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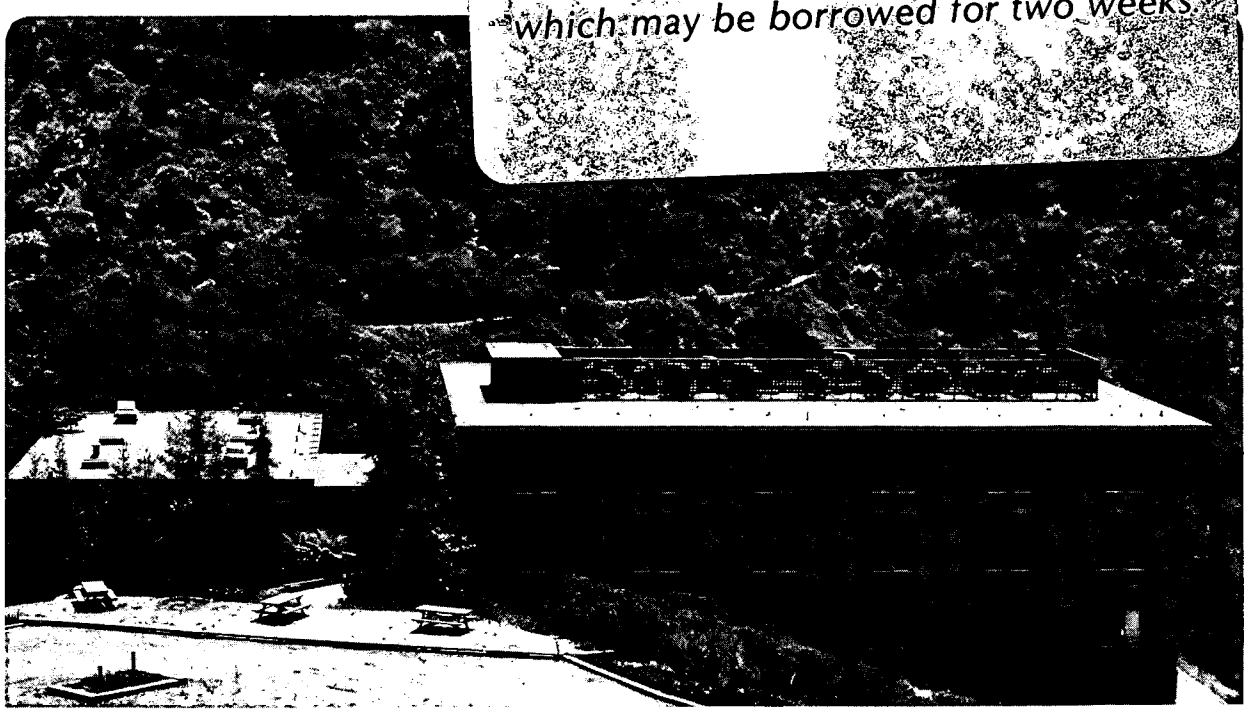

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# HOMOGENEOUS, HETEROGENEOUS AND ENZYMATIC CATALYSIS

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## HOMOGENEOUS, HETEROGENEOUS AND ENZYMATIC CATALYSIS

### INTRODUCTION

Catalysts have been employed by mankind since antiquity in such activities as wine, bread and cheese making. In many cases it was found that the addition of a small portion from a previous batch, a "starter", was necessary to begin the next production. In 1835 Berzelius published an account which tied together earlier observations by chemists such as Thénard, Davy and Döbereiner by suggesting that minute amounts of a foreign substance were able to greatly affect the course of chemical reactions, both inorganic and biological. Berzelius attributed a mysterious force to the substance which he called catalytic (1,2,3). In 1894 Ostwald proposed that catalysts are substances that accelerate the rate of chemical reactions without themselves being consummed during the reactions (4,5). This definition is still applicable today.

The scope of catalysis is enormous. Catalysts are widely used in the commercial production of fuels, chemicals, foods and medicines. They also play an essential role in processes in nature, like nitrogen fixation, metabolism and photosynthesis.

### CLASSIFICATION

Catalysts can be protons (6,7), ions (8,9,10), atoms (11,12), molecules (11) or larger assemblages. Traditionally, catalysts have been classified as homogeneous, heterogeneous and enzymatic, reflecting this increasing hierachy of complexity.

