

CHAPTER II

THEORY

2.1 Composition of Petroleum

Petroleum is a mixture of a tremendous number of organic compounds of different basic structures and varying molecular weights. Most of them are hydrocarbons. They consist of a normal and branched-chain paraffins, naphthenes, and aromatics. Higher cyclic compounds such as polyalkylindanes and higher aromatics such as polyalkylanthracenes and phenanthrenes as minimum are believed to occur as well, together with other even more highly condensed and much higher molecular weight compounds.

Petroleum also contains sulfur and its compounds in varying amounts. A "sour" crude contains dissolved hydrogen sulfide. Sulfur itself may be present in elementary form. The most common of organic sulfur compounds are mercaptans, disulfides, sulfides, and thiophenes.

Nitrogen compounds also occur in petroleum. In general these comprise more highly condensed structures, such as the alkylquinolines. Oxygen can also occur in similar condensed structures and in such compounds as the naphthenic acids. In addition there are traces (usually parts per million) of metalorganic compounds that contain such elements as iron, vanadium, nickel, and arsenic.

These, then, are the general structures of the types of compounds present in petroleum. Within each structural type, molecular weights vary tremendously. When petroleum is distilled, first at atmospheric pressure and then under vacuum, series of compound mixtures are obtained. Most volatizes are the dissolved gases, which are low-molecular-weight hydrocarbons (up to about C₅). Next in boiling point are gasoline and solvent naphtha, followed by kerosene. Then come diesel oils and light and heavy fuel oils . The last to distil are the heavy mineral oils, lubricating oils, petrolatum, road oils, asphalt, and coke. Each fraction is a mixture of a tremendous number of different compounds, which have the basic structures indicated above [5,6,7].

2.2 Catalysis

Catalysis is the science of accelerating chemical reactions that under normal conditions proceed only slowly or not at all. The rate of a chemical reaction can be controlled by a few parameters only: temperature, pressure and composition. In addition, the choice of a suitable catalyst may change the reaction pathway. As a consequence, the overall reaction rate may be increased and / or new pathways, and therefore new products, may become feasible. A chemical reaction is the result of a collision of two or more molecules or atoms. The function of a catalyst is merely to capture the participants of the reaction, to bring them in close contact and thus to guide them through some reaction pathway. The combination of catalyst and reactant(s) dictates the pathway. The characteristics

are important in describing a catalyst. First of all, its activity that is the rate at which the products are generated. The higher activity is the better catalyst. Secondly, it is the selectivity. In most cases, a catalyst produces a wide range of products, some of which are useful and others are not. By selectivity in general we mean the fraction of useful products, usually expressed as a percentage. A high selectivity indicates that the catalyst produces mainly the desired products.

2.2.1 Definitions of Catalyst

The basic concept of a catalyst is that of a substance that in small amount causes a large change. More precise definitions of catalysis and of what constitutes a catalyst have gradually evolved as understanding of the cause of catalytic phenomena has grown. Even today there is no universal agreement on definitions, the point of view varying somewhat depending upon the investigator; for example, as between the fundamental investigator and the practitioner, and among researchers concerned with heterogeneous catalysis, homogeneous catalysis, polymerization reactions, and enzymes. For purposes however our definition is: a catalyst is a substance that increases the rate of reaction without being appreciably consumed in the process [8].

This basic concept, stemming from the chemical approach to catalysis, is that a reaction involves a cyclic process in which a site on a catalyst forms a complex with reactants, from which products are then desorbed, thereby restoring the original site. This leads to the idea that a catalyst is unaltered by the reaction it catalyzes, but this is misleading. A catalyst may undergo major changes

in its structure and composition as part of the mechanism of its participation in the reaction. A pure metal catalyst will frequently change in surface roughness or crystal structure on use. The ratio of oxygen to metal in a metal oxide catalyst will frequently change with temperature and composition of the contacting fluid.

2.2.2 Categories of Catalysts

Catalysts are known in many varieties, but in principle they can be classified into two categories [9]: homogeneous and heterogeneous catalysts. Homogeneous catalysts can be mixed perfectly with the reactants. i.e., up to molecular scale. Homogeneous catalysis mainly occurs in the liquid phase. All the enzymes at work in our body are homogeneous catalysts. In heterogeneous catalysis, the catalyst, the reactants, and the products are in separate phases and therefore the mixing is far from perfect. The catalyst is usually a solid and the reactants are liquids or gases. The automotive catalyst is an example of a heterogeneous catalyst. The reactants, hydrogen, carbon monoxide and nitric oxides, and the products, water, carbon dioxide and nitrogen, are gaseous while the active catalyst is a combination of several precious metals supported on some (inert) support.

2.2.3 Catalytic Activity

The activity of a catalyst refers to the rate at which it causes the reaction to proceed to chemical equilibrium. The rate may be expressed in any of several ways. The performance of an industrial reactor is frequently given in term

of a space-time yield (STY), which is the quantity of product formed per unit time per unit volume of reactor.

With Mars and Krevelen mechanism bearing in mind one can expect a relation to exist between the metal-oxygen bond strength and the catalytic activity. Also the coordination of the metal ion (tetrahedron and octahedron), the crystallographic structure of the oxide and the acidity of the oxide, which plays a role in abstraction of H-atoms, can influence the activity of a catalyst[10].

2.3 Reaction Pathways

Consider a gas-phase reaction, which may occur either homogeneous or heterogeneous, the two reaction pathways occur simultaneously. In order for the catalyzed reaction to be observed it must occur measurably faster than the homogeneous reaction.

The rate of a single elementary step of a homogeneous reaction is proportional to a rate constant k that varies with temperature according to the Arrhenius relationship, $k = Ae^{-E/RT}$, where E is the activation energy and R is the gas constant. The preexponential factor A is a constant that in collision theory is identified as a collision number for bimolecular processes and, for unimolecular processes, as a frequency factor or the probability of reaction of an activated molecule.

The ability of a catalyst to increase a reaction rate can be ascribed in a general way to its causing a reduction in the activation energy of the reaction.

But even for the simplest kind of reaction, the single-step conversion of A to B, the situation is considerably more complicated than this simple statement may imply. The catalyzed reaction involves three rate processes: adsorption, the formation and breakup of an activated complex, and desorption of products. Each of these has its own activation energy. The rate of each is also determined by the total surface area of the catalyst present (or, more precisely, the number of active sites) and by the concentration on the catalyst surface of various adsorbed species. The idealized homogeneous reaction has single activation energy, and its rate is a function of the gas-phase concentration.

