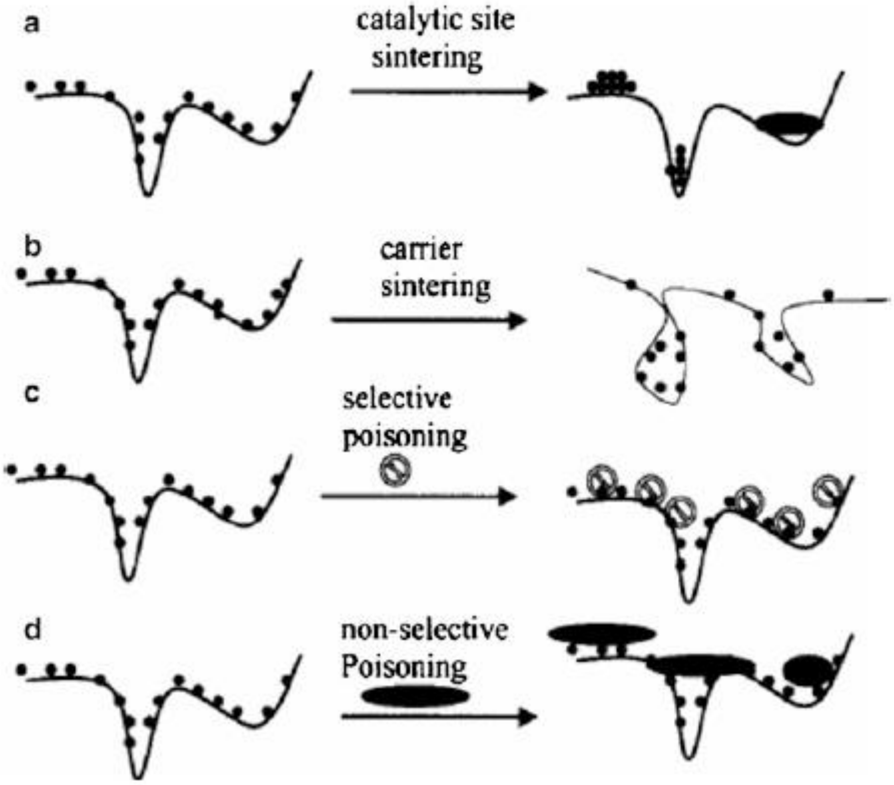


**Fig. 6.7** Idealized poisoning mechanism: (**a**) sintering of the catalytic components, (**b**) sintering of the carrier, (**c**) selective poisoning, and (**d**) nonselective poisoning

*Sintering of the Active Components*. Catalytic scientists and engineers go to great lengths to disperse the active catalytic species over the surface of a carrier to maximize the number of sites available to the reactants. Small particles or crystallites have a high surface-to-volume ratio that is a highly unstable thermodynamic condition. The simple principle of Ostwald ripening indicates that small crystallites tend to grow to larger ones to bring the surface to volume condition to a favorable low free energy state. This is depicted in Figure 6.7a in cartoon form. Thermal sintering occurs when small particles of active catalyst migrate over the surface of the carrier and agglomerate to form larger particles. There are other mechanisms of sintering, but conceptually this is the easiest to understand. The net effect is the loss of catalytic surface area that leads to loss of activity. The most frequently encountered cause is high temperature. This condition is encountered in Pt-, Pd-, and Rh-containing catalytic converters present in automobile exhausts where temperatures above to 1,000°C are commonly experienced. An oxidizing environment promotes the sintering of Pt by the formation of highly mobile or volatile Pt oxides. PdO, on the other hand, forms a bond with the $Al_2O_3$ surface and thus sintering is not significant at temperatures below about 800oC. Above this temperature the oxide decomposes to the metallic or reduced state and Pd readily sinters. Naturally it also sinters in a reducing environment as is the case in hydrogenation reactions. A catalytic species strongly bound to the surface (i.e. Al-OH) is less likely to sinter. For this reason, a carrier such as $SiO_2$, which contains few OH groups on the surface relative to $Al_2O_3$, leads to sintering of the supported metal or metal oxide more readily. Catalyst companies have incorporated “rare earth stabilizers” into the formulations to minimize the rate of growth of the metal and metal oxide components. Stabilizers slow the rate of sintering, but do not completely prevent it due to the thermodynamic nature of the phenomenon. The goal is to minimize the rate to ensure acceptable life of the catalyst.

*Carrier Sintering*. The purpose of the carrier is to provide a high surface area upon which the catalytic components can be dispersed. The high surface area leads to sintering by collapse of the pore structure that subsequently blocks (or occludes) the active sites by preventing access of the reactant. A cartoon depiction of this phenomenon is shown in Figure 6.7b. For some carriers such as $Al_2O_3$, there are changes to the crystal structure that occur as its exposure temperature is increased. The most common is the conversion of high surface area (gamma) $\gamma$-$Al_2O_3$ (200 $m^2/g$) to low area (alpha) $\alpha$-$Al_2O_3$ (1–5 $m^2/g$) at temperatures greater than about 1000°C. This process occludes the catalytic components within the carrier and prevents the reactants from having access to them. High temperatures and steam are two of the most significant contributors to carrier sintering. Catalyst companies have incorporated metal oxides, such as Ba and La in precise percentages, into the carrier to minimize the sintering rate.

*Poisoning*. Specific components present in the reactant feed can adsorb selectively onto active catalytic sites rendering them inactive as shown in Figure 6.7c. For heterogeneous catalysts, sulfur compounds are the most universal poisons for both base metal catalysts and to a lesser extent precious metals. Sulfur compounds present in petroleum, chemical, and environmental streams adsorb on the surface of Ni, Cu, Co, etc. forming metal sulfides that have little activity. In general, poisoning by sulfur compounds is irreversible but can be reversed at high temperature however this may introduce additional sintering. For this reason upstream filtration processes are used to reduce the sulfur to acceptable levels to preserve the life of the catalyst.

Sulfur oxides ($SO_2$ and $SO_3$) present in flue gases from upstream combustion operations adsorb onto the catalyst surface and in many cases form inactive metal sulfates. It is the presence of sulfur compounds in petroleum-based fuels that prevent the super-sensitive base metal oxide and metallic catalysts (i.e., Cu, Ni, Co, etc.) from being used as the primary catalytic components for many environmental applications. Precious metals are inhibited by sulfur and lose some activity, but usually reach a lower steady-state activity. Furthermore, the precious metals are reversibly poisoned by sulfur compounds and can be regenerated simply by removing the poison from the gas stream or raising the temperature. Heavy metals such as Pb, Hg, As, etc. alloy with precious metals and permanently deactivate them. Basic compounds such as $NH_3$ can deactivate an acidic catalyst such as an $Al_2O_3$ or zeolite by adsorbing and neutralizing the acid sites but again this poison can be desorbed at elevated temperatures. Water is a reversible poison in that it will weakly adsorb (physically adsorb) on sites at low temperature, but readily desorbs as the temperature is increased.

One interesting example of different selective poisoning mechanisms is that of $SO_3$ deactivation of Pt on $Al_2O_3$ used for abating emissions from combustion reactions. The Pt oxidizes the $SO_2$ to $SO_3$ and the latter adsorbs onto the $Al_2O_3$ forming a sulfate. Slowly the carrier surface becomes so sulfated that it occludes the Pt within the pores and the catalyst slowly deactivates. By using a non-sulfating carrier such as $TiO_2$ or $ZrO_2$, deactivation can be prevented. In contrast, $SO_3$ directly adsorbs selectively on Pd sites and deactivation occurs rapidly.

There are processes where a catalyst is intentionally poisoned to decrease activity towards an undesirable reaction. In the hydro-desulfurization and de-metallization of a petroleum feedstock, the catalyst is pre-sulfided prior to introducing the feed to decrease its activity and minimize cracking reactions that will produce unwanted gases. Another is the use of ammonia to slightly poison a Pt catalyst used in the hydrogenation of fats and oils to decrease undesirable oversaturation of the double bonds.

Nonselective poisoning or masking is caused by debris depositing on the surface of the catalyst physically blocking sites (Figure 6.7d). Corrosion products from the reactor walls and contaminants such as dust, oil, etc. can be eliminated by careful filtration upstream, but this mechanism of deactivation is a constant problem in many applications. Regeneration is possible for precious metal oxidation catalysts designed to abate volatile organic compounds (VOC) from flue gases. The reactor is bypassed when the activity begins to decline to unacceptable levels. High-velocity air is passed through the catalyst bed and loosely held debris is dislodged. Chelating solutions are sometimes used to selectively solubilize the metal contaminants such as oxides of Fe without destroying the catalyst. Coking is a common phenomenon when petroleum and/or high molecular weight chemical compounds are processed. Hydrogen-deficient-hydrocarbons are formed from undesirable side reactions and block access to the catalytic sites deep within the pores of the catalyst. This deactivation mode has been positively integrated into the fluid catalytic cracking process for converting heavy oils to useful products. The coked catalyst is continuously recycled from the catalytic reactor to a regenerator where a small amount of air is injected to oxidize the coke. The heat liberated is used to preheat the feed as it enters the catalytic cracking reactor.

## Catalyst Characterization

The goal of catalyst characterization is to relate the physical and/or chemical properties of the catalyst to performance. Some of the most important catalytic properties are physical surface area, pore size distribution, active catalytic surface area, the morphology or crystal structure of the carrier and active components, the location of the active components within the carrier, and the presence of contaminants or poisons on the surface. Fortunately, there are many instrumental tools readily available in modern laboratories to measure these properties for both fresh and spent (deactivated) catalysts. There are many reference books and monographs available that describe the strengths and limitations of the instrumental methods used in characterizing catalysts [13, 14].

The chemical composition can be measured by traditional wet and instrumental methods of analysis. Physical surface area is measured using the $N_2$ adsorption method at liquid nitrogen temperature (BET method). Pore size is measured by Hg porsimetry for pores with diameters larger than about 3.0 nm (30 Å) or for smaller pores by $N_2$ adsorption/desorption. Active catalytic surface area is measured by selective chemisorption techniques or by X-ray diffraction (XRD) line broadening. The morphology and structure of the carrier is viewed by electron microscopy and XRD, respectively. The active catalytic component crystal size can also be measured by XRD, but there are certain limitations once its size is smaller than about 3.5 nm (35 Å). For small crystallites, transmission electron microscopy (TEM) is most often used. The location of active components or poisons within the catalyst is determined by electron microprobe. Surface contamination is observed directly by X-ray photoelectron spectroscopy (XPS).

Making the characterization measurements is of critical importance in the diagnostics of the catalysts, but interpreting those most responsible for changes in activity or selectivity requires experience and good comparative kinetics for fresh and aged materials. It should be standard practice to compare fresh and aged catalytic performance with the changes observed in your characterization diagnostics. Measuring rate-limiting steps and activation energies will provide invaluable insight into the major causes of deactivation.

## Homogeneous Catalytic Reactions

In a homogenous catalytic reaction, the reactants and catalysts are in the same phase, usually liquid. The catalyst is a metal (Rh, Co, Ni, etc.) chelated with both inorganic or organic ligands (often phosphine-containing) soluble in the reaction media, and because no carrier is used to support the catalyst, pore diffusion does not occur. However, bulk mass transfer is a concern especially when for hydrogenation reactions where gaseous $H_2$ must be first dissolve in the liquid and make contact with the reactant (s) at the catalyst site. This is accomplished by using high pressure and vigorous stirring. The kinetics of these reactions was described earlier. Homogeneous catalysis is most often used in the pharmaceutical industry where the desired selectivity can only be achieved with active complexes. A significant issue is separation of the catalyst from the final product to achieve the required purity. Furthermore, recovery of the catalyst is most often necessary especially for expensive precious metal containing complexes such as Rh. Distillation is sometimes used, provided there is a significant difference in vapor pressure of the product and catalyst. The catalyst is also recovered by ion exchange with a suitable sequestering agent such as amine compounds. The efficiency of the separation allows for catalyst reuse and is essential for an economic process. An example will be given in “Commercial Applications.”