The first four species above may be considered examples of **homogeneous** catalysts (13). In addition, metal complexes and organometallic compounds are important members of this class of catalysts (14,15,16). As the name implies, these catalysts are uniformly dispersed or dissolved in a gas or liquid phase together with the reactant of the reaction.

In contrast to homogeneous catalysts, **heterogeneous** catalysts are usually solid surfaces, attached to solid surfaces, or part

of insoluble matrices such as polymers, and are, thus, phase-separated from the fluid medium surrounding them. Regardless of their form, the active catalytic component is located at the interface between the solid and the fluid and may consist of a wide diversity of species. Examples are: one or two atoms of the total surface (17), a larger ensemble of such surface atoms (18,19,20,21,22), an organometallic compound attached to the surface by covalent bonds (23), or a molecular cluster lying on the surface (24,25).

**Enzymatic** catalysts are like homogeneous catalysts in being dissolved in liquid media, but enzymatic catalysts are of biological origin and possess the highest level of complexity among the three types (26,27,28,29,30,31,32). Ironically, as mentioned in the opening sentence, they were probably the first catalysts utilized by man. Enzymatic catalysts are proteins composed of repeating units of amino acids, often twisted into helices, and in turn folded into 3-dimensional structures. The protein structures often surround a central organometallic structure.

**FUNDAMENTALS**

The action of catalysts will be illustrated by an example, the water gas shift reaction catalyzed by iron and chromium oxides.

$$H_2O + CO \quad ----> \quad H_2 + CO_2$$

This reaction is used in the production of hydrogen in several commercial processes. It is an example of a heterogeneous catalytic reaction, but the principles derived from it are also applicable to homogeneous and enzymatic catalytic reactions. A simplified scheme for the reaction is presented below.

$$H_2O + * \quad ----> \quad H_2 + O*$$

$$CO + O* \quad ----> \quad CO_2 + *$$

In the first step, one of the reactants, $H_2O$, reacts with an empty catalytic site, denoted by *, to produce a product, $H_2$, and a reactive intermediate consisting of an oxygen atom associated with the site, denoted by O*. In the second step, the other reactant, CO, reacts with the intermediate to produce the product, $CO_2$, and regenerating the catalytic site, *. The energetics associated with this process are given in Figure 1. A key aspect of this scheme is that it represents a cycle which occurs many times as the reaction proceeds. Each repetition of the cycle is called a **turnover**. A good catalyst will have millions of turnovers. In contrast, a stoichiometric reactant will have only one. Several important points are to be made concerning the energetics and scheme presented above.

1.) The energy level diagram shows that the catalyzed reaction has a **lower activation barrier** (33) than the uncatalyzed thermal reaction. This is the origin of the

enhancement in the rate and it applies both in the forward and reverse directions of the reaction.

2.) Regardless of the details of the mechanism and the energetics of the transformation of R into P, their relative energies, as shown by $\Delta H^{o}_{reaction}$, do not change (34). This means that the thermodynamic equilibrium between them does not change. Catalysts increase the **rate of approach to equilibrium** but not the thermodynamic equilibrium value itself.

3.) As shown by the overall reaction stoichiometry, there is **no net consumption or production** of the catalytic site, *. The reaction proceeds by repetition of the catalytic cycle or chain, with the catalytic species remaining **unchanged** at the end. This explains the observation noted earlier that miniscule amounts of catalyst can give rise to very large amounts of product.

4.) The intermediate, O*, must be **neither too stable or too unstable**. If it is too stable, it will not decompose to form the product; if it is too unstable, it will not form in the first place.

**NOMENCLATURE**

The performance of catalysts is generally described by their activity, conversion, selectivity and yield. **Activity** is a measure of the rate at which the catalyst is able to transform reactants into products and is given in terms of an extensive property of the catalyst, such as mass, volume or number of moles. **Active sites** are the atomic or molecular species responsible for catalytic activity (represented by the symbol * in the previous section). Their identity and number are in general very difficult to measure. Various examples of the type of entities they might be are given in the definitions of the three kinds of catalysts. **Turnover frequency**, also known as turnover number or turnover rate, is the most fundamental measure of the activity, and represents the rate at which the catalytic cycle proceeds. It is equivalent to the number of molecules undergoing transformation per active site per unit time. The term **conversion** refers to the percentage of a reactant that is reacted to form all products. The term **selectivity** is applied to a specific product and refers to the percentage of that product among the total products formed. Equivalently, it is equal to the the percentage of the product formed of the total reactant consumed. A high selectivity implies little waste of reactant. **Yield** is the product of conversion and selectivity, and is a measure of the efficiency of carrying out a particular transformation. **Specificity** is used mainly with enzymatic catalysts and describes their propensity to carry out only one type of reaction or to act upon only one isomer of a particular compound.