In order for a reaction to be noticeably catalyzed, the various factors that determine the overall rate of the heterogeneous reaction must in the entirety of their interactions outweigh that of the different group of factors that determine the rate of the homogeneous reaction. Generally the most important effect of the catalyst is to provide a pathway whereby the activation energy for the formation of the intermediate surface complex is considerably less than for the homogeneous reaction. Because the activation energy appears in the rate equation as an exponent, a slight change in activation energy has a marked effect on the rate.

The rate of catalyzed reaction is proportional to the active surface area, and the rate of a homogeneous reaction is proportional to the volume of fluid. Hence the maximum ratio of the catalyzed rate to the homogeneous rate occurs with the use of high-area (porous) catalyst pellets packed in a reactor. Catalysts such as those frequently utilized in practice have areas of the order of

100 m²/g or more. Arguments based on the absolute theory of reaction rates show that, although there is not usually observed, there is entirely possible for the observed rate of a catalyzed reaction to proceed faster than the corresponding homogeneous reaction even when the activation energy for the rate-limiting step on the catalyst is on less than that for the homogeneous reaction [11].

The changes in energy associated with the different steps in a simple exothermic reaction can be depicted as shown in Figure 2.1. E_{hom} is the activation energy for the homogeneous reaction, E_{ads} for adsorption of reactants onto the catalyst, E_{cat} for the formation of the activated complex, and E_{des} for the desorption of products. λ_{ads} is the heat of adsorption of reactants, taken to be exothermic, and λ_{des} is the heat of desorption of products, taken to be endothermic. The overall energy change upon reaction is ΔH and is, of course, the same for the two pathways.

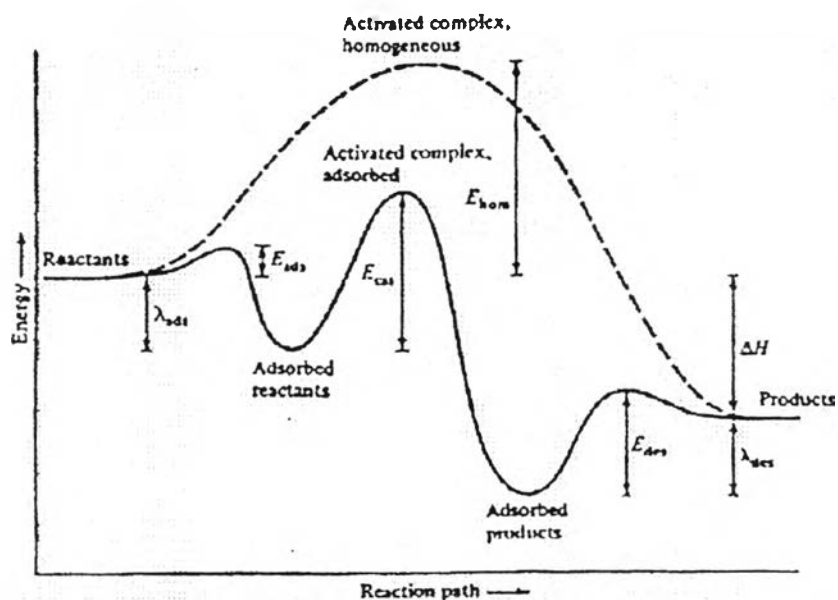


Figure 2.1 Energy changes associated with individual steps of a reaction[11]

From experimental rate data, an “apparent activation energy” can be calculated from the slope of the reciprocal of the absolute temperature. To proceed from this calculation of the activation energy of a surface process in the general case requires a knowledge or assumption of the mechanism of the surface reaction, identification of the rate-controlling step, and heats of adsorption and desorption. This treatment also shows that there is no reason why a straight-line relationship between $\log k$ and $1/T$ should be expected to be encountered over a substantial range of temperature. It will usually be found that the apparent or effective activation energy for a catalyzed reaction is less than that for the same reaction proceeding homogeneously, both being determined from the slope of an Arrhenius plot. It is to be emphasized, however, that there is no fundamental reason why this should always be the case. Nevertheless, a consequence of this

common behavior is that with increased temperature a point will usually be reached beyond which the rate of a catalyzed reaction will be exceeded by the rate of the homogeneous reaction.

With some endothermic reactions high temperatures are required in order for a substantial amount of the product to be present at equilibrium, and it may be found that these temperatures are so high that any catalyst achieves no significant increase in rate. An example is the dehydrogenation of ethane to form ethylene and hydrogen, in which a temperature of about 725 °C is required for 50 percent conversion to equilibrium at atmospheric pressure. Little increase in rate is obtained with a heterogeneous catalyst, For conversion of higher paraffin such as butene, however, a specified degree of conversion to equilibrium can be obtained at considerably lower temperatures than with ethane, and a substantial increase in rate is observed with use of a catalyst.

2.4 Zeolites

Zeolites are crystalline, hydrated aluminosilicates of group I and group II elements, in particular, sodium, potassium, magnesium, calcium, strontium, and barium. Structurally, the zeolites are framework aluminosilicates, which are based on an infinitely extending three-dimensional network of AlO_4 and SiO_4 tetrahedron linked to each other by sharing all of the oxygens [12].

Zeolites may be represented by the formula $\text{M}_{2/n}[(\text{AlO}_2)_x(\text{SiO}_2)_y] \cdot w\text{H}_2\text{O}$ where cations M of valence n neutralize the negative charges on the aluminosilicate framework.

Zeolites are categorized based on their structures [13,14]. The tetrahedra (so called primary building units) are linked together to form several types of secondary building units, such as a double 4-ring (D4R), a double 6 ring (D6R), or a sodalite cage (truncated octahedron or β cage). Only the positions of Si and Al are shown at the corners of each building unit shown in Figure 2.2. The oxygen atoms lie near the lines connecting the metal atoms. The connection of these building units in various ways results in different structures, i.e. different types of zeolites.