## Commercial Applications

There are literally hundreds of commercial catalytic processes carried out for high and low volume premium products. Only a few have been selected below as examples of everyday products. Table 6.1 presents a short listing of some of the major catalytic processes however the reader is directed to a more complete description [10].

## Petroleum Processing

*Hydro-Demetallization (HDM) and -Desulfurization (HDS) of Heavy Oils*. Crude oils are composed of a variety of hydrocarbons fractions with varying boiling ranges as well as inorganic compounds that require removal in order to produce high quality products. The hydrocarbon fractions are separated by distillation where the molecules are separated in accordance to their boiling ranges. The inorganic impurities, most often concentrated in large molecular weight organometallic molecules such as nickel, vanadium, and sulfur-containing compounds, must be removed to make high-suitable products both functionally and environmentally. The high-boiling fractions (higher molecular weight) contain the highest concentration of metals and sulfur [15, 16]. Metals, if present in gasoline or diesel, will create significant engine wear and sulfur would produce sulfur oxides during combustion and ultimately sulfuric acid in the atmosphere. Furthermore, they will deactivate the catalysts used in the petroleum upgrading processes and in their ultimate application as a fuel will damage the performance of the abatement catalyst.

Crude oil contains about 0.01% metals and up to 5% sulfur present in large aromatic structures. These levels are highly dependent on the origin of the crude. For example, California crude is relatively low in sulfur but higher in metals than crude from Kuwait. Any process to remove them must be economical with little destruction of the hydrocarbons and minimum consumption of $H_2$. The catalyst is Co, Mo/$Al_2O_3$ with particles a few mm in diameter. Although sulfur is usually a poison for catalytic reactions, it is used here to control selectivity. It is pre-sulfided (S-Co, Mo/$Al_2O_3$) to decrease initial activity towards excessive consumption of $H_2$ that leads to unwanted saturation of aromatic molecules. Some generalized hydro-demetalization and desulfation reactions are shown below. R = an organic host molecule and M = (Ni and/or V)

$$\text{R-M} + H_2 \rightarrow \text{M} + \text{R-H}$$
$$\text{R-S} + H_2 \rightarrow H_2S + \text{R-H}$$

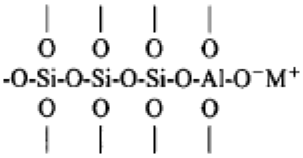
Metals deposit and accumulate within the catalyst pore structure for the hydro-demetalization while $H_2S$ gas is formed during hydro-desulfurization and removed by adsorption downstream.

The de-metallization hydrogenation process is carried out at ~ 500°C and pressures in excess of 30 atm. in fixed bed reactors containing a series of catalysts with varying physical properties to accommodate the metal deposition that occurs during the reaction. In some systems moving bed reactors are used where spent catalyst is continuously removed and fresh catalyst added. The first reactor contains the Co, Mo deposited on a low surface area $Al_2O_3$ with large pores to allow deep penetration of the metals into the particle. The second bed (also with Co, Mo catalytic components) will treat a feed with less Ni and/or V so the $Al_2O_3$ pore size is smaller and surface area slightly larger to enhance activity. The metal penetration here is less deep than in the first bed and allows for some hydro-desulfurization. The final bed contains Co, Mo supported on an $Al_2O_3$ with high surface area and small pores designed to perform primarily hydro-desulfurization.

The catalyst is regenerated from coke accumulation frequently during its useful life, but once spent it is leached and the metals recovered for other uses.

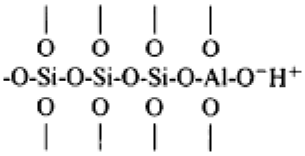
*Crude oil and Catalytic Cracking for the Production of Useful Fuels*. The composition and molecular weight distribution of the crude oil depends on its origin, but generally less than 50% is within the molecular and boiling range for transportation and heating fuels. Gasoline and diesel fuel, home and commercial heating oil, kerosene, jet fuel, etc. are all produced by catalytically cracking the larger molecular weight fractions into smaller sizes and low boiling ranges. The crude oil is distilled in large vertical towers where the various fractions present are separated according to their boiling ranges. The light gases (C1- $C_4$ ) are distilled first at ~ 50°C while the light/heavy naphtha fraction ($C_5$ to $C_{10}$), the precursors to gasoline, are distilled between roughly 70 and 200°C. The precursors to diesel fuel and heating oils ($C_{10}$-$C_{18}$) are collected between 200 and 340°C. The higher molecular weight hydrocarbons (classified as > $C_{20}$) are mostly catalytically cracked to lower molecular weight ranges to be used for the more useful products. The very heavy hydrocarbons ($C_{40}$) are high boiling (called vacuum distillates) and are used for lubricants and road pavement. Therefore, the catalyst may be thought of as the heart of the refining industry.

*Cracking Catalysts*. The catalysts used for cracking are called zeolites [17, 18]. They are $SiO_2$–$Al_2O_3$ materials in which Si, in its tetrahedral $SiO_2$ structure, is replaced with Al cations. They are produced by reacting sodium silicate with a water-soluble salt of Al followed by hydrothermal treatment sometimes in an autoclave. The zeolite is unique in that it has a well-defined crystal structure with a precise pore size (or aperture) ranging typically from 0.3–4 nm or 3–40 Å. This unique pore structure is responsible for separating gaseous molecules in accordance with their cross-sectional area. A molecule, larger than the aperture, cannot enter the interior of the zeolite. Hence, the term molecular sieve is used to describe zeolites used extensively for separating gaseous molecules. The aperature or pore size can be varied giving rise to a large number of different zeolites with different crystal structures. They are usually identified by the Si/Al ratio, the crystal structure, and the size and shape of the pore. The $Si^{+4}$ is bonded to $4O^{-2}$ and each is bonded to another $Si^{+4}$ establishing charge neutrality. Substituting $Al^{+3}$ for Si cation causes an imbalance in charge neutrality and requires another positive charge to satisfy the oxygen ion charge.



$$-O-Si-O-Si-O-Si-O-Al-O^{-}M^{+}$$

Neutrality is satisfied by a positive charged species such as a $H^{+}$ or $M^{+}$, such as $Na^{+}$ derived from the salts used in the synthesis. When the cation is a proton, an acid site is created. This is the key active site for catalytic cracking. The first exchange of the Na+ is with $NH_4{}^{+}$ which when heat-treated decomposes to $NH_3$ with the $H^{+}$ retained on the zeolite. The acid zeolite is designated HZ.



$$-O-Si-O-Si-O-Si-O-Al-O^{-}H^{+}$$

The active zeolite for cracking reactions is called Faujasite and is classified as an X zeolite (HX). It has a has a Si/Al ratio of 1.0–1.5 with a pore size of 0.74 nm or 7.4 Å forming an aperture composed of 12 oxygen anions as shown in Fig. 6.8. The midpoint of each line represents an $O^{-2}$ bonded to either $Si^{+4}$ or $Al^{+3}$. It is the $AlO^{-}$ site that requires a cation for charge balance. For cracking catalysts these sites are $H^{+}$. The higher the Al content (lower Si/Al), the greater the number of acid sites, but the lower the thermal stability. Y-zeolites are also used and characterized by a Si/Al or 2-5 which increases zeolite structure stability important during the exothermic coke regeneration process. The zeolite is embedded within an amorphous $SiO_2$–$Al_2O_3$ matrix structure that initiates the cracking of the large molecules, but also contains additives that capture impurities such as organic compounds containing Ni and V that will severely deactivate the zeolite. The matric has its own acid sites and therefore functions to break large molecules into smaller sizes where the zeolite can polish them to desired products. Catalyst particle sizes vary between 50 and 100 μm depending on the fluidization dynamics of the process.

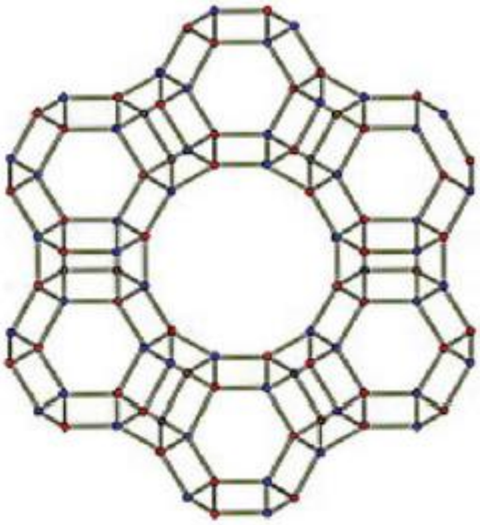


**Fig. 6.8** Faujasite zeolite

During the fluidized catalytic cracking (FCC) process, a C–C bond is broken and a proton transferred from the catalyst to the molecule forming a positively charged carbocation. This ion can react with other hydrocarbons transferring its proton generating new carbo cations. Ultimately the large molecule is cracked to a smaller alkane and alkene with the regeneration of the protonated zeolite completing the catalytic cycle. A cracking and de-alkylation reaction are shown below. Note that olefins are formed in both reactions

Paraffin cracking: $C_{26}H54 \longrightarrow C_{13}H_{28} + C_{13}H_{26}$
Dealkylation: $C_2H_5\text{-}C_6H_5 \longrightarrow C_6H_6 + CH_2{=}CH_2$

The reactions above can be intermediates where additional H is lost from the structure leading to formation of hydrogen-deficient, high-boiling compounds called coke. Coking reactions are catalyzed by acid. The coke masks the surface and blocks the pores of the catalyst preventing access of the feed molecules and thus a loss in activity.

Cracking is carried out in a fluid bed process as shown in Fig. 6.9. Catalyst particles are mixed with heated feed and fluidized with steam up-flow in a riser reactor where the net endothermic reactions occur at around 500°C. The active life of the catalyst is only a few seconds because of coke formation. The deactivated catalyst particles are separated from the product in a cyclone and injected into a regenerator coke is combusted (coke burn-off) with a limited amount of injected air. The regenerated catalyst is mixed with the incoming feed which is preheated by the heat of combustion of the coke.

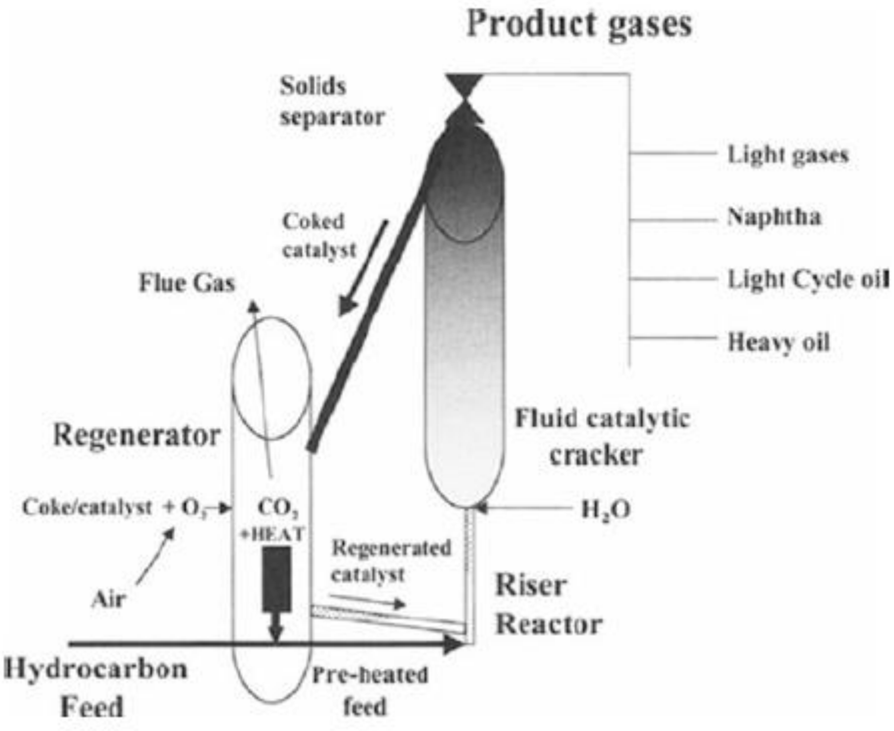


**Fig. 6.9** Schematic of Fluid Catalytic Cracking (FCC) reactor with catalyst regenerator

Zeolites play a major role as catalysts and/or adsorbents in the petroleum, chemical, and lately in a growing number of environmental applications. The reader should consult references available [18].