Other terms chiefly pertain to industrial applications of catalysts. **Stability** and **lifetime** refer to the ability and length of time that a catalyst is able to maintain the conversion and selectivity necessary to run a process. **Deactivation** refers to the loss of catalytic function by any of

a number of causes such as decline in surface area, decomposition of active species, or poisoning. **Denaturization** describes the deactivation of an enzyme by the loss of its 3-dimensional folded structure. This is generally caused by extremes in temperature or pH. **Poisoning** is a type of deactivation caused by the strong binding of a foreign substance to the active site of a catalyst in competition with the reactant. **Regenerability** refers to the ability to chemically or physically treat a catalyst that has lost its activity.

## INDUSTRIAL USAGE OF CATALYSTS

The following section describes the most important catalysts employed commercially in the world as listed in Tables 1 and 2. The section dealing with **fuels** covers the major operations used in the refining of petroleum. The section involving **chemicals** describes a few of the major processes used to produce industrial chemicals. The section covering **foods and medicines** deals exclusively with enzymes.

### FUELS(35)

#### Catalytic cracking (36)

These catalysts are used to refine a moderately heavy crude oil fraction known as gas oil to gasoline. The net result of the process is a lighter product with a high content of branched-chain and aromatic hydrocarbons, the species responsible for raising gasoline octane levels. The transformations are complex, but can be considered to involve the following major acid-catalyzed reactions:

1. C-C bond breaking: $C_{18}H_{38}$ ----> $C_{10}H_{22}$ + $C_8H_{16}$
   paraffin — paraffin + olefin
2. Dealkylation: $ArC_4H_9$ ----> $C_4H_8$ + $ArH$
   alkyl aromatic — olefin + aromatic
3. Hydrogen transfer: $C_6H_{12}$ + $3C_8H_{16}$ ----> $C_6H_6$ + $3C_8H_{18}$
   cycloparaffin + olefin — aromatic + paraffin
4. Isomerization: $n\text{-}C_{10}H_{20}$ ----> $i\text{-}C_{10}H_{20}$
   olefin — isoolefin

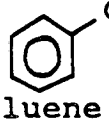
The heterogeneous catalysts employed in cracking are acidic materials composed of 3 to 25 weight percent zeolites embedded in a silica-alumina matrix. Zeolites are crystalline alumino-silicates possessing a network of uniform pores whose walls hold the catalytically active acid sites. The reactant molecules pass through the pores and react within the zeolites.

Reforming (36,37,38,39,40)

The catalysts are employed to treat naphtha, a fraction of crude oil somewhat lighter than gas oil and containing large amounts of straight-chain paraffins. Several examples of typical reactions carried out by these catalysts are given below. The result of these reactions is to reconstruct or "reform" the hydrocarbons in the feed so as to increase the octane level. The catalysts here differ from cracking catalysts because they tend not to alter the carbon number of the reactants and because they produce a substantial amount of byproduct hydrogen gas.

1. Isomerization: $n\text{-}C_7H_{16}$ ----> $CH_3\text{-}CH_2\text{-}CH_2\text{-}C(CH_3)_2\text{-}CH_3$

n-heptane 2,2-dimethylpentane

2. Dehydrocyclization: $n\text{-}C_7H_{16}$ ---->  + $H_2$

n-heptane toluene hydrogen

3. Aromatization:  ---->  + $3H_2$

methylcyclohexane toluene hydrogen

These heterogeneous catalysts consist of multimetallic clusters, containing metals such as platinum, iridium or rhenium, supported on porous acidic oxide supports such as alumina. The catalysts are said to be bifunctional because both the metal and the oxide play a part in the reactions. The metal is believed to carry out reversible dehydrogenation of paraffins to olefins, while the oxide is believed to carry out isomerization.