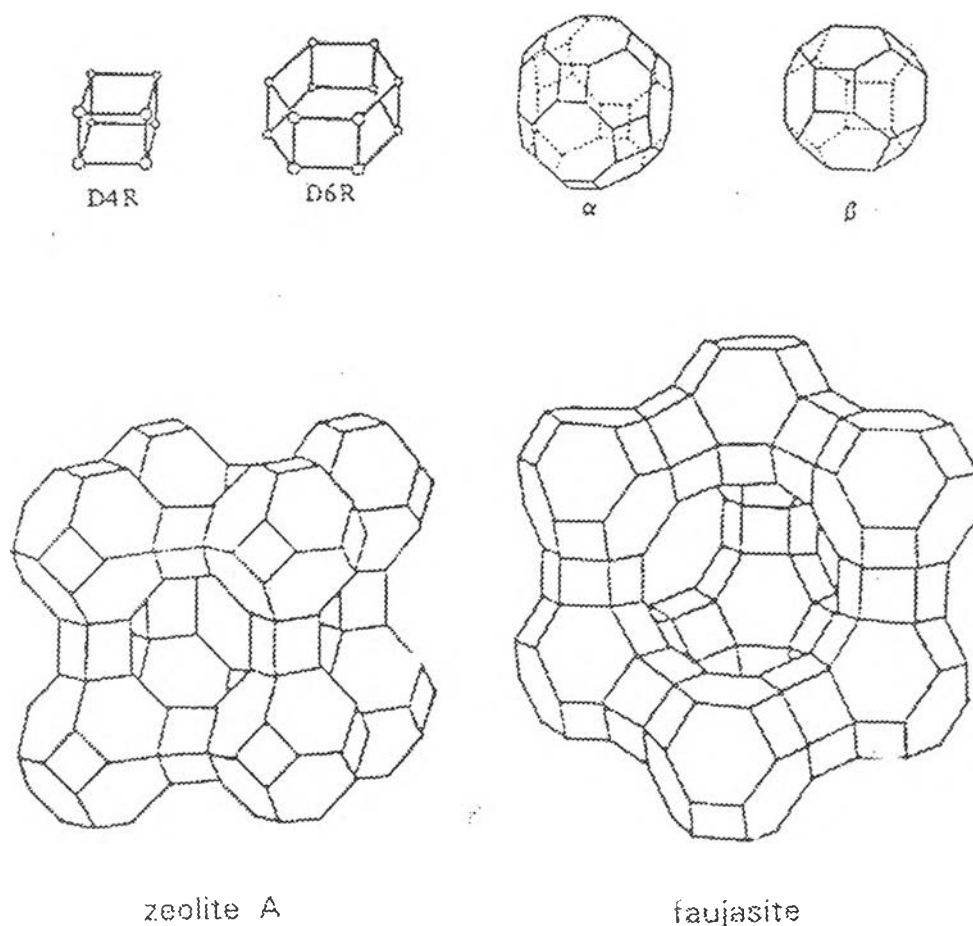


Figure 2.2 Topologies of the structural building units and the structures of zeolite A and faujasite-type zeolites.

For example, Figure 2.2 illustrates the building units and structures of zeolite A and faujasite (including zeolite X and Y). The structures are formed by connecting the sodalite units with double 4 rings or double 6-rings. A new larger cage is formed at the center, which is called supercage (α cage) for both types of structure. The supercage type I belongs to zeolite A structure and supercage type II for faujasite and both are shown in Figure 2.2. Zeolite X and Y have similar structure but different Si/Al ratio. The Si/Al ratio varies from 1 to 1.5 for zeolite X and from greater than 1.5 to 3 for zeolite Y.

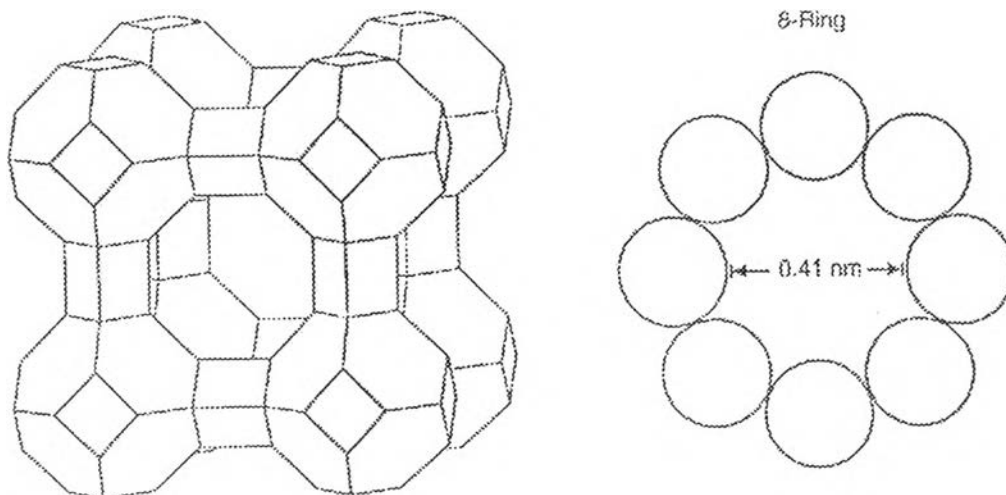


Figure 2.3 Framework structure of zeolite A with α -cage

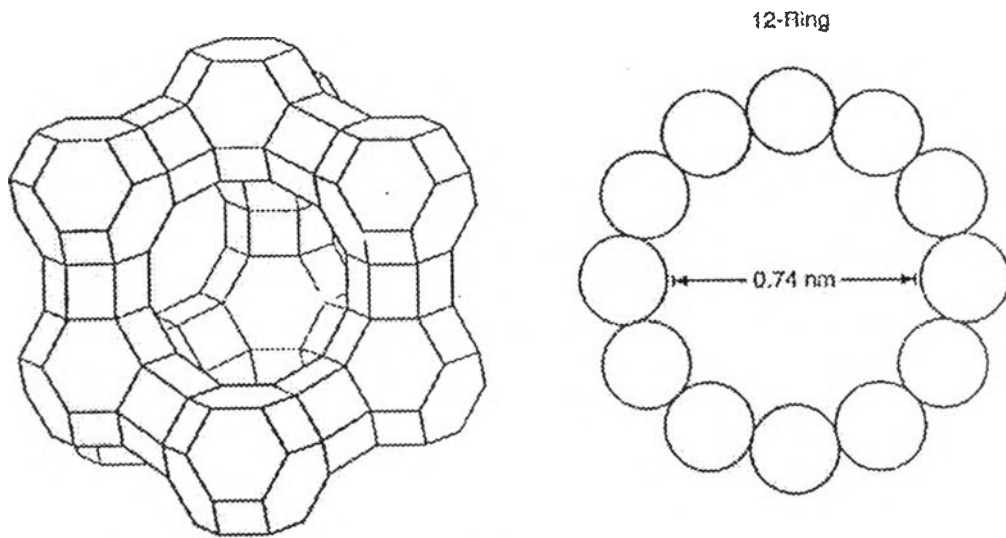


Figure 2.4 Y zeolite (faujasite)