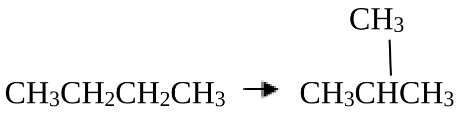
*Naphtha Reforming for High-Octane Gasoline*. In the internal combustion engine gasoline is volatilized, combined with air and injected into the cylinders where it is ignited under compression by a spark plug in the power stroke. Maximum power is achieved when the cylinder reaches top dead center (maximum compression) and the mixture ignited by the spark plug. The heat increased gaseous volume generated drives the piston down in the work stroke. High-octane gasoline is formulated to not pre-ignite, during compression when the temperature rises to avoid the pinging or "knocking" sound that detracts from power. Before the mid-1970s, tetraethyl lead was added to quench pre-ignition reactions, but because lead is no longer permitted the gasoline must be formulated to resist combustion until initiated by the spark. High-octane compounds such as aromatics and branched-paraffins are used in place of lead compounds. Today oxygenates, such as ethanol, are added to boost octane. Octane is a measure of resistance to pre ignition.

Fuel-quality gasoline is made by a process called catalytic reforming [19, 20] in which molecules in the gasoline boiling range (called naphtha) are isomerized, dehydrogenated, and aromatized to make high-octane products. The most widely used reforming catalyst is Pt, Re on chlorinated $Al_2O_3$ particles (3–5 mm diameter). The Pt is the active component primarily for dehydrogenation and aromatization reactions and the Cl adds to the acidity of the carrier which is the active site for isomerization. The Re minimizes coke formation and Pt sintering. Dehydro-isomerization requires both metal and acid functions. Some reactions are endothermic (dehydrogenation and dehydro-isomerization) and others are exothermic (isomerization and dehydro-aromatization). One can see below that the reactions lead to an increase in octane number.

The endothermic dehydrogenation of cyclohexane to benzene and $H_2$ increases the octane number from 75 to 106. The reaction is catalyzed by Pt.

$$C_6H_{12} \rightarrow C_6H_6 + 3H_2$$

Acid catalyzed isomerization of *n*-butane to *i*-butane increases octane from 94 to 101.



$$CH_3CH_2CH_2CH_3 \rightarrow CH_3\overset{\overset{CH_3}{|}}{C}HCH_3$$

Heptane has a defined octane number of 0 and when exothermic dehydro-aromatization (Pt and acid catalyzed) occurs toluene and $H_2$ are formed with an octane number of 116.

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_3 \rightarrow CH_3\text{-}\ C_6H_5 + 4H_2$$

The formation of benzene and $H_2$, from methyl cyclopentane, is catalyzed by both Pt and acid producing the gasoline component with an octane increase from 76 to 106. The net reaction is endothermic

$$CH_3\text{-}C_5H_9 \rightarrow C_6H_6 + 3H_2$$

The reforming process operates with three or four reactors in series. The feed is delivered at 500°C to the first reactor charged with the only 5 % wt. of the total catalyst present. It operates with a high space velocity to perform the easy but highly endothermic dehydrogenation reactions. To minimize coke that forms in all reactions, a small amount of $H_2$ is recycled from the product to the feed. The products and unreacted feed are then reheated to 500°C and fed to a second bed containing about 15% of the total catalyst charge where isomerization reactions occur. The unreacted feed and product are then reheated to 500°C where the more difficult dehydro-isomerization reactions take place with 20% of the total catalyst charge. The final reactor contains 60% of the total catalyst charge and performs dehydro-cyclization which is the most difficult of all the reactions and thus requires the lowest space velocity. The $H_2$ produced is exported to other processes in the refinery (i.e. hydrogenation). Swing reactors are in place to allow the process to continue as each bed is being regenerated by coke burn-off. Following coke burn off the catalyst is rejuvenated by the addition of chloride (lost in regeneration) followed by reduction of the metal to its active state.

## Alternative Fuels

A secure energy supply and the need for reduction of greenhouse gas emissions will continue to be technological goals for the world throughout future decades. It has become apparent that we need a fossil free energy supply. Solar, wind geothermal, hydroelectric, tidal, etc. are natural sources of energy that are being utilized for stationary power generation. Hydrogen powered fuel cells and battery propelled vehicles are also being commercialized very slowly. While these technologies are being improved we need a transitional approach for liquid fuels for vehicular applications. Biofuels, derived from plants, are already making an impact partially replacing fossil fuels in both gasoline and diesel applications [21]. In the US, ethanol is commonly added (10%) to gasoline, while biodiesel additions to fossil derived diesel can range from 2 to 100% depending on the locations and country of use.

Ethanol is derived primarily for corn and other starchy plants, is produced by the well-known fermentation process where enzymes (nature's catalysts) accelerate the conversion of starch to ethanol. Bio diesel is synthesized by the homogeneous alkali catalyzed transesterification of triglyceride oils derived from plants such as soy and canola. Both alternative fuels are derived from edible plants which conflict with the food chain.

For this reason, there is a strong interest in utilizing non-edible portions of the plant, called lignin-cellulose as a source of fuel, especially ethanol. Algae oils are also under investigation. One of the main issues is the efficient penetration of the lignin (un-reactive aromatic polymer) portion of the plant which exists as a protective fiber surrounding the hemi cellulose and cellulose (sugar polymers of glucose), both of which are somewhat reactive towards enzymatic catalyzed fermentation to ethanol. This problem has stimulated the chemical and biochemical approach of developing new pretreatment techniques, including new enzymes, which can breakdown the lignin without destroying the cellulose to be used in the production of ethanol. Alternatively, the thermal-chemical approach of gasification or pyrolysis of lignin-cellulose to produce gases and oils is being explored as a source of fuel. The gaseous and liquid products will require improved catalysts for upgrading bio oil to useable fuels.

Biodiesel can be derived also from non-edible plants such as jathropa and pennycress, both of which are rich in triglyceride oils. These plants grow on arid lands during summer and winter seasons with little need for fertilizers. Processing these plants to useful fuels is highly desirable but at this time success has been limited but worthy of future research.

## Catalysts for Controlling Automotive Emissions

*Oxidation Catalysts to Abate Unburned Hydrocarbon and CO Emissions:* Catalytic converters were first installed in U.S. gasoline fueled cars in 1976 [22, 23]. They were passive devices fixed in the exhaust. It catalyzed the oxidation of the unburned hydrocarbons ($C_xH_y$) and carbon monoxide (CO) to $CO_2$ and $H_2O$ at moderate temperatures. A 90% reduction of these two pollutants using Pt and Pd relative to the uncontrolled un-catalyzed (1970) vehicle was obtained.

$$CO + 1/2O_2 \rightarrow CO_2$$

$$C_xH_y + (1+y/4)\,O_2 \rightarrow xCO_2 + y/2H_2O$$

The presence of the catalyst provides a lower-energy chemical conversion path than that offered by a non-catalytic thermal reaction. A catalyst accelerates the conversion of hydrocarbon/carbon monoxide/air mixture, whose composition lies outside the flammability range. For a thermal reaction to be sustained the fuel-air composition must be within the flammable range which often requires the addition of fuel which adds expense and higher green-house gas emissions than that which is catalyzed. This is only one reason why catalysts are very suitable for conversion of low levels of pollutants for both stationary and mobile sources applications. An excellent example is the oxidation of CO with and without a catalyst. Without a catalyst, the rate-limiting step in CO oxidation is $O_2$ dissociation at 700°C followed by reaction with gas phase CO. In the presence of a Pt, $O_2$ dissociation is rapid at room temperature and the rate-limiting step becomes the surface reaction between adsorbed O atoms and CO occurring below 100°C. Thus the catalyst decreases the energy demand, expense of added fuel and reactor materials of construction and therefore is a logical solution to destroying pollutants. The low temperature insures abatement of pollutants during the early phases of driving. The catalyst experiences temperatures up 1000ºC depending on the mode of operation.

Two approaches were used in the design of the first converters, both of which were positioned in the exhaust physically under the driver's seat. Both used precious metals (Pt and Pd) as the active catalytic components dispersed on $Al_2O_3$ (stabilized against carrier sintering with 1–2% $CeO_2$ and sometimes alkaline earth metal oxides). One major automobile company used catalyzed $Al_2O_3$ beads (4 mm in diameter) and a spring-loaded radial design reactor with a large entry diameter to decrease the linear velocity and thus pressure drop which detracts from power by offering less resistance to flow. Another used a catalyzed ceramic monolithic structure with hundreds of parallel channels (see Fig. 6.4). A coating (washcoat) of stabilized $Al_2O_3$ containing the active precious metals is deposited on the walls of each channel. The cordierite structure ($2MgO–5SiO_2–2Al_2O_3$) has a melting point over 1,300°C sufficiently high to withstand the expected temperatures in the exhaust. The extruded structure has excellent resistance to breakage due to thermal shock experienced during the transient temperature operations during driving. The cellular structure had between 200 and 400 cells per square inch (cpsi) parallel to the flow. With channel diameters of 0.059 in. (200 cpsi) and 0.044 in. (400 cpsi), they had open frontal areas of about 70%, offering little resistance to flow and thus low back pressure. It was incorporated into the exhaust system with retainer rings and surrounded by layers of insulation to minimize breakage due to vibration and heat. The regulations required that the converter have a life of 50,000 miles. To ensure this life, it was necessary to remove the tetraethyl lead from the gasoline, used to boost octane, because the Pb poisoned the Pt and Pd by catalysts.

Oxidation catalysts were used until 1979 in both the particulate (bead) and monolith structures. Particulate beds proved to be less mechanically stable and underwent slow attrition and loss of effectiveness. They were all replaced exclusively with washcoated monoliths found to be highly reliable.

## Three-Way Catalytic Conversion

In 1980, additional regulations imposed by the U.S. Environmental Protection Agency (EPA) required control of $NO_x$ (NO, $NO_2$, $N_2O$) emissions in addition to CO and HC. The removal of $NO_x$ coupled with the need to decrease CO and $C_xH_y$ proved to be quite challenging because the latter had to be oxidized and the former reduced. Thus, it appeared both oxidation and reducing environments would be needed. This problem was solved by the development of the three-way catalyst or TWC capable of catalyzing the conversion of all three pollutants simultaneously provided the exhaust environment could be held within a narrow air-to-fuel range.  This is shown in Fig. 6.10.