Hydrocracking (41,42,43)

Hydrocracking catalysts are used to reduce the molecular weight of a feedstock. A typical use is the conversion of light gas oil to naphtha for gasoline production through reforming. An example of a characteristic reaction is given below.

$$n\text{-}C_{16}H_{34} + H_2 \text{ ----> } n\text{-}C_7H_{16} + i\text{-}C_9H_{20}$$

n-hexadecane n-heptane iso-nonane

These heterogeneous catalysts contain nickel, cobalt, molybdenum, tungsten, platinum or palladium on acidic aluminum silicate or zeolite supports. As with reforming catalysts, the catalysts here are also believed to be bifunctional with the metal component carrying out the reversible dehydrogenation of paraffins to olefins. Hydrocracking is carried out in the presence of hydrogen and produces saturated products.

Hydrotreating (36,44,45,46,47)

Hydrotreating comprises a mild hydrogenolysis of nitrogen,

oxygen and sulfur compounds prior to catalytic cracking. Typical reactions carried out in this step are illustrated below.

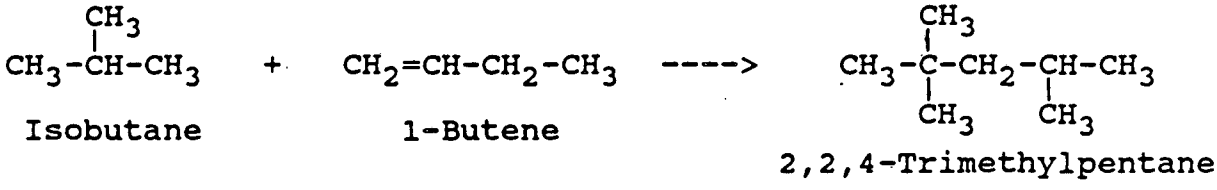
1. Desulfurization: $R\text{-}SH + H_2 \longrightarrow RH + H_2S$

2. Denitrogenation: $R\text{-}NH_2 + H_2 \longrightarrow RH + NH_3$

Hydrotreating catalysts are composed of cobalt or nickel molybdate or nickel tungstate on an alumina or zeolite support. The materials are sulfided with $H_2S$ before use but the final catalyst may retain some oxide and be of complex composition.

Alkylation

Alkylation converts isobutane and butylenes produced in the catalytic cracking step into a mixture of dimers known as alkylate. This product is a gasoline blending stock of high octane value. Alkylation catalysts are homogeneous liquid catalysts, either sulfuric or hydrofluoric acids.




Isobutane 1-Butene 2,2,4-Trimethylpentane

CHEMICALS (36,48,49,50,35)

Polymerization (36,51)

These catalysts are employed in the production of polymers such as linear low-density polyethylene (LLDPE). An example of these catalysts are Ziegler-Natta catalysts, combinations of titanium halides with aluminum and magnesium alkyls.

$$n\ CH_2{=}CH_2 \longrightarrow -(-CH_2\text{-}CH_2)_n-$$

ethylene LLDPE

Alkylation (49)

These catalysts are used to make carbon-carbon bonds, as in the liquid phase alkylation of benzene to ethylbenzene, a styrene precursor. The catalyst in this case is aluminum chloride.

$$C_6H_6 + CH_2{=}CH_2 \longrightarrow C_6H_5\text{-}CH_2\text{-}CH_3$$

benzene ethylene ethylbenzene

Hydrogenation (52,53)

These catalysts are used to add hydrogen to unsaturates, as in the hydrogenation of vegetable oils to form hardened oils. Most catalytic systems consist of nickel or a noble metal on a

support.

$CH_3(CH_2)_4CH=CH-CH_2-CH=CH(CH_2)_7COOH$ ----->

linoleic acid $CH_3(CH_2)_7CH=CH(CH_2)_7COOH$

oleic acid

Dehydrogenation (49,54)

These catalysts are used to remove hydrogen from hydrocarbons. Many catalysts have been developed, including metals and oxides. An example of the latter is chromia-alumina used in the dehydrogenation of butane.

$CH_3-CH_2-CH_2-CH_3$ ----> $CH_2=CH-CH=CH_2$

butane butadiene

Oxidation, ammoxidation and oxychlorination (55,56,57, 58,59,60,61)

Numerous catalysts have been developed for a number of processes that fall under this category. Examples are supported vanadium oxide, complex multimetallic oxides and supported cupric chloride, respectively, for the reactions listed below.