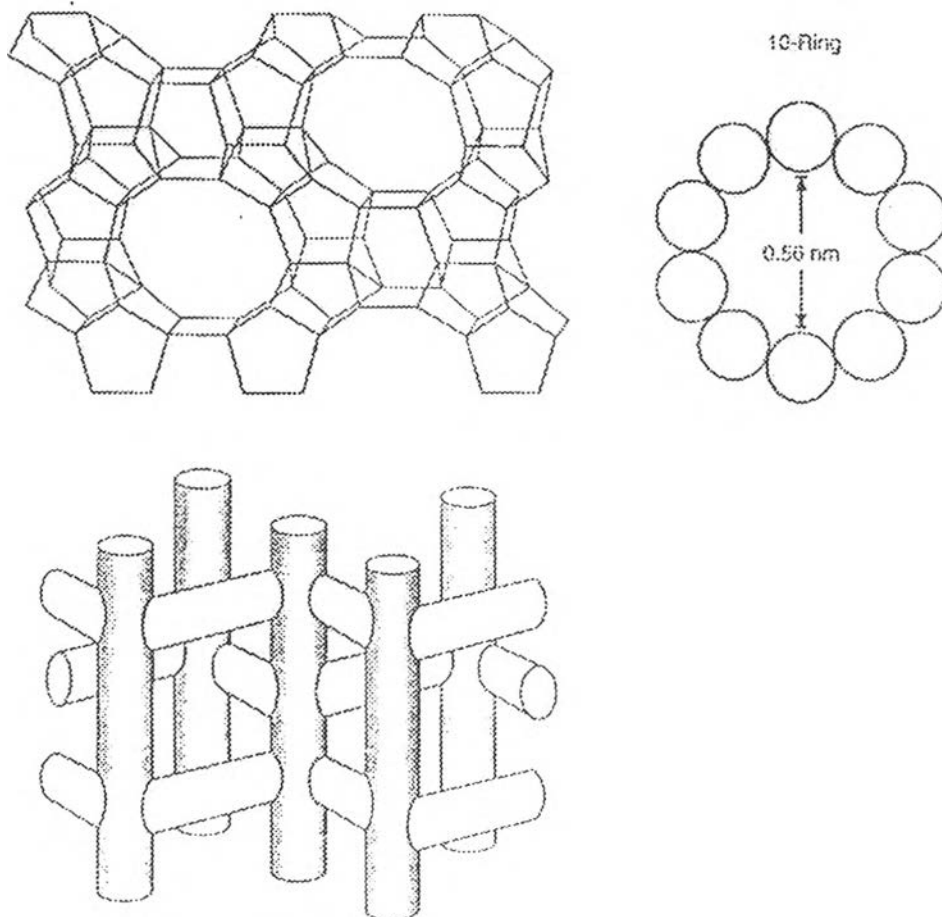


Figure 2.5 Pentasil zeolite with channel structure

Representatives of the medium-pore zeolites are the so-called pentasils, which belong to the silicon rich zeolites. In contrast to the structures described above, their polyhedra are composed of 5-rings as secondary building units. These so-called 5-1 units are structurally analogous to methylcyclopentane. Linking of the resulting chains gives a two-dimensional pore system in which linear or zig-zag channels are intersected by perpendicular linear channels (Fig.2.5). An advantage of these zeolites is the uniform channel structure, in contrast to the zeolites A and Y, in which the pore windows provide access to larger cavities. A well known representative of this class of zeolites is ZSM-5 (from Zeolite Socony Mobil no. 5). Table 2.1 shows the important zeolites.

Table 2.1 Characteristics of important zeolites

Type	Pore diameter [nm]	Pore aperture
Zeolite Y (faujasite)	0.74	12-ring
Pentasil zeolite	0.55 x 0.56	10-ring (ellipsoid)
Zeolite A	0.41	8-ring
Sodalite	0.26	4-ring

2.4.1 Catalytic Properties of the Zeolites

In 1962, the zeolites were introduced by Mobil Oil Corporation as new cracking catalysts in refinery technology. They were characterized by higher activity and selectivity in cracking and hydrocracking. At the end of the 1960s, the concept of shape-selective catalysis with zeolites was introduced to petrochemistry (Selectoforming process), and zeolites became of increasing importance in catalysis research and applied catalysis [15].

Since then chemists worldwide have prepared numerous “tailor-made” modified zeolites, and the synthetic potential for the production of organic intermediates and high-value fine chemicals are enormous. How can the success of this new class of catalysts in industry and academy be explained? It is due to the outstanding catalytic properties of the zeolites. No other class of catalysts offers so much potential for variation and so many advantages in application. Their advantages over conventional catalysts can be summarized as follows:

- Crystalline and therefore precisely defined arrangement of SiO_4 and AlO_4^- tetrahedra. This results in good reproducibility in production.
- Shape selectivity: only molecules that are smaller than the pore diameter of the zeolite undergo reaction.
- Controlled incorporation of acid centers in the intracrystalline surface is possible during synthesis and/or by subsequent ion exchange.
- Above 300°C pentasils and zeolite Y have acidities comparable to those of mineral acids.

- Catalytically active metal ions can be uniformly applied to the catalyst by ion exchange or impregnation. Subsequent reduction to the metal is also possible.
- Zeolite catalysts are thermally stable up to 600°C and can be regenerated by combustion of carbon deposits.
- They are well suited for carrying out reactions above 150°C, which is of particular interest for reactions whose thermodynamic equilibrium lies on the product side at high temperatures.

Let us first take a closer look at the most important properties of the zeolites:

- Shape selectivity
- Acidity

2.4.2 Shape selectivity

We have seen that the inner pore system of the zeolites represents a well-defined crystalline surface. The structure of the crystalline surface is predetermined by the composition and type of the zeolite and is clearly defined. Such conditions are otherwise found only with single-crystal surfaces [16].