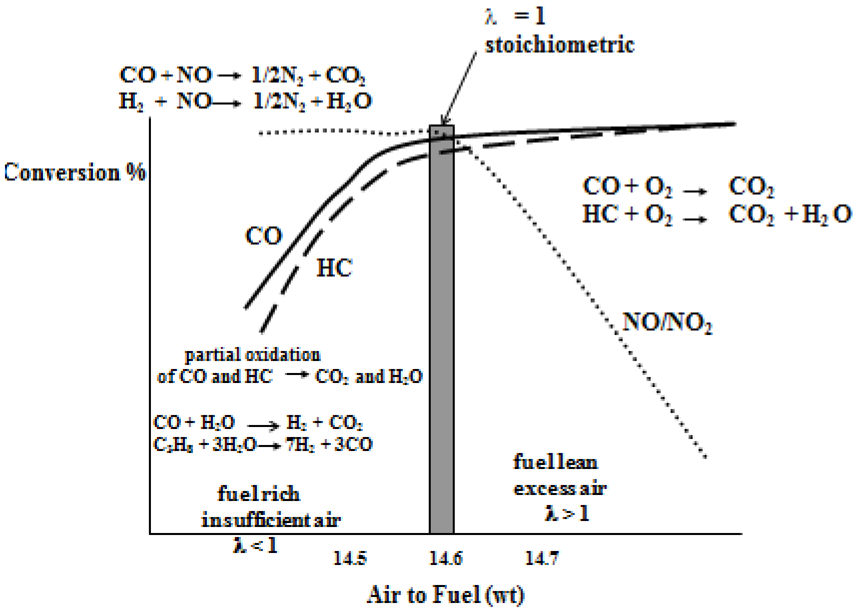


**Fig. 6.10** Three-way catalytic (TWC) converter profile for conversion vs. the air-to-fuel ratio.

This range was defined between the fuel-lean and fuel-rich sides of the stoichiometric point. The exhaust air to fuel ratio divided by the stoichiometric air to fuel ratio is defined as $\lambda$. At $\lambda = 1$ the amount of $O_2$ is precisely sufficient for oxidizing all of the fuel entering the engine. This control required $O_2$ in the exhaust be continuously measured. This led to the development of an $O_2$ sensor discussed below.

In the original TWC, the Pt function primarily as catalysts for the CO and $C_xH_y$ oxidation while Rh catalyzes the $NO_x$ reduction shown below where the $NO_x$ is presented as NO.

$$CO\ (H_2) + NO \longrightarrow 1/2N_2 + CO_2 + (H_2O)$$

The $H_2$ for NO reduction requires it be produced catalytically (mostly by Rh) by the steam reforming of excess hydrocarbon (shown as $C_3H_8$ below) and/or the water gas shift reaction (catalyzed mainly by Pd).

Steam reforming: $C_3H_8 + 3H_2O \longrightarrow 7H_2 + 3CO$

Water gas shift: $CO + H_2O \longrightarrow H_2 + CO_2$

*$O_2$ Sensor*. The control of the exhaust composition was essential to maintain the air-to-fuel ratio close to stoichiometric for simultaneous conversion of all three pollutants. This control came about with the invention of the $O_2$ sensor [23, 24]. The sensor head is installed in the exhaust immediately at the inlet to the catalyst and was able to measure the $O_2$ content instantly and precisely. It generates a voltage consistent with the Nernst

equation in which the partial pressure of $O_2$ $(PO_2)_{\text{exhaust}}$ in the exhaust develops a voltage ($E$) relative to a reference. The exhaust electrode was Pt deposited on a solid oxygen ion conductor of yttrium-stabilized zirconia ($ZrO_2$). The reference electrode, also Pt, was deposited on the opposite side of the solid electrolyte, but physically mounted outside the exhaust and senses the partial pressure $(PO_2)_{\text{ref}}$ in the atmosphere. $E_o$ is the standard state or thermodynamic voltage. $R$ is the universal gas constant, $T$ the absolute temperature, $n$ the number of electrons transferred in the process, and $F$ the Faraday constant.

$$E = E_o + RT / nF[\ln(PO_2)_{\text{ref}} / (PO_2)_{\text{exhaust}}]$$

The CO and $C_xH_y$ catalytically react with the $O_2$ at the surface of the Pt electro-catalyst. When the $O_2$ content is below stoichiometric, the electrode surface is depleted causing an increase in the $(PO_2)_{\text{ref}}/(PO_2)_{\text{exhaust}}$ generating a large voltage. When the $O_2$ content in the exhaust is higher than stoichiometric, the voltage is decreased. Thus, the electrodes must also function as catalysts. The voltage signal generated continuously fluctuates as the $O_2$ content is adjusted from sub to excess stoichiometric. Naturally, the exhaust electrode must be resistant to exhaust poisons and temperature variations, so it was engineered with great care. The voltage signal is fed back to the air/fuel intake system through an electronic control unit that sends a signal to the engine to maintain $\lambda \sim 1$.

Given the finite time necessary for the feedback system to function, a perturbation in the $\lambda$ occurs. To address the $O_2$ variation $CeO_2$, an oxygen storage component (OSC), capable of storing and releasing $O_2$, was added to the TWC formulation. When the engine momentarily delivers less $O_2$ than the stoichiometric amount the OSC is reduced by the unreacted CO (first reaction). During higher $O_2$ spikes the excess is stored on the OSC via oxidation according to the second reaction below.

Fuel rich ($\lambda < 1$): $2CeO_2 + CO \longrightarrow Ce_2O_3 + CO_2$

Fuel lean ($\lambda > 1$): $Ce_2O_3 + 1/2O_2 \longrightarrow 2CeO_2$

The current OSC material is $CeO_2$–$ZrO_2$ (proprietary promoters are added to stabilize it against sintering) where the oxidation state of the cerium is sufficiently labile to respond to the requirements for the OSC. The $ZrO_2$ is added to enhance thermal stability of the OSC.

U.S. federal regulations require that the driver be alerted to a malfunctioning catalyst by a signal on the dashboard. Currently, there is no instrumentation commercially available to sense the effectiveness of the catalyst to meet the onboard diagnostic requirement. An indirect solution is to place a second $O_2$ sensor at the exit of the catalytic converter. If the OSC in the catalyst is working properly, its voltage signal would have virtually no fluctuations because the $O_2$ content would be always zero. If the OSC is not functioning properly, $O_2$ will break through at the exit and the sensor would undergo similar fluctuations as the inlet sensor. Comparing these two signals generates the diagnostic that informs the operator of a malfunction.

To further decrease large emissions during a cold start a small close couple TWC is positioned very close to the engine exhaust ports. This catalyst becomes hot quickly to initiate conversions and insure a low emissions profile.

A modern converter with dual $O_2$ sensors (one at the inlet and one at the outlet) is shown as Fig. 6.11. In modern vehicles the $O_2$ sensor is located at the inlet to the close couple catalyst. This further discussed below.

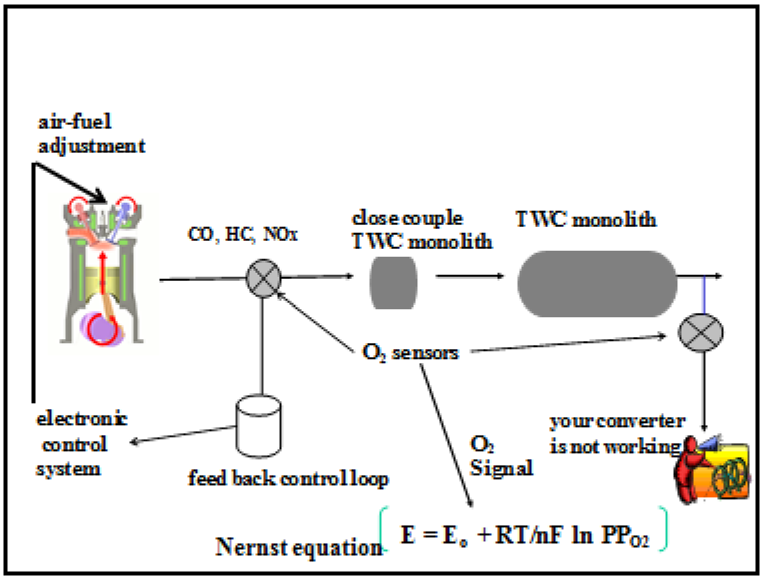


**Fig. 6.11 Cartoon s**chematic of the gasoline exhaust system with a TWC close couple and TWC catalyst. The system is equipped with dual $O_2$ sensors, one at the inlet and one at the outlet of the TWC converter for on-board diagnostics

### Modern Catalytic Converter Systems

Modern TWC-equipped vehicles are required to meet minimum emission standards for 150,000 miles [23, 24]. It should be understood that after this time period the catalyst is still extremely active, but may have lost sufficient activity to no longer meet the stringent EPA standards. The source of deactivation is sintering of the catalytic metals (Pd, which has replaced Pt, and Rh), the OSC and the carrier due to the extremely high temperatures (~1,000°C) experienced in the exhaust. The steam produced from combustion enhances the sintering. There are proprietary stabilizers added to the formulations that minimize sintering. Poisoning effects by sulfur and oil components (Zn, P, Ca, S, etc.) have been minimized by reductions in fuel sulfur and careful design of the washcoat to prevent contact of the poisons with the catalytic components. These catalyst improvements, coupled with enhanced engine control, have resulted in lifetimes that often exceed the life of the car itself.

At start-up, the catalyst is cold and there is a substantial emission of hydrocarbons. It is during the first 1 or 2 min of cold-start operation that the vehicle can fail the federal test procedure. During cold start the reactions are kinetically controlled. Once the catalyst is sufficiently warm, the reaction exotherm quickly raises the temperature and the reaction becomes limited by bulk mass transfer. So manufacturers have designed the catalyst for both kinetic control and bulk mass transfer conditions. The cold-start issue was addressed by positioning a small oxidation catalyst (close coupled) up against the exhaust ports of the engine to ensure rapid heat up and light-off. This is shown in Fig. 6.11. The newest cordierite monoliths have lower weights, thin walls for faster light-off and high geometric areas (600–900 cpsi) to ensure adequate bulk mass transfer area and lower pressure drop to meet modern driving demands and ever-increasing regulations. The space velocity varies between 5,000 (idle) and 75,000 $h^{-1}$ at high speed.

It is truly remarkable that catalysts can function so well in the exhaust of the modern high-speed vehicle. This fact has raised confidence in industry to use different monolithic (ceramic and metal) structures as supports for catalysts for other environmental applications such as diesel exhausts, power and chemical plants, restaurants, and even on wide-body aircraft.

## Controlling Emissions from Diesel Engines

The diesel engine was invented by Rudolph Diesel in the latter part of the nineteenth century. Due to significant benefits in fuel economy, they have enjoyed a surge in popularity in recent years, particularly in Europe where they represent approximately 50% of new cars sold. Diesel trucks are used throughout the world due to their long life and high fuel economy. Although improved fuel efficiency is the key driver, improvements in the drivability of diesel vehicles as well as a reduction in their tailpipe emissions have also helped improve their image and spurred further growth. Unlike gasoline emissions that are gaseous in nature, diesel emissions from passenger cars, buses, and trucks contain solid, liquid, and gaseous components. The composition of diesel fuel and operation of the engine differ significantly from gasoline spark ignited engines and therefore their emission profiles are much more complicated. Diesel fuel has a boiling range from 200 to 350°C. The four-stroke engine compresses air and at maximum compression (top dead center) injects liquid fuel into the compressed air where combustion occurs driving the piston downward in the work stroke. Diesel engines operate with a large excess of air ($\lambda \gg 1$) and therefore three-way catalysts, which operates at ($\lambda \sim 1$), will not catalyze the reduction of $NO_x$. Furthermore, the reduction of total particulate matter (TPM) is addressed mainly via filtration [23].