1. Butane oxidation: $C_4H_{10} + O_2$ ----> $C_4H_2O_3$

butane maleic anhydride

2. Ammoxidation: $C_3H_6 + O_2 + NH_3$ ----> $CH_2=CH-CN$

propylene acrylonitrile

3. Oxychlorination: $C_2H_4 + Cl_2 + O_2$ ----> $ClCH_2-CH_2Cl$

ethylene 1,2-dichloroethane

Ammonia, hydrogen and methanol production (62,63,64, 65,66,67,68,69)

The ammonia synthesis catalyst is metallic iron promoted with $Al_2O_3$, $K_2O$, MgO and CaO. The hydrogen-producing (methane reforming) catalyst is supported nickel. The methanol synthesis catalyst is ZnO promoted with $Cr_2O_3$ or Cu(I)-ZnO promoted with $Cr_2O_3$ or $Al_2O_3$. The respective reactions are cited below.

1. Ammonia synthesis: $N_2 + 3H_2$ ----> $2NH_3$

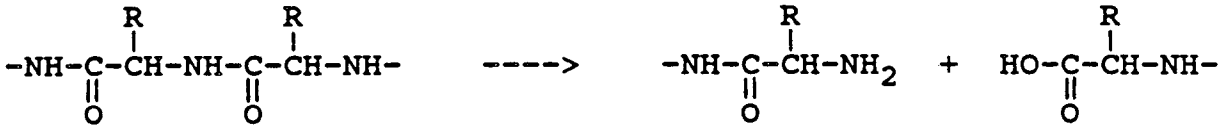
2. Methane reforming: $CH_4 + H_2O$ ----> $CO + 3H_2$

3. Methanol synthesis: $CO + 2H_2$ ----> $CH_3OH$

FOODS, MEDICINES AND OTHER PRODUCTS (35,78)

Proteases (70)

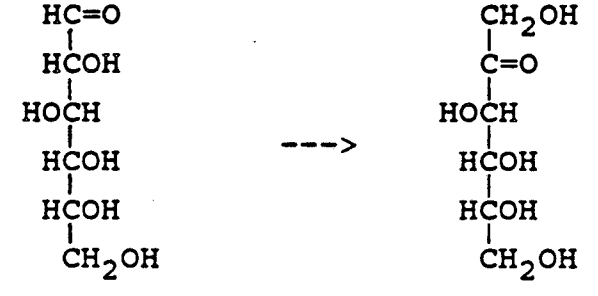
The function of these enzymes is to hydrolyze the peptide bond in proteins. Considerable variety exists in source, specificity, and reaction conditions for these enzymes.



1.) Alkaline proteases are derived from bacteria. They find wide application in detergents, leather tanning, protein hydrolysis, brewing and silver recovery from film.
2.) Papain (71) is a plant protease derived from the papaya fruit. The enzyme is employed in digestive aids, wound debridement, tooth-cleaning and, most importantly, as a meat tenderizer.
3.) Bromelain is another plant protease with similar uses to that of papain. It is obtained from the stumps left over from pineapple harvests.
4.) Rennet (72) or rennin is an animal protease derived from the stomachs of calves as well as from microorganisms. It is employed in the manufacture of cheese to clot milk.

Glucose isomerase (73)

This enzyme is found in many organisms and in practice is used in the form of entrapped cells or bound to ion-exchange resins. It converts glucose to fructose, one of the principal components of table sugar.

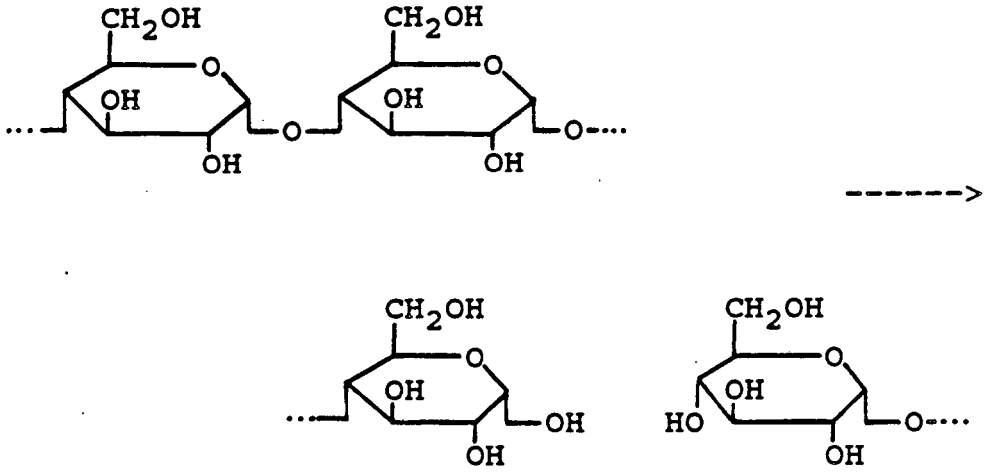


D-Glucose D-Fructose

Leather bating enzymes

These enzymes are employed in leather manufacture to remove flesh from hides. They are generally derived from hog and beef pancreas and consist of mixtures of enzymes that attack both proteins and lipids.