The accessibility of the pores for molecules is subject to definite geometric or steric restrictions. The shape selectivity of zeolites is based on the interaction of reactants with the well-defined pore system. A distinction is made between three variants, which can, however, overlap:

- Reactant selectivity
- Product selectivity

- Restricted transition state selectivity

Figure 2.6 shows these schematically with examples of reactions.

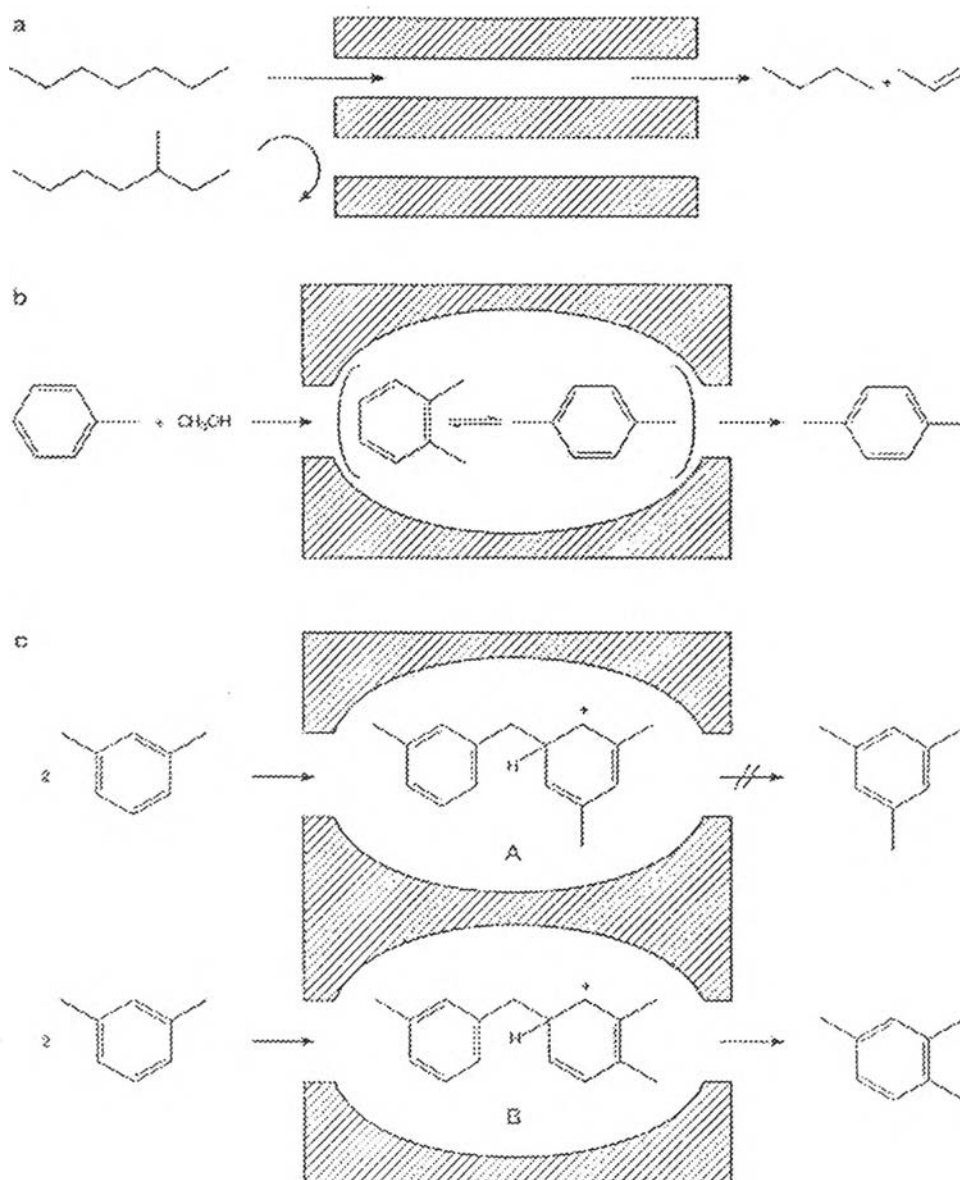


Fig 2.6. Shape selectivity of zeolites with examples of reactions

- a) Reactant selectivity: cleavage of hydrocarbons
- b) Product selectivity: methylation of toluene
- c) Restricted transition state selectivity: disproportionation of *m*-xylene

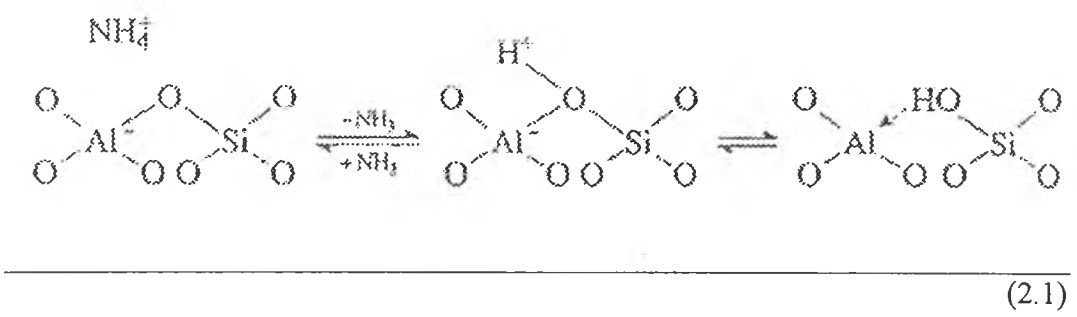
Table 2.2 Molecular diameters and pore sizes of zeolites[17]

Molecule	Kinetic diameter [nm]	Zeolite	Pore size [nm]
He	0.25	KA	0.3
NH ₃	0.26	LiA	0.40
H ₂ O	0.28	NaA	0.41
N ₂ ,SO ₂	0.36	CaA	0.50
Propane	0.43	Erionite	0.38 x0.52
<i>n</i> -Hexane	0.49	ZSM-5	0.54x0.56/0.51x0.55
Isobutane	0.50	ZSM-12	0.57 x 0.69
Benzene	0.53	Ca-X	0.69
<i>p</i> -xy ^l ene	0.57	Mordenite	0.67-0.70
CCl ₄	0.59	NaX	0.74
Cyclohexane	0.62	AIPO-5	0.80
<i>o</i> -, <i>m</i> -Xylene	0.63	VPI-5	1.20
Mesitylene	0.77		
(C ₄ H ₉) ₃ N	0.81		

2.4.3 Acidity of Zeolites

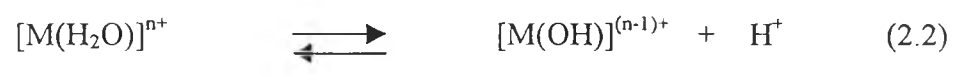
Zeolites in the H form are solid acids whose acid strength can be varied over a wide range by modification of the zeolites (ion exchange, partial dealumination, and isomorphic substitution of the framework Al and Si atoms)

[18]. Direct replacement of the alkali metal ions by protons by treatment with mineral acids is only possible in exceptional cases (e.g., mordenite and the high-silicon zeolite ZSM-5). The best method is exchange of the alkali metal ions by NH_4^+ ions, followed by heating the resulting ammonium salts to 500-600°C (deammonization; Equation 2.1).