Based on the combustion characteristics of lean burn compression ignition diesel engines, the focus of emission regulations is on two key tailpipe pollutants—TPM and $NO_x$. Both of these are produced in large quantities during combustion. Since diesel fuel is less volatile than gasoline and is injected directly into the cylinder as a liquid, combustion initiates before the fuel droplets have sufficient time to vaporize and mix completely with the air. As a result, combustion begins at the gas–liquid interface of the fuel spray and then progresses towards the center of the droplet. This “diffusion combustion” phenomenon results in the production of significant amounts of $NO_x$ at the fuel liquid–gas interface where the local temperature and oxygen concentrations are high. In contrast, large amounts of soot (mostly dry carbon) are generated in the interior of the droplet where the temperature and oxygen concentrations are lower. This phenomenon is called pyrolysis where fuel is heated in the absence of air. As a result, both soot and $NO_x$ are produced simultaneously in large amounts from diesel engines. The relationship between combustion temperature-particulates and $NO_x$ is called the $NO_x$-particulate trade-off. When $NO_x$ emissions are high (e.g., at high combustion temperatures), particulate emissions are low. In contrast at lower combustion temperatures $NO_x$ emissions are low but particulate emissions are high. Regulations required that both particulate and $NO_x$ emissions be reduced to close to zero from 2010 and beyond in the US with other countries following closely.

Due to the adverse health effects associated with diesel soot and the ozone forming potential of $NO_x$, both are the major focus for emissions regulations. Although CO and

HC are also regulated, the amounts produced by diesel engines are generally low. Due to the large excess of air meeting their emission regulations can be easily addressed. This is particularly true for heavy duty diesel applications.

The solids emitted from diesel engines are essentially dry soot (carbon rich particles). The liquids are primarily unburned diesel fuel and lubricating oils (the combination is commonly referred to as soluble organic fraction or SOF) and to some extent sulfates originating from the combustion of the sulfur compounds present in the diesel fuel. The combination of solid and liquids is referred to as particulates or TPM. Note that $H_2SO_4$ is included since it is a liquid at the collection conditions for TPM. The gaseous pollutants are primarily CO, HC, and $NO_x$.

Total Particulate Matter

- Dry soot
- Liquids (oil, fuel) called SOF
- $H_2SO_4$

Gases

- CO, HC, $NO_x$

## Diesel Oxidation Catalysts

The diesel oxidation catalyst (DOC) has two primary functions; 1. oxidize the CO, HC's and NO to $NO_2$ emitted from the engine and 2. oxidize injected diesel fuel to generate heat for regenerating the particulate filter (to be discussed below). This catalyst is primarily a mixture of Pt and Pd on stabilized $Al_2O_3$ deposited on a ceramic monolith.

Regulations for dry soot reduction led to the introduction of a wall flow or diesel particulate filter (DPF). It is primarily a cordierite honeycomb structure with alternating adjacent parallel channels plugged at opposite ends. Exhaust enters the open channels, but only the gaseous components can pass through the porous wall exiting via the adjacent open exit channel. Soot that is entrained in the exhaust stream is trapped on the wall while the gaseous components pass unrestricted. Periodically (e.g., every 1,000 km of driving), the filter is heated to a temperature high enough (ca. 500°C) to combust the soot and regenerate the filter. This heat is generally provided by oxidizing the diesel fuel injected into the DOC with the exotherm generating at least 500°C to initiate combustion of the soot. Alternatively, for vehicles without a DOC, fuel is injected into the cylinders during the exhaust stroke to promote combustion in the exhaust manifold, thereby raising the exhaust and DPF temperature. For the light duty market, DPF are usually silicon carbide or aluminum titanate.

A DPF may also contain a Pt containing catalyst (i.e., a catalyzed soot filter or CSF) to assist with the combustion of soot and to oxidize CO generated during the soot regeneration process.

## Controlling $NO_x$ in Diesel Engines

The US and European standards require the reduction of all three phases of diesel emissions (i.e., solids, liquids, and gases). In particular, reduction of $NO_x$ offers considerable challenge due to the lean nature (large excess air) of the exhaust. Two of the most promising technologies for controlling $NO_x$ are Selective Catalytic Reduction (SCR) and lean $NO_x$ Traps (LNT). Both utilize catalytic processes to eliminate $NO_x$ reducing it to $N_2$.

SCR, which is mostly used in trucks, relies on the reduction of $NO_x$ by ammonia ($NH_3$) over either metal exchanged zeolite catalysts supported on a monolith. The current

$NO_x$ reduction catalysts are a combination of Cu on chabazite zeolite and Fe on a beta zeolite. The 3 major desired reactions occurring are

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$$

$$4NH3 + 2NO_2 + O_2 \rightarrow 3N_2 + 6H_2O$$

$$2NH_3 + NO_2 + NO \rightarrow 2N_2 + 3\,H_2O$$

Although commonly used in stationary source applications, SCR needed to be modified for vehicle applications. Since handling gaseous ammonia is not practical in automobiles or trucks, an ammonia surrogate such as urea is utilized to generate ammonia in-situ in the vehicle exhaust. Typically, an aqueous solution of 30% urea is injected into the exhaust stream before the SCR catalyst, and is hydrolyzed to ammonia. In addition, an ammonia "cleanup" monolithic catalyst (usually a Pt on $Al_2O_3$) may be required to remove any ammonia "slip" that may pass through the SCR catalyst. Depending on the specific application, an oxidation catalyst (DOC), a CSF, an SCR catalyst, and an ammonia destruction catalyst (AMOX) may all be required to meet the combined CO, HC, and $NO_x$ and soot regulations for heavy duty trucks. Sophisticated engine controls are required to ensure proper operation of all components within the system. The schematic in Fig. 6.12 shows the catalytic unit operations for meeting diesel emission standards using an SCR system for trucks.

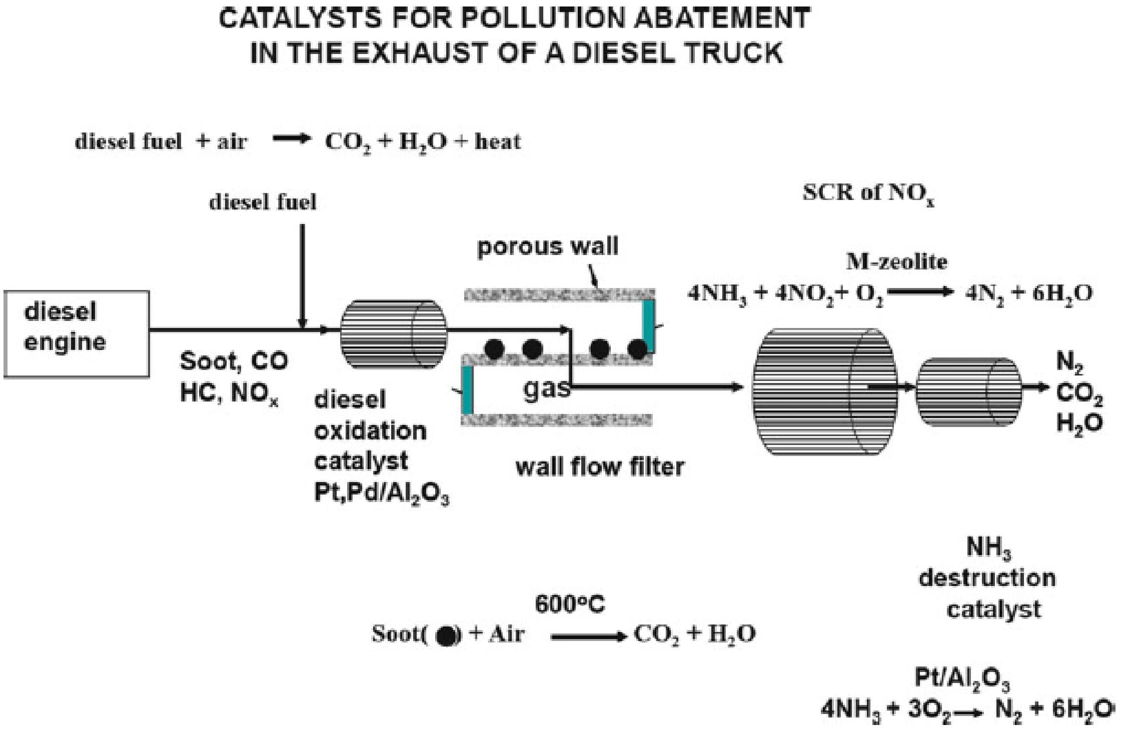


**Fig. 6.12** Simplified diesel exhaust after-treatment system for heavy duty trucks. A diesel oxidation catalyst, wall flow filter, selective catalytic reduction, and ammonia decomposition catalyst are shown. M zeolite for SCR is a combination of Cu/chabazite zeolite and Fe/beta zeolite

The alternative technology for controlling $NO_x$, mainly for passenger cars, is a lean $NO_x$ trap (LNT). The technology utilizes a Pt and Rh-based TWC in combination with an $NO_2$ trapping agent (e.g., an alkaline earth compound such as BaO). During the normal lean operation (for enhanced fuel economy) NO is oxidized to $NO_2$ at the Pt site and the $NO_2$ is adsorbed by BaO within the catalyst washcoat. Periodically (e.g., every 60–120 s), the trap is regenerated by introducing a “rich pulse” of reductant (e.g., diesel fuel) into the exhaust stream or by switching the engine operating mode to slightly rich of stoichiometric for 1–2 s. This rich pulse provides the necessary $H_2$ (via hydrocarbon steam reforming) to convert the adsorbed nitrate to nitrogen over the Rh catalyst.

Lean mode catalyzed by Pt: $NO + 1/2O_2 \longrightarrow NO_2$

$NO_2$ trapping: $NO_2 + BaO \longrightarrow BaO\text{---}NO_2$

Rich mode catalyzed by Rh: $BaO\text{---}NO_2 + 2H_2 \longrightarrow 1/2N_2 + 2H_2O + BaO$

LNT technology is commonly used for light duty passenger vehicle applications; however, its primary disadvantages are high Pt levels to maintain sufficient catalyst durability and a fuel penalty (ca. 3–5%) resulting from the periodic trap regeneration. In addition, the $SO_x$ derived from the fuel-borne sulfur forms $BaSO_4$ that is much more stable than the corresponding nitrates and not removed during the slightly rich of stoichiometric operation mode. Therefore, the trap becomes progressively poisoned by sulfates. Complicated engine control strategies have been developed to desulfate the poisoned trap by operating the engine at a high temperature (>550°C) and rich of the stoichiometric air/fuel ratio for a short period of time. In addition, the air-to-fuel ratio must be carefully controlled to avoid the formation of $H_2S$ during excessive rich conditions. LNT technology has the capability of removing up to 90% of the $NO_x$ in the exhaust. Having lower sulfur fuels available will favor high $NO_x$ conversion levels and also reduce the requirements for desulfation.

## Catalytic Hydrogenation of Vegetable Oils for Edible Food Products

### Triglycerides

Plant-derived oils such as soy, cottonseed, peanut, canola, corn, etc. are natural sources of edible products such as baking dough for cakes, cooking oils, salad dressing, chocolates, margarine, etc. Non-edible products such as lubricants, creams, lotions, etc. can also be produced depending on the processing of the oils. Natural oils are composed of combinations of chains of fatty acid esters called triglycerides a typical one shown in Fig. 6.13. The triglyceride chains are polyunsaturated, the degree of which influences their stability against oxidation in air.

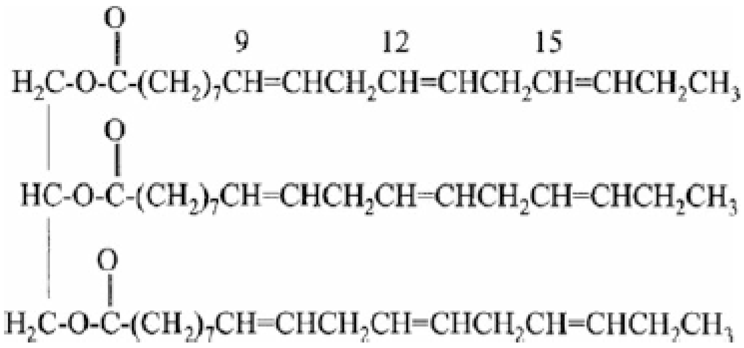


**Fig. 6.13** An unsaturated triglyceride molecule. Example shown is linolenic oil

Catalytic hydrogenation of the double bonds improves the stability against air and raises the melting point such that solids can be produced. Thus, the precursor to chocolate candy, margarine, or a cake mix is liquid oil that upon hydrogenation becomes an edible solid at room temperature. The more double bonds hydrogenated (the more saturated) the more resistant it is to air oxidation, the higher its melting point but more injurious to our health by deposition of saturated fats in our blood vessels. The goal of a good catalyst coupled with the proper process conditions is to produce a reasonably healthy product with the desired melting range with sufficient air stability to permit a reasonable shelf life.