Amylases (70,74)
These enzymes hydrolyze the D-glycosidic linkage in starch.



1.) Glucoamylase is found in blood, molds and bacteria. It produces glucose by removing the end glucose unit in long-chain carbohydrates such as starch, glycogen, dextrins and maltoses. Its main commercial use is in the production of glucose syrup, glucose paste and crystalline glucose.
2.) Other amylases, constituting a large family of enzymes that act on different substrates, are found in saliva, animal tissues, plants, yeasts and other microorganisms. They find wide use in the manufacture of glue, starchy syrups, and in various steps in the production of brewery and bakery products.

Pectinases (70)
These enzymes carry out the hydrolytic degradation of the D-glycosidic linkage in pectins. The latter substances, also known as pectic substances, are polymeric components of plant cell walls and like starch are composed of sugar residues linked by glycosidic bonds. The chemistry is the same as shown for the amylases above. The main application of pectinases is in the production of fruit juices, wines, and other food products.

**ECONOMIC IMPACT OF CATALYSIS**
Catalysts have a subtantial economic role in modern society. U.S. sales of process catalysts (those involving refining and chemical processes) amounted to 4.86 billion lb in 1985 corresponding to a value of $955 million. These figures are forecasted to rise to 5.4 billion lb in 1990 corresponding to a value of $ 1.12 billion (75). The inclusion of emission and pollution control catalysts raises these numbers by $510 million in 1985 and by $620 million in 1990 (76). Table 1 provides a breakdown of these figures among the various catalyst categories. The addition of sales from the fermentation industry adds several hundred millions of dollars to these

figures (77).

The figures above are for the U.S. market. Inclusion of sales for Western Europe and Japan raises the total worldwide sales value to $2.5 billion in 1985, predicted to rise to $4-5 billion in 1990 (76).

Acid catalysts for alkylation in the liquid phase dominate the production of commodity fuels and chemicals. These homogeneous catalysts, in the form of aluminum chloride, sulfuric, phosphoric and hydrofluoric acids, account for 90% of the total volume of process catalysts (Table 1). In terms of value, however, heterogeneous catalysts amount to 80% of total sales.

In comparison to fuel and chemical process catalysts, enzymes have smaller markets in volume and sales (Table 2). In 1980 the estimated value of worlwide enzyme sales was $290 million (78). In 1983 another estimated value was $350-400 million (79). These figures do not include the value of enzymes used internally by food and pharmaceutical producers. By 1990 total sales are predicted to rise to nearly $500 million (Table 2).

## PERSPECTIVES ON CATALYSIS

Although homogeneous liquid-phase acids are the industrial catalysts used in the highest volume (Table 1), they have low specificity, and, thus, limited use in new reactions requiring high product selectivity. As new catalysts, organometallic compounds are particularly attractive because of the possibility of systematically varying their organic ligands so as to obtain desired catalytic properties. (14-16) Advances in precise inorganic and organometallic synthesis are making possible the design of engineered catalysts (80). From an industrial standpoint homogeneous catalysts are difficult to use because they are not readily separable from the products which are formed in the same phase. However, advantages in activity, selectivity or severity of reaction conditions override these considerations. New technologies involving immobilization (81) and phase transfer catalysis (82,83,84,85,86,87,88) will be used to overcome the separations problems.

From an engineering standpoint heterogeneous catalysts are the easiest catalysts to handle because they are stable at high temperature and phase-separated from the reactants and products. They thus find widespread use in industry. Despite their importance they have been difficult to understand from a fundamental standpoint. New advances are rapidly changing this. The techniques of surface science (89,90,91) which allow the use of surface-sensitive spectroscopies such as low energy electron spectroscopy (LEED), x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES), allow the examination of model catalysts in the form of single crystals (92,93). Spectroscopic techniques such as Fourier transform infrared spectroscopy (FTIR), extended x-ray absorption fine structure