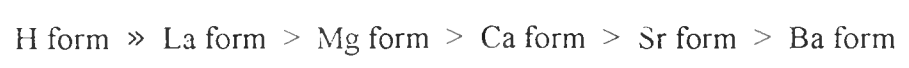


Infrared investigations have shown that the protons are mainly bound as silanol groups but have a strongly acidic character due to the strongly polarizing influence of the coordinately unsaturated aluminum center. Brønsted acid centers are generally the catalytically active sites of H-zeolites.

Weak to moderately strong acid sites can be generated in zeolites by ion exchange with multivalent cations. Owing to the polarizing effect of the metal cations, water is dissociatively adsorbed, and the equilibrium of Equation 2.2 is established.



The following order of Brønsted acidity is given for cation-exchanged zeolites:



The incorporation of transition metal ions into zeolites leads to interesting bifunctional catalysts in which metal and acid centers can act simultaneously.

Another major influence on the acidity of zeolites is the Si/Al ratio. The zeolites can be classified according to increasing Si/Al ratio and the associated acid/base properties (Table 2-3).

Since the ion-exchange capacity corresponds to the Al^{3+} percentage of the zeolites, those with lower Si/Al ratios have higher concentrations of active centers.

Zeolites with high concentrations of protons are hydrophilic and have high affinity for small molecules that can enter the pores. Zeolites with low H^+ concentrations, such as silicalite, are hydrophobic and can take up organic components (e.g., ethanol) from aqueous solution. The boundary lies at a Si/Al ratio of around 10.

The stability of the crystal lattice also increases with increasing Si/Al ratio. The decomposition temperatures of zeolites are in the range 700-1300 °C. Zeolites of low aluminum percentage are produced by dealumination with a reagent such as SiCl_4 , which is produced by this method or by hydrothermal treatment with steam at 600-900 °C, is regarded as ultrastable and is employed in cracking catalysts.

The highest proton-donor strengths are exhibited by zeolites with the lowest concentrations of AlO_4^- tetrahedra such as H-ZSM-5 and the

ultrastable zeolite HY. These are superacids, which at high temperatures (ca. 500 °C) can even protonate alkanes. It was found that the acid strength depends on the number of Al atoms that are adjacent to a silanol group. Since the Al distribution is nonuniform, a wide range of acid strengths results.

Table 2-3 Classification of acidic zeolites according to increasing Si/Al ratio [18]

Si/Al ratio	Zeolite	Acid/base properties
Low (1-1.5)	A, X	relatively low stability of lattice; low stability in acids; high stability in bases; high concentration of acid groups of medium strength
Medium (2-5)	Erionite Chabaxite Chinoptilolite Mordenite Y	
High (ca. 10 to ∞)	ZSM-5; Dealuminated Erionite, mordenite, Y	relatively high stability of the lattice; high stability in acids; low stability in bases; low concentration of acid groups of high strength

2.4.4 Metal-Doped Zeolites

Zeolites are especially suitable as support materials for active components such as metals and rare earths. With rare earths, the activity of the catalyst and its stability towards steam and heat can be increased. Suitable metals are effective catalysts for hydrogenations and oxidations, whereby the shape selectivity of the carrier is retained. Important factors influencing the reactions of such bifunctional catalysts are the location of the metal, the particle size, and the metal-support interaction[17].

The bifunctionality of metal-doped zeolite catalysts is explained here for the important example of isomerization and hydrogenation. The metal percentage facilitates the hydrogenation and dehydrogenation steps, while the acid-catalyzed isomerization step takes place under the restricted conditions of the zeolite cavities (Scheme 2-1).

Bifunctional catalysts are used in many reactions, including hydrocracking, reforming and dewaxing processes. They usually contain ca. 0.5% Pt, Pd, or Ni. An advantage of nickel-containing hydrocracking catalysts is their lower hydrogenolysis activity compared to conventional catalysts.

A further example is acid-catalyzed disproportionation with [Pt]H-ZSM-5 as catalyst. The metal performs the hydrogenative cleavage of more highly aggregated molecules that would otherwise cause coking of the catalyst.