Oils are classified by the length of the glyceride chain and degree of poly-unsaturation. Typically, nature produces oils with a mixture of chain length between 12 and 22 carbons with up to three unsaturated bonds per chain usually all in the *cis*-form. Triglycerides with 18 carbons per length and three double bonds at positions 9, 12, and 15 counting from the first carbon in the ester group are called linolenic and designated C18:3. This structure is shown in Fig. 6.13. The outermost double bond is so reactive towards air that oils with three double bonds in the alkyl chain are rare. Therefore, the most prevalent in nature have double bonds at positions 9 and 12 and are referred to as linoleic (C18:2). Its reactivity is about half that of linolenic. The least reactive is oleic (activity 1/20 that of linolenic) with only one double bond per length at position 9 (C18:1). Stearic is the term used for glycerides with all bonds saturated (C18:0). Not surprisingly, this form has virtually no reactivity towards air, has a high melting point, and is unhealthy.

The source of the oils plays a major role in producing a product with the desired melting point, stability, and health consequences. Cotton, sunflower, corn, and soy bean oils are a mixture of the four basic triglycerides with 50–70% C18:2 being the most dominant followed by 20–30% C18:1 with less than 1% C18:3. Less than 10% are other saturated oils such as C16:0. Palm kernel and coconut oils have almost 80% saturated triglycerides (C12:0, C14:0, and C16:0), have high melting points, and are stable against air. They are primarily used for protecting the skin against excessive sun exposure. Olive oil has up to 80% C18:1 and is therefore relatively healthy.

The most common oil hydrogenation catalysts are 20–25% Ni on $Al_2O_3$ and $SiO_2$. The nickel salts are either impregnated or co-gelled with a carrier precursor such as a soluble Al or Si salt. The catalytically active state of Ni is the reduced (metallic) form. Reduction is performed during manufacture at which time the catalyst is coated with a fatty gel to protect it from air oxidation during shipment.

Less than 1% by weight of catalyst is added to the batch reactor where the fatty protective gel slowly dissolves and the hydrogenation reaction commences. Temperatures of 100°C and $H_2$ pressures of 3–5 atmospheres are used to ensure adequate dissolution of the $H_2$ into the feed stream. Reactions are carried out between 100 and 160°C. Stirring is vigorous to maximize $H_2$ dissolution and diffusion to the catalyst surface. The catalyst particles are small to minimize pore diffusion resistance and increase liquid–solid mass transfer area. The kinetics for a batch slurry phase reaction were presented early in the review.

Cu supported on $Al_2O_3$ is less active than Ni and this property is used to "brush" hydrogenate. Only minimum hydrogenation occurs maintaining the melting point but sufficient to improve stability against air. This is sometimes used for producing salad oils.

The reaction profile is generally sequential with hydrogenation first occurring on the most active double bonds followed by those less active [24–26]. Time distribution shows the linoleic form decreasing as the oleic form increases. After extended reaction time, the stearic begins to form as the oleic is slowly hydrogenated. It is imperative the time be controlled to produce the desired product distribution.

Hydrogenation of the linoleic structure, with a melting point of −13°C, will produce an oleic product with a melting point of 5.5°C very suitable for consumption. During the partial hydrogenation process, it is desirable to minimize isomerization to the *trans* isomer (the hydrocarbon groups are *trans* to each other across the remaining unsaturated bonds) because this structure raises the "bad" cholesterol or LDL (low-density lipids). A partially hydrogenated *cis*-structure may have a melting point of 6°C, whereas it's *trans* isomer at 40°C. The *trans* isomer is more readily formed at high reaction temperatures, high Ni catalyst loadings, and at low hydrogen pressures (low concentration of $H_2$ at the catalyst surface). Pt containing oil hydrogenation catalysts produce considerably less *trans* than Ni; however, their high activity causes excessive hydrogenation of the double bonds. To minimize this effect, $NH_3$ is intentionally added to the feed or catalyst to slightly poison its activity towards hydrogenation. By so doing, low *trans* oil is produced without excessive saturation of the double bonds. In 2006, the U.S. Food and Drug Administration required labels that report the amount of *trans* components present in edible products.

Catalyst deactivation is mainly caused by mechanical attrition due to the rigorous stirring. In most cases, adsorption guard beds are used upstream to remove impurities such as sulfur and phosphorous often found in the feed. Recognizing that some poisons may break through, the catalyst has an average pore size sufficiently large to admit the triglycerides but smaller than the average size of the organic compounds containing P and S. The spent catalyst is separated from the product by filtration. Given the increasing cost of Ni, it is recovered, refined, and used to make fresh catalyst.

## Fertilizers and Hydrogen Generation

*General Reactions:* Ammonium nitrate ($NH_4NO_3$) and urea ($CO(NH_2)_2$) are two major sources of the world's fertilizers. The nitrate is produced by reaction of ammonia and nitric acid.

$$NH_3 + HNO_3 \rightarrow NH_4NO_3$$

Urea is produced by the reaction of $NH_3$ with $CO_2$ and its subsequent decomposition by heating.

$$2NH_3 + CO_2 \rightarrow NH_2CO_2NH_4 \rightarrow NH_2CONH_2 + H_2O$$

Ammonia is produced by the Fe catalyzed hydrogenation of $N_2$ with $H_2$

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

Hydrogen is produced by a series of catalytic reactions, the first of which is hydrocarbon reforming catalyzed by Ni and the second is water gas shift catalyzed by a Cu. Considering natural gas ($CH_4$) as the starting hydrocarbon

$$CH_4 + H_2O \rightarrow 3H_2 + CO$$

$$CO + H_2O \rightarrow H_2 + CO_2$$

Nitric acid is produced by the selective catalytic oxidation of $NH_3$ to NO using a PtRh alloy gauze. Upon cooling NO is oxidized to $NO_2$ and its subsequent hydration forms nitric acid.

$$2NH_3 + 7/2O_2 \rightarrow 2NO + H_2O$$

$$NO + 1/2O_2 \rightarrow NO_2$$

$$3NO_2 + 1H_2O \rightarrow 2HNO_3 + NO$$

Each catalytic step will be discussed in this section.

*Hydrogen Generation for the Production of $NH_3$:* Producing $H_2$ from hydrocarbons such as natural gas is currently practiced in the chemical industry [27–30] under steady state conditions with carefully controlled catalytic unit operations. The overall process is as shown in Fig. 6.14.

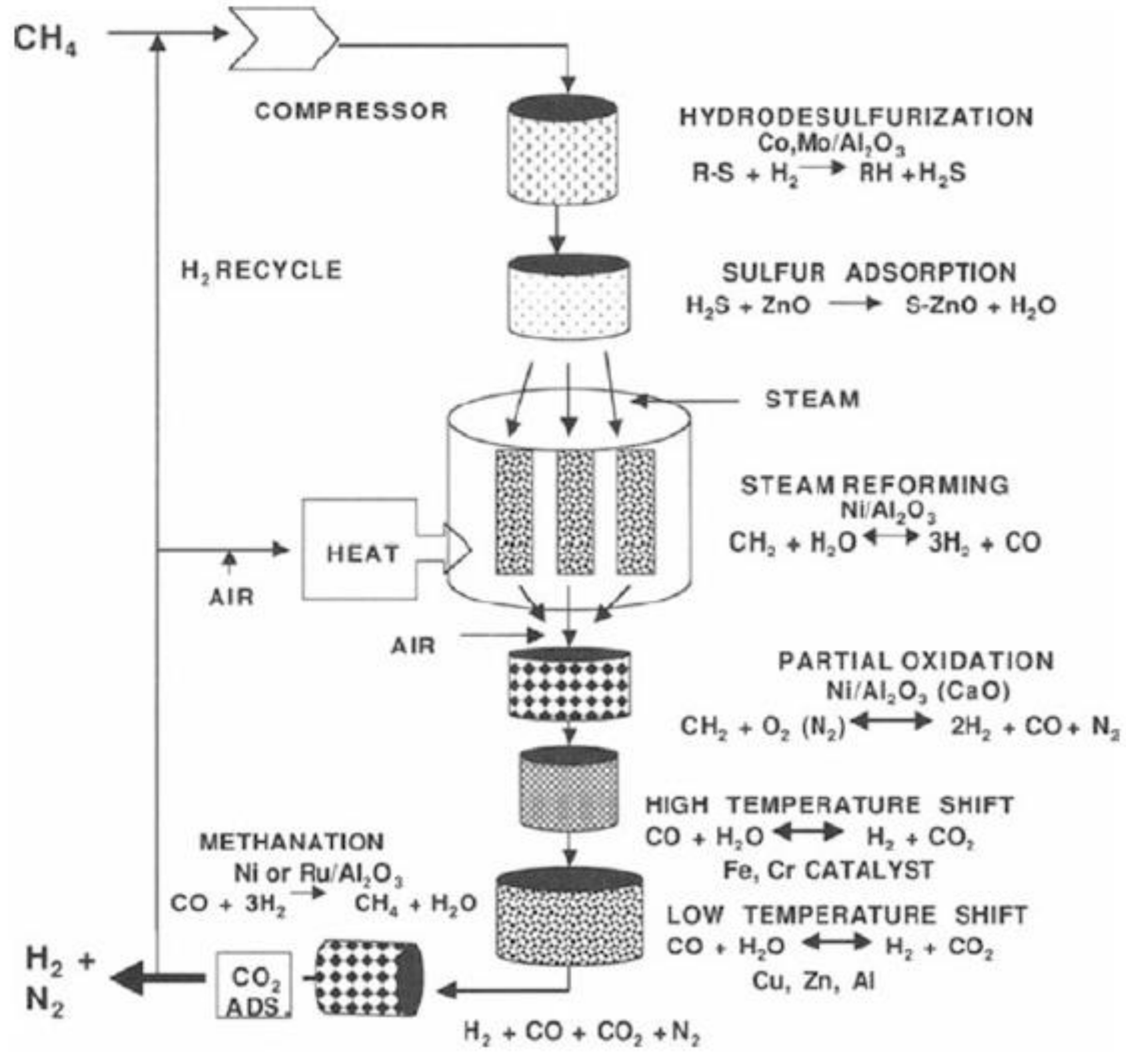


**Fig. 6.14** The catalytic synthesis of hydrogen from natural gas for ammonia synthesis using hydrodesulfurization, steam reforming, partial oxidation, water gas shift, methanation, and $CO_2$ scrubbing

Traces of organic sulfur compounds such as mercaptans, thiosulfides, and alkyl sulfides are added to natural gas to impart odor for detection of leaks. Because sulfur compounds are poisons to the downstream catalysts, they must be removed. The technology of choice is hydro-desulfurization or HDS. This is similar to the petroleum desulfation process but under less severe conditions.

$$R\text{-}S + H_2 \longrightarrow H_2S + R\text{-}H$$

The reaction is carried out around 300–400 psig and 300–400°C. The catalyst is 3% Co, 15% Mo deposited on spheres (25–75 $m^2/g$) $Al_2O_3$ with diameters of 2–3 mm. The catalyst is pre-sulfided to decrease its activity towards undesirable side reactions such as coking. The $H_2S$ produced is removed downstream from the HDS reactor by adsorption on ZnO particles at about 400–500°C.

$$H_2S + ZnO \longrightarrow ZnS + H_2O$$

Primary reforming of the sulfur-free natural gas (i.e., $CH_4$) is the first step to produce a $H_2$-rich gas.