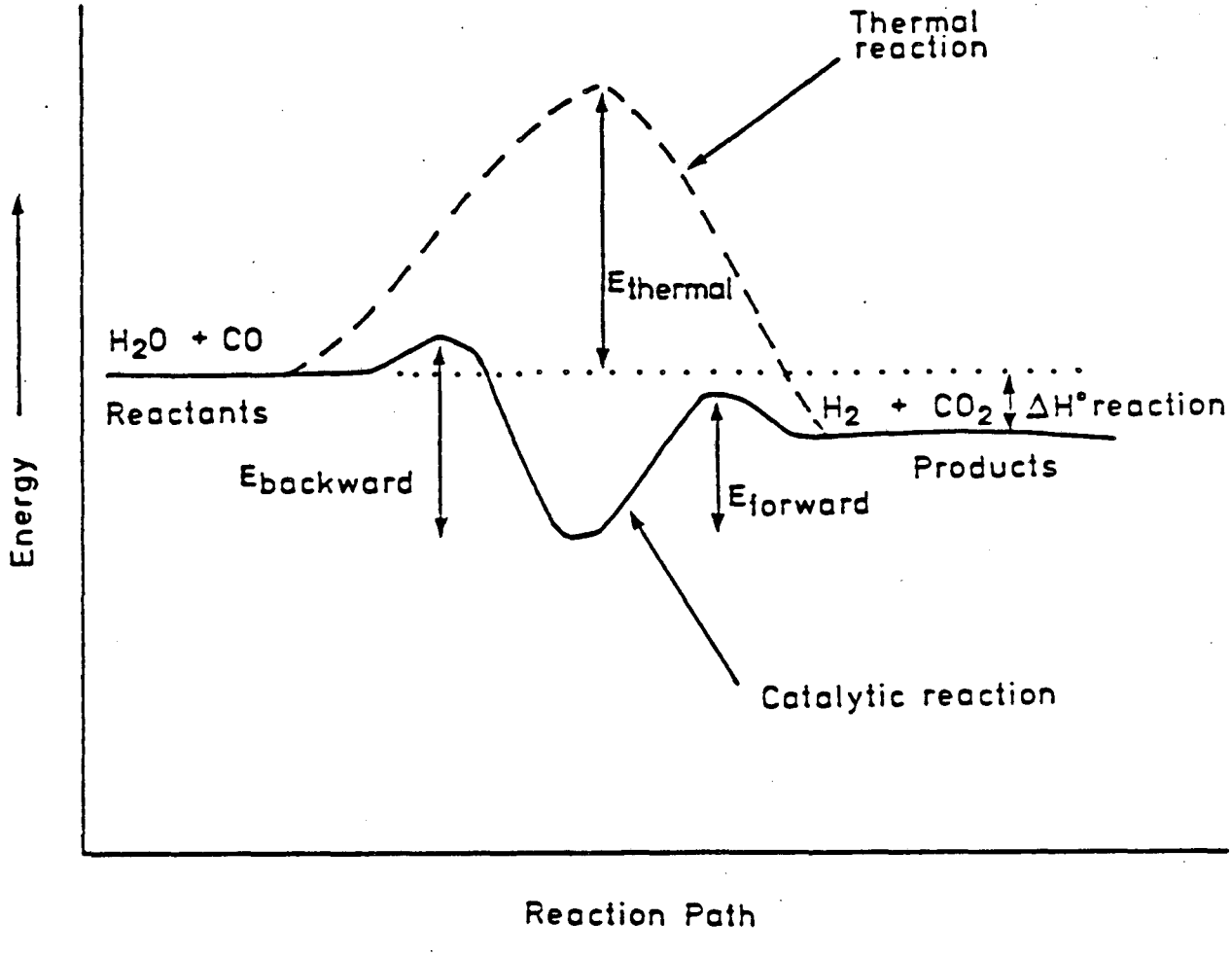
(EXAFS) and laser Raman spectroscopy and the use of dynamic techniques (94) allow the examination of the catalyst surface at reaction conditions.

The active surface on heterogeneous catalysts provides a different environment from the active sites on homogenous or enzymatic catalysts. On a surface the presence of adjacent sites and the possibility of surface diffusion (95) allows numerous reactive species to come together or a single reactive intermediate to migrate from site to site. On homogeneous metal complexes or in enzymes the need for coordinatively open sites create much more stringent requirements on the number of species that can react at an active site. Furthermore, because surfaces can have a wide range of energetically different sites (96,97) and because variations in coverage can change the energetics of the entire surface (98), surfaces have a built-in adaptability to reaction conditions (99).