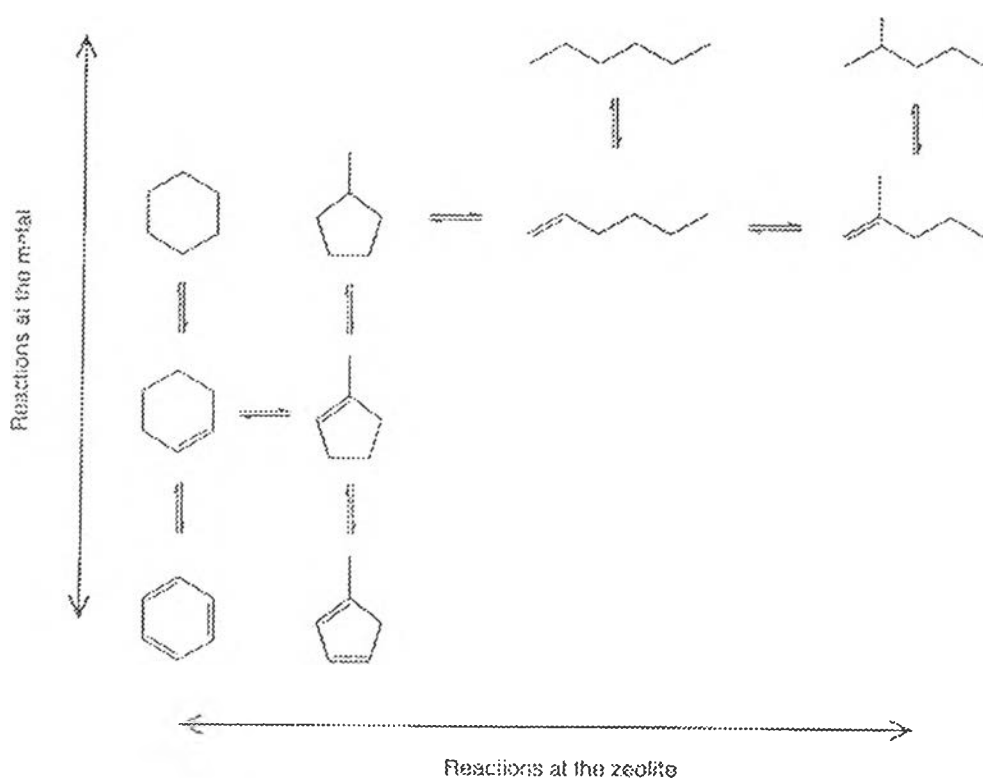


Figure 2.7. Bifunctionality of metal-doped zeolites: isomerization and hydrogenation

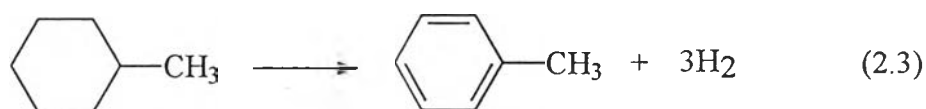
2.5 Catalytic Cracking and Aromatization

Thermal cracking is nothing but straight pyrolysis. Catalytic cracking is pyrolysis in the presence of a catalyst such as silica-alumina, processed clay, or a combination of silica-alumina and zeolite. Because of the irregularities in its crystal structure, a silica-alumina catalyst is strongly acidic [5].

Catalytic cracking has the advantage over thermal cracking in that it is easier to control and takes place at a lower temperature and there by requires less energy. Recently cracking in the presence of hydrogen has been developed as

a means of obtaining a greater yield of low-boiling materials from the very high-boiling fractions.

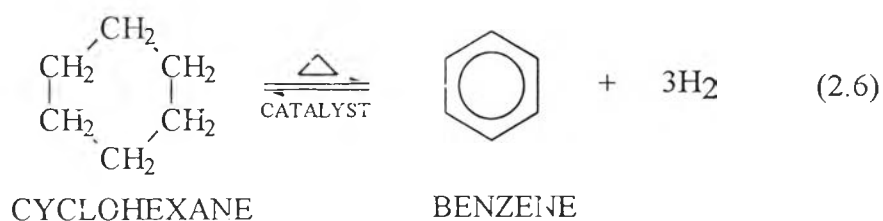
Aromatization is form of dehydrogenation. In petroleum refining, molecular rearrangement often occurs along with aromatization. The process is broadly called reforming, of which there are several variations. Perhaps the most common catalyst in reforming is platinum on alumina. Following are some typical reactions that occur during reforming.



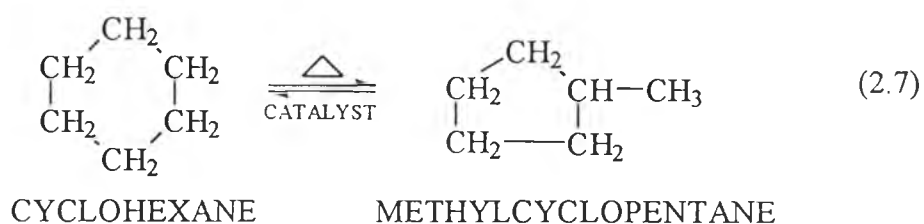
2.6 Reactions

The main reactions that occur during the aromatization process are naphthene dehydrogenation, naphthene isomerization, dehydrocyclization, paraffin isomerization, and hydrocracking. Examples of each of these reactions are shown below [19].

1. Naphthene dehydrogenation



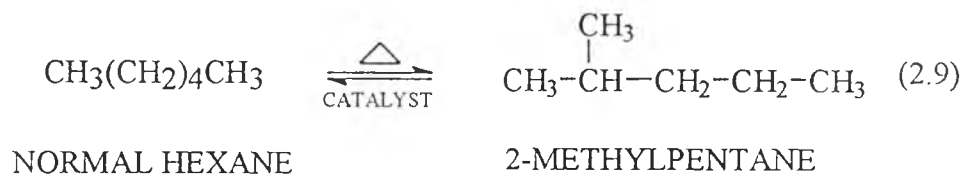
2. Naphthene isomerization



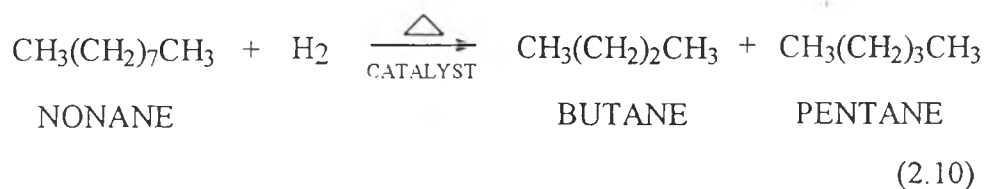
3. Dehydrocyclization



4. Paraffin isomerization



5. Hydrocracking



2.6.1 Naphthene Dehydrogenation

Naphthene dehydrogenation is a relatively fast reaction in which naphthenes are converted to aromatics. Most of the naphthene dehydrogenation is completed in the first reactor of the reformer. Because this reaction is highly

endothermic, there is a substantial reduction in temperature across the first reactor. Temperature decreases in excess of 100°F are common for midcontinent-type naphtha. The precious metal portion of the catalyst catalyzes this reaction. This reaction produces hydrogen, and its rate is shown by high hydrogen partial pressures. The conversion of naphthenes to aromatics produces an increase in product density.

2.6.2 Naphthene Isomerization

Naphthene isomerization reactions proceed quickly by action with both the acidic (halogen) portion of the catalyst and, to a lesser degree, the precious metal portion of the catalyst. This reaction produces a rearrangement of the molecule with no addition or loss of hydrogen; therefore, the reaction rate is virtually unaffected by pressure. The exothermic temperature effects associated with naphthene isomerization are usually small enough to go undetected in a commercial reforming unit.