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO$$

The reaction is highly endothermic and thus is favored at high temperatures. The maximum temperature achievable is limited by metallurgy of the reactor. Given the increase in gas volume, the reaction is favored by low pressures. The catalyst is about 30% Ni with about 14% CaO on highly densified alpha alumina ($\alpha$-$Al_2O_3$) with a surface area about 2–5 $m^2/g$. The CaO reacts with the $Al_2O_3$ forming $CaAl_2O_4$ for added mechanical strength under the severe operating conditions of 800°C and 300–400 psig and a steam environment up to 75%. The reaction rate is limited by a combination of heat transfer and pore diffusion, the latter due to the inadequate accessibility of the reactants to the catalyst interior. Enhanced heat transfer to the center of the reactor is achieved by using small diameter tubes containing the catalyst. To counter pore diffusion limitations, the catalyst is manufactured as a donut with two to three holes to increase the external contact area and decrease the diffusion path. The space velocity is between 1,000 and 2,000 $h^{-1}$. The active catalyst is Ni metal, so it must be reduced carefully with $H_2$ prior to introducing the feed. The reaction is carried out in a series of tubular parallel reactors located in a large fired box furnace to provide the necessary heat.

Deactivation is due mostly to the slow accumulation of sulfur that breaks through the upstream HDS/ZnO guard beds. Sulfur irreversibly decreases the activity of the Ni that allows the methane decomposition rate to become significant leading to the accumulation of hydrogen-deficient carbon or “coke.” This builds up within and between catalyst particles, leading to its fracture and an increase in pressure drop. During process shut down, the catalyst must be “passivated” to protect against air oxidation of the Ni and a subsequent fire due to its strong exotherm creating a safety hazard at the plant site. This is accomplished by periodically injecting small amounts of air and carefully oxidizing the surface of the Ni while monitoring the exotherm.

Equilibrium limits conversion of the $CH_4$, so partial oxidation or secondary reforming of the unreacted $CH_4$ is used to generate more heat and $H_2$ in a secondary reforming step. The addition of air also serves the purpose of providing the required $N_2$ for the subsequent ammonia synthesis reaction. Secondary steam reforming also uses a high-temperature resistant Ni containing catalyst that must retain its strength after prolonged exposure to close to 1,200°C due to the oxidation in the front end of the bed. The catalyst used is $\alpha$-$Al_2O_3$ impregnated with about 18–20% Ni and 15% CaO. The unbalanced reaction is shown below

$$CH_4 + \text{Air}\ (N_2 + 1/5O_2) \rightarrow H_2 + CO + CO_2 + N_2$$

The exit from the secondary reformer contains about 10–12% CO, is cooled to about 350°C, and fed to a high-temperature water gas shift (HTS) reactor.

$$CO + H_2O \leftrightarrow H_2 + CO_2$$

The high temperature water gas shift catalyst is a particulate composed of 90% Fe and 10% Cr. The Cr minimizes sintering of the active Fe phase. The catalytic reaction is limited by pore diffusion, so small particles are used. The exit process gas contains about 2% CO as governed by the thermodynamics and kinetics of the reaction. This reaction is slightly exothermic and thermodynamics favor low temperatures that decrease the reaction rate. It is therefore necessary to further cool the mix to about 200°C where it is fed to a low-temperature shift reactor (LTS) containing another particulate catalyst composed of 30–35% Cu, 45% ZnO, and 13–20% $Al_2O_3$. The catalyst is active in the reduced form, so it must be carefully activated with $H_2$ avoiding excessive overheating which will cause sintering. The Zn and $Al_2O_3$ are added to stabilize the Cu because it is sensitive to sintering. The CO is decreased to its thermodynamic limit as imposed by the temperature and gas compositions. Typically, the CO is reduced to less than about 0.5%. The catalyst deactivates by traces of sulfur and sintering of the active Cu phase. Because of the necessity to operate at low temperatures, the reaction rate is slow and large volumes and low space velocities (1,500–2,500 $h^{-1}$) are used.

The active Cu-containing catalyst is also very air sensitive (like the Ni reforming catalyst) and will spontaneously oxidize generating uncontrolled reaction heats. Thus, it must be passivated before discharged and exposed to air. A small amount of air is added to the reactor and the temperature monitored. This process is continued until the exotherm is small enough that the catalyst can be safely removed from the reactor.

The remaining CO, which poisons the downstream ammonia synthesis catalyst, is removed by methanation using either a Ni on $Al_2O_3$ catalyst at 300°C which is the reverse of the steam reforming reaction.

$$CO + 3H_2 \longrightarrow CH_4 + H_2O$$

The $CO_2$ must be removed since it is also a poison to the ammonia synthesis catalyst. It is scrubbed in an amine solution and recovered for other uses especially methanol synthesis (below).

## Ammonia Synthesis

The Haber process for the synthesis of ammonia from $H_2$ and $N_2$ has been practiced since the beginning of the twentieth century always with a massive Fe catalyst [31].

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

The reaction is mildly exothermic, so the reaction is thermodynamically favored at lower temperatures but at high pressures due to the contraction of gaseous product volume. To obtain reasonable rates, the process is operated at about 450°C and pressures approaching 5,000 psig at a space velocity of 10,000–15,000 $h^{-1}$. The process is operated in a recycle mode, so ammonia is continuously removed aiding the equilibrium. The active catalyst is 75–80% Fe metal, 10% $Fe_2O_3$, 4% $Al_2O_3$, less than 5% alkali and alkaline earth (Li, Ca, and Mg), with 1% $SiO_2$ added to minimize sintering of the Fe. The promoters are added to a melt of magnetite ($Fe_2O_3$). The solid mass is then ground to 1 mm particles, charged to the fixed bed reactor, and slowly reduced with $H_2$ at 500°C. The reduction generates active Fe metal with some porosity due to liberation of oxygen forming $H_2O$. The internal surface area is increased from about 1 $m^2/g$ to about 20 $m^2/g$. The small particle size of the finished catalyst is necessary to minimize pore diffusion limitations. Special precaution is necessary during discharge from the reactor because air exposure will

spontaneously oxidize the Fe surface generating large quantities of heat.
The catalyst is poisoned by CO, $CO_2$, and $H_2O$, so they must be rigorously removed upstream in the hydrogen synthesis process. Oxygen-containing molecules are permanent poisons. Other poisons such as sulfur, arsenic, halides, and phosphorous must be carefully removed upstream in as much as they too are permanent poisons.

### Nitric Acid Synthesis

Nitric acid is produced by the selective oxidation of $NH_3$ over a gauze catalyst composed of 90%Pt, 10%Rh (some gauze is 90% Pt, 5% Rh, and 5% Pd) [32]. The product NO and O2 is cooled and converts to NO2 which is hydrated to form HNO3. The first reaction was used in the “Selectivity” section to demonstrate the high efficiency with which PtRh leads to NO production as opposed to more thermodynamically favored $N_2$.

Desired reactions: $2NH_3 + 7/2O_2 \rightarrow 2NO + H_2O$

$NO + 1/2O_2 \rightarrow NO_2$

$3NO_2 + 1H_2O \rightarrow 2HNO_3 + NO$

Undesired $4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$

The low-pressure process (15–30 psig) produces NO with a selectivity of 98% and the high-pressure process (150 psig) a selectivity of 94%. The high-pressure plant allows for a smaller reactor (and smaller gauze diameter of about 3 ft) compared to 12 ft diameter for the low-pressure process.

The feed is composed of 10–12% $NH_3$ in air and is fed to the reactor at an inlet temperature of about 250°C and a space velocity approaching 50,000 $h^{-1}$. For a high-pressure plant, the exotherm generates a temperature of 900°C. The NO product is cooled and non-catalytically converted to $NO_2$ which reacts with $H_2O$ forming $HNO_3$.

The finished alloy catalyst is manufactured by a knitting process to form wire gauze that looks like a door screen. The Rh is added to impart mechanical strength during the wire drawing operations. During reaction, the catalyst undergoes an unusual morphology change. The Pt forms an oxy–nitrogen species and volatilizes from the gauze. The smooth wires become roughened and sprout occurs. The surface area of the gauze increases by 20 times during the sprouting process. The loss of Pt enriches the surface with Rh and the catalyst slowly loses activity. After approximately 90 days of operating a high-pressure plant, the Pt content of the gauze is reduced to 50%. The volatile Pt is captured downstream on a “getter gauze” made of Pd. The Pd surface catalytically decomposes the gaseous oxy–nitro Pt species and a Pt–Pd alloy forms that allows for recovery of the precious metals. The spent catalyst is returned to the supplier where the precious metal is recovered for future use.

Another source of deactivation is Fe contamination originating from the corrosion of upstream equipment depositing on the gauze. Another source is from the Fe-containing ammonia synthesis catalyst.

Although the largest use for nitric acid is $NH_4NO_3$ fertilizers, it is also used for explosives and nylon polymers.

## Pure Hydrogen Generation with Pressure Swing Adsorption Purification

For applications in which $N_2$ is not needed, such as $H_2$ or alcohol production, pressure swing adsorption (PSA) is used as a final step. The process flow diagram is shown in Fig. 6.15.

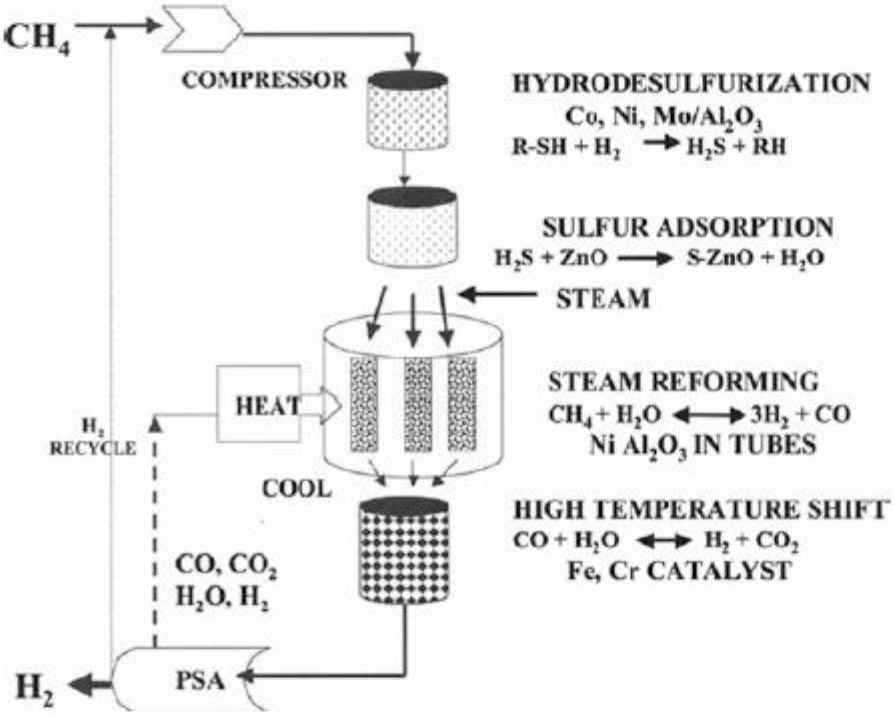


**Fig. 6.15** The catalytic synthesis of hydrogen from natural gas using hydrodesulfurization, steam reforming, water gas shift, and pressure swing absorption (PSA)

## Fuel Cells:

There is a renewed interest in hydrogen generation for the developing hydrogen economy with the anticipated use of fuel cells as a power source for stationary and vehicle applications [33]. The fuel cell generates electricity and heat by electrochemically oxidizing $H_2$ and reducing $O_2$. Pt/carbon electro-catalysts are used for both the anode and cathode reactions but of different compositions and designs due to the specific reactions to be catalyzed. The proton exchange membrane (PEM) fuel cell operates at about 70-80°C. The electrons produced at the anode travel to an external circuit where they perform useful work before returning to the cathode to complete the circuit. The protons produced at the anode permeate through a proton exchange membrane (PEM) where they combine with $O_2$ from air and electrons to complete the reaction. Figure 6.16 is a cartoon of a single cell PEM fuel cell. They are stacked in series to increase the output voltage for the required appliance. Heat generation accompanies the electrochemical reaction so heat exchange fluids are utilized in the stack design.