Enzymes possess extremely high specificity and activity. Their complexity makes them very difficult to understand. In many cases they are able to react with only one particular group in a substrate, even in the presence of other very similar groups. They show very high activity, being able to carry out reactions at physiological temperatures, that heterogeneous catalysts can only carry out at elevated temperatures. From an industrial standpoint, because like homogeneous catalysts enzymes are dispersed in solution, their separation from the reaction products is difficult. Techniques such as immobilization are being developed to solve this problem (100,101,102). However, in many cases enzymes are used to break bonds in massive or insoluble substrates, and for this purpose immobilization is detrimental. Other limitations are that enzymes are difficult to obtain in pure form, tend to work in a narrow temperature and pH range and are sensitive to strong chemicals. A possible solution to these problems may be designed synthetic enzymes produced through such techniques as genetic engineering (103). Synthetic enzymes could offer ease of purification, increased stability to heat or denaturizing agents, use in non aqueous solvents and even catalysis of new reactions (104,105,106).

FIGURES

Figure 1. Energy level diagram for the hypothetical catalytic and thermal water gas shift reaction. The overall heat of reaction is given by $\Delta H^{o}_{reaction}$, the activation barriers in the forward and backward direction by $E_{forward}$ and $E_{backward}$, respectively, and the activation barrier for the thermal reaction by $E_{thermal}$.



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34. Again, strictly speaking it is a free energy of reaction, $\Delta G^{o}$. The equilibrium constant is given by $K = \exp(-\Delta G^{o}/RT)$.

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Table 1
**Estimated U.S. Catalyst Volume and Sales**

| | 1985 | | 1990 | |
|---|---|---|---|---|
| | Volume ($10^6$ lb) | Value ($10^6$ $) | Volume ($10^6$ lb) | Value ($10^6$ $) |
| **PETROLEUM REFINING**[a] | **4670** | **545** | **5160** | **620** |
| Catalytic cracking | 370 | 250 | 405 | 275 |
| Reforming | 4.5 | 23 | 4.7 | 24 |
| Hydrocracking | 1.8 | 36 | 2.0 | 40 |
| Hydrotreating | 28 | 77 | 38 | 104 |
| Alkylation | 4265 | 160 | 4710 | 177 |
| **CHEMICAL PRODUCTION**[a] | **190** | **410** | **230** | **500** |
| Polymerization | 50 | 175 | 60 | 220 |
| Alkylation | 90 | 50 | 110 | 60 |
| Hydrogenation | 9.6 | 35 | 11 | 40 |
| Dehydrogenation | 3.7 | 10 | 4.6 | 12 |
| Oxidation, ammoxidation, and oxychlorination | 11 | 85 | 14 | 105 |
| Ammonia, hydrogen, and methanol production | 26 | 55 | 31 | 60 |
| **EMISSION AND POLLUTION CONTROL**[b] | N/A | **510** | N/A | **620** |
| **TOTAL** | **4860**[c] | **1465** | **5390**[c] | **1740** |

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[c] Do not include emission and pollution control figures.

N/A Not available.

Table 2

**Estimated Worldwide Enzyme Volume and Sales**

| | 1980 | | 1990 | |
|---|---|---|---|---|
| | Volume[a] ($10^6$ lb) | Value[b] ($10^6$ $) | Volume ($10^6$ lb) | Value[c] ($10^6$ $) |
| **ENZYME** | | | | |
| Alkaline protease | 1.0[b] | 80 | N/A | 220 |
| Glucose isomerase | 0.1 | 45 | N/A | 40 |
| Leather bating | N/A | 30 | N/A | N/A |
| Papain | 1.2[b] | 30 | N/A | N/A |
| Rennets | 0.02 | 30 | N/A | 75 |
| Glucoamylase | 0.7 | 25 | N/A | 50 |
| Other amylases | 0.7 | 21 | N/A | 25 |
| Pectinase | 0.02 | 6 | N/A | N/A |
| Bromelain | 0.08[b] | 3 | N/A | N/A |
| All others | N/A | 20 | N/A | N/A |
| **TOTAL** | **3.82** | **290** | N/A | **499**[d] |

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[c] D. Owings, Eur. Chem. News, Chemscope, p. 23, October, 1984.

[d] Assumes 1980 figures for unavailable 1990 figures.

N/A Not available

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