2.6.3 Dehydrocyclization

Dehydrocyclization, an important octane-enhancing reaction in which paraffins are converted to aromatics, is a relatively slow reaction catalyzed by both the precious metal and the acid portions of the catalyst. This endothermic reaction usually occurs in the middle to the last reactors of the reformer unit. Dehydrocyclization produces hydrogen, and its rate is inhibited by high hydrogen partial pressure. Dehydrocyclization reactions increase the density of the product.

2.6.4 Paraffin Isomerization

Paraffin isomerization is a relatively fast reaction catalyzed mainly by the acid function of the catalyst. Like naphthene isomerization, this reaction produces a rearrangement of the molecular structure with no net change in hydrogen production. The rate of paraffin isomerization is not strongly affected by hydrogen partial pressure. Exothermic temperature effects associated with paraffin isomerization are not usually detected in a refinery reformer.

2.6.5 Hydrocracking

Hydrocracking, breaking long-chain paraffins into smaller-chain paraffins, is mostly catalyzed by the acid function of the catalyst. This relatively slow reaction is generally undesired, since it produces excessive quantities of light ends—C₄ and lighter hydrocarbons and coke and consumes hydrogen that could be used elsewhere in the refinery. The rate of hydrocracking is enhanced by high unit pressure. Hydrocracking is exothermic and normally occurs in the last reactor. In some cases enough hydrocracking occurs to produce a temperature increase across the last reactor. Hydrocracking reactions reduce the density of the product.

2.7 Reactors

There are two main types of reactors used for carrying out reactions continuously in the liquid phase, *tubular reactors*, and *stirred flow reactors* (see Fig. 2.7) [20].

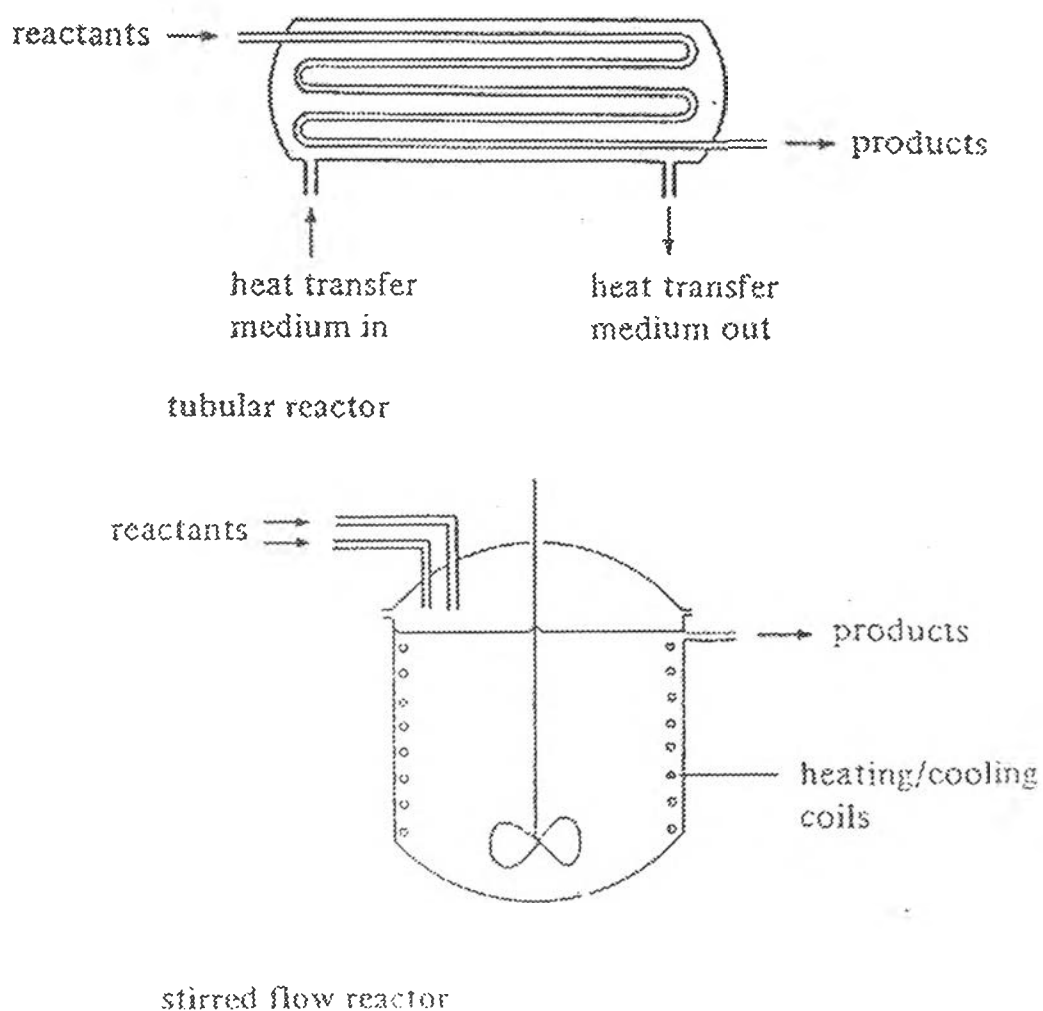


Figure 2.8 Reactors for continuous processing in the liquid phase

Tubular reactors consist, as the name implies, of a tube, or tubes, through which the reaction mix turns flows. Usually, provision is made for the addition or removal of heat by a heat transfer medium circulating round the tubes.

A stirred flow reactor consists of a vessel with an agitator and provision for continuously adding reactants and removing products. Heat transfer may be provided for by a variety of means, e.g. by a jacket, or by coils immersed in the reaction mix turns.

The type of reactor used for gas phase processes depends on whether the reaction involved is carried out in contact with a solid catalyst or not. Non-catalytic gas phase reactions are carried out in tubular reactors broadly similar to those used for liquid phase reactions. With reactions over solid catalysts, considerations of heat transfer become dominant. Beds of catalyst are poor transmitters of heat, so that there is a tendency for large temperature gradients to be set up.

2.7.1 Petrochemical Process Technology

Petrochemicals are usually made-by *continuous processing*, that is, raw materials are continuously fed into the plant, and products are continuously taken from it. This contrasts with most laboratory preparations, which are carried out by *batch processing*. Continuous processing is used because it has a number of advantages for large-scale chemical manufacture, notably, it is easier to automate, it allows better energy conservation, and it allows short reaction times to be used [20].