Anode: $H_2 - 2e^- \longrightarrow 2H^+$ $E^o = 0$

Cathode $1/2O_2 + 2e^- + 2H^+ \longrightarrow H_2O$ $E^o = 1.23$ volts

Net reaction $H_2 + 1/2O_2 \longrightarrow H_2O$ $E^o = 1.23$ Volts

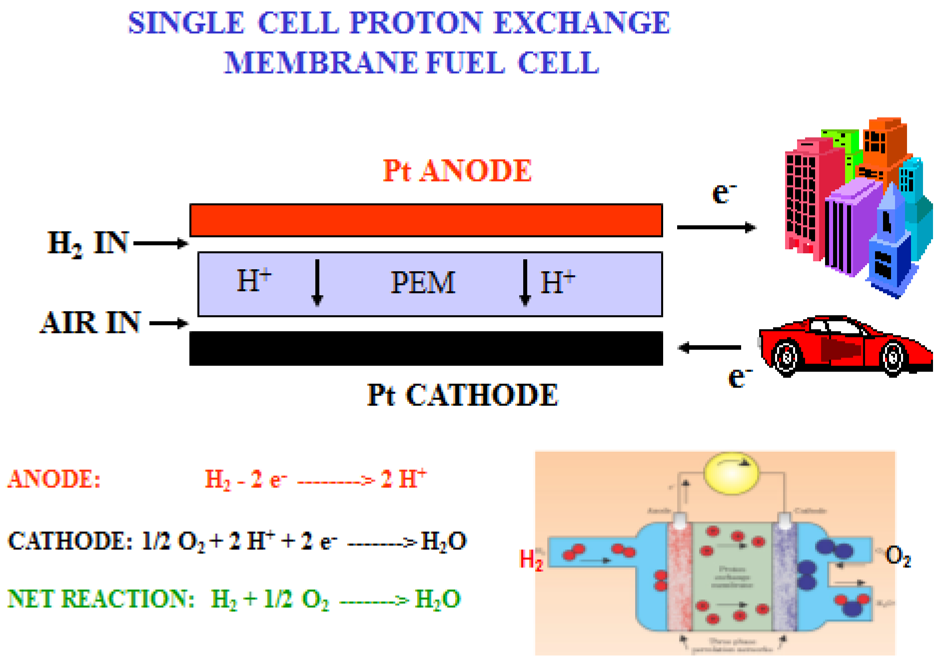


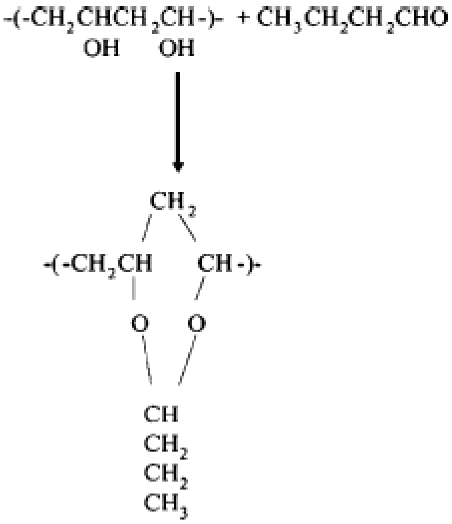
Figure 6.16 Shows a simply proton exchange membrane fuel cell providing electricity for stationary and vehicle applications. The voltages for each reaction are at standard states.

Because the fuel cell directly converts chemical to electrical energy without using the traditional mechanical steps (heat engine cycles) of piston-driven engines and turbines for power generation, it is more efficient, cleaner, decreases our dependence on oil and generate less greenhouse gas. The small-scale generation of $H_2$ for cost-effective use in the home for domestic electricity and heat production is now being actively practice mainly in Japan. Natural gas, a widely available infrastructure fuel, is converted to $H_2$ by steam reforming. The fuel cell powered vehicle will require an infrastructure similar to gasoline and diesel service stations. Hydrogen refueling stations are being constructed near large cities to accommodate $H_2$/fuel cell vehicles. The hydrogen will produced by steam reforming of natural gas but ideally it will someday be derived from water by electrolysis using renewable energy sources such as solar, wind, and geothermal energy on a large scale..

Given the need for smaller size reformers to be operated in local communities, safety will be an elevated concern [34].

## Production of Butyraldehyde: A Homogeneous Catalytic Reaction

*Butyraldehyde:* The incorporation of an inner layer of poly (vinyl butyral) or (PVB) in the glass of an automobile windshield protects against serious head injuries when a passenger strikes it during an accident. The strongly adherent coating is optically transparent and maintains the glass intact (anti-shattering agent) when a foreign object hits the surface. Thus, the glass does not shatter when a stone strikes its surface. PVB is produced by reaction of polyvinyl alcohol (PVA) with linear butyl aldehyde ($CH_3CH_2CH_2CHO$).



Another important application of butylraldehyde is in the production of oxo-alcohols for use as plasticizers used to improve mixing of solid compounds that must be molded or extruded into specific shapes. The hydrogenation catalyst is $Ni/Al_2O_3$.

$$CH_3CH_2CH_2CHO + H_2 \longrightarrow CH_3CH2CH_2CH_2OH$$

Butyl aldehyde is produced by a homogeneous catalytic process called hydro-formulation in which CO and $H_2$ are added to liquid propylene using a soluble cobalt-containing complex catalyst $Co(CO)_6$. The desired product is the linear form. The reaction is carried out with a butanol solvent

$$CH_3CH{=}CH_2 + H_2 + CO \longrightarrow 80\%\ CH_3CH_2CH_2CHO\ \text{(linear)} + 20\%\ \text{isomers}$$

The conditions needed to catalyze the reaction are very severe; pressure = 3,000–4,500 psig and 150°C. The high pressure maintains the propylene in solution, ensures sufficient solubility of the $H_2$ and CO, and maintains the Co-carbonyl complex stable against decomposition. The product distribution is 4:1 linear to other isomers.

Much less severe conditions can be used with the Wilkinson homogeneous catalyst rhodium tricarbonyl triphenyl phosphate, $HRh(CO)_3(PC_6H_5)_3$. Pressures equal to 225 psig and temperatures of 100°C selectively produce the more useful linear form [35]. The milder conditions more than compensate for the more expensive Rh (1,000 times that of Co). The aldehyde product is distilled leaving the catalyst in the solvent ready for reuse.

Homogeneous catalysts are structurally well-defined complexes and, because they are soluble in the reaction mix, are not subject to pore diffusion limitations as are heterogeneous catalytic materials. They are usually highly selective towards desired products. The main consideration is that the complex be stable and reactor conditions chosen such that all the gaseous reactants are adequately dissolved and mixed in the liquid phase. Homogeneous catalysts are easily characterized by standard instrumental methods for compound identification such as XRD or spectroscopy. Deactivation is associated with attack by traces of carboxylic acidic byproducts and impurities in the feed such as $O_2$ and chlorides that attack the ligand groups.

## Polyethylene and Polypropylene for the Production of Plastics

*Polyethylene:* Specially prepared plastics are replacing traditional metal components because of their strength, transparency, resilience, lighter weight, and corrosion resistance. The largest volume products are polyethylene and polypropylene. Each has its own contributions to the marketplace where the former is primarily used for low-strength applications such as milk and food containers while polypropylene is used when enhanced strength, higher melting temperatures, and greater resistance to chemicals such as chemical holding tanks and automobile bumpers are required.

There are two prevalent methods of producing polyethylene, both of which involve heterogeneous catalysts. A slurry phase process utilizes chromium oxide deposited on $SiO_2$ dispersed in a solvent such as cyclohexane at 80–150°C, a pressure between 300 and 500 psig. The process operates in a recycle mode with a residence time of 2–3 h. The product containing the solvent and polymer is flashed leaving the polymer. The catalyst is usually left in the polymer because its concentration is extremely low. The operating conditions are adjusted to produce both high- and low-density polyethylene. The active site is $Cr^{+2}$ produced by the reduction of $Cr^{+6}$ by ethylene. The reaction mechanism proposed is that the polymer coordinates with one of the $Cr^{+2}$ sites and the incoming ethylene coordinates with another site. Insertion of the ethylene into the double bond of polymer propagates its growth.

A second method of production utilizes the Ziegler–Natta $TiCl_4$ catalyst with liquid co-catalysts such as an alkyl aluminum halide. This is a reactive catalyst that must be prepared at the exclusion of air and water. The alkyl group of the co-catalyst coordinates with the $Ti^{+3}$ sites. The polymer grows by insertion of the ethylene into the double bond of the adsorbed polymer on another site.

*Polypropylene:* The most modern production route for polypropylene (PP) is also the Zeigler–Natta catalyst [36–38]. The catalyst is $TiCl_4$ supported on $MgCl_2$ along with aluminum alkyl halide co-catalyst such as diethyl aluminum fluoride $(CH_3CH_2)_2AlF$. The $MgCl_2$ is milled to a very disordered but active structure and the $TiCl_4$ is deposited on it. Production is carried out in a fluidized gas phase reactor between 50 and 100°C and 100–600 psig. Ethyl benzoate is also used as part of the catalyst preparation and functions to reduce the $TiCl_4$ to active $TiCl_3$. The role of the alkyl component of the co-catalyst is to coordinate with the $Ti^{+3}$ site where it inserts into the adsorbed polypropylene continuing the chain growth. The amount of catalyst used is so small it is retained in the final polymer product with no negative consequences. Unreacted gases are removed and recycled at the completion of the process. The most desirable product for the largest market is the isotactic form in which all $CH_3$ groups are on the same side of the polymer chain. Typically, it has a density of 0.9 $g/cm^3$, a melting point of 170°C, and an average molecular weight of 500,000. The polypropylene product is mixed in a separate reactor with ethylene to make a block polymer with enhanced mechanical properties.

Water, CO, and $O_2$ are the most significant poisons and are carefully removed upstream of the process.

The catalyst preparation and the production process are far more complicated than presented here, so the reader is encouraged to refer to more detailed references [36–38].

## Catalyst Challenges

Catalysts will have additional challenges as we advance in the twenty-first century. In this author's mind, one of the most critical is the need to balance our rapidly expanding energy needs with the environment. Catalysts are already playing a dominant role in pollution abatement and in the production of specialty petroleum and chemical products. The main challenge will be to use bio-renewable energy sources (Chap. 33) as well as solar, wind, geothermal, etc. with the specific goal of freeing us from the use of fossil fuels. A hydrogen economy coupled with the fuel cells holds great promise as one road to meet this challenge [33] especially for stationary energy sources as well as vehicle applications.

We are slowly moving towards more renewable and sustainable sources of energy however it is necessary that the use of fossil fuels will continue for the for-see-able future. Therefore we must address climate change and the growth of $CO_2$ resulting from combustion of carbon based fuels. Capture and sequestration technologies are being advanced however major breakthroughs are still needed. Many of these new technologies will involve catalysts for economic conversion of $CO_2$ to useful products. This will be an exhilarating ride as we find our way to clean energy.

Another area of great importance is the application of bio-catalysis using enzymes to produce a growing number of pharmaceutical agricultural products and fuels such as ethanol. This subject is outside the scope of this review so other sections of this Handbook (see Chap. 31) should be consulted.

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