# CHAPTER III
THEORY

3.1 Nitrogen Oxides [Fritz and Pitchon (1997)]

3.1.1 Origins of Nitrogen Oxides

The major source of nitrogen oxides is the combustion of fossil fuels such as coal in electrical power plants or petroleum in the engines of vehicles and airplanes. In both cases, the processes are so fast that the thermodynamic equilibrium (CO_2+H_2O) is not reached. For this reason, the exhaust gases contain products of an incomplete combustion such as soot or carbon monoxide. Nitrogen oxides are also formed. Among them, nitrogen monoxide (NO) accounts for 95% of all nitrogen oxide emissions. From a thermodynamic point of view, this compound is unstable. The majority of NO is formed by the reaction between nitrogen and oxygen following the mechanism.

$$N_2 + O^* \longrightarrow NO + N^*$$
$$N^* + O_2 \longrightarrow NO + O^*$$

$$N_2 + O_2 \longrightarrow 2NO$$
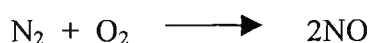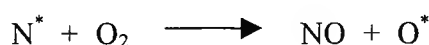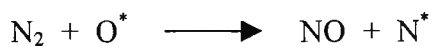
3.1.2 Effects of Nitrogen Oxides

In recent years, studies from within a variety of the biological sciences have converged to reveal the importance of NO to the living organism. One of these reports described NO as an essential messenger, which transmits the necessary information to the white corpuscles within the bloodstream to destroy cells and assorted bacteria and, in a second role, to the neurotransmitters to dilate the blood vessels. However, while the biologically active NO is a poisonous product of the in vivo enzyme-catalyzed transformation of the amino acid, arginine, and is maintained only at beneficent concentrations, that emitted freely from a car engine presents a real hazard of toxicity.

In the presence of air NO is oxidized to NO_2, which is rapid conversion at high concentration, further accelerated in the presence of sunlight and hydrocarbon from unburned gasoline. This oxide is poisonous for the respiratory system, provoking both lung infection and respiratory allergies since it is able to diffuse through the alveolar cells and capillary vessels of the lungs and damage their structure through their propensity towards oxidation. Epidemiological studies have revealed that concentrations of nitrogen oxides having hazardous effects for people in good health are above 0.05 ppm for an exposure of over 24 h. Nevertheless, this value is often exceeded in towns with dense traffic during peak hours or during the summer.

Nowadays, the deforestation of the hemisphere by contamination is considered one of the most important ecological problems. Although responsibility might be directed towards a variety of factors, that of acid rain remains a major contributor among them. In this process, nitrogen oxides play an influential role in the photochemistry of both strotosphere and stratosphere. Figure 3.1 illustrated the various chemical transformations of nitrogen oxide in our atmosphere that lead to air pollution problems.
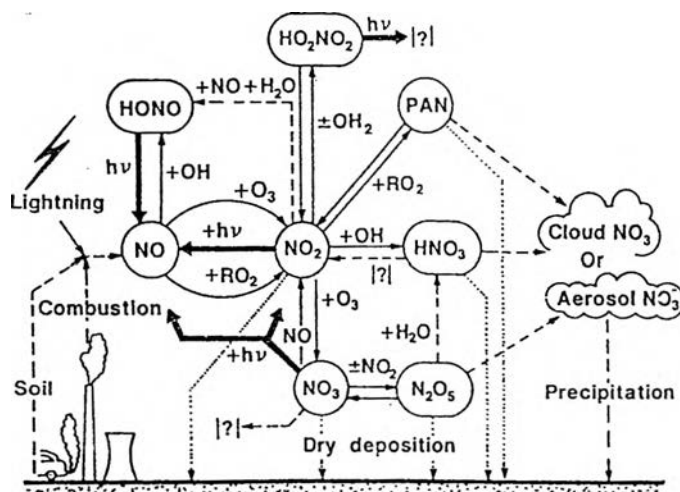

Figure 3.1 Upper atmospheric chemistry of nitrogen oxide [Fritz and Pitchon (1997)]

===> : photochemical processes

——> : thermal gas-phase processes

......> : dry deposition

----> : heterogeneous reactions

3.1.3 Nitrogen Oxides Removal

There are a number of commercial approaches to nitrogen oxides removal (Figure 3.2) which include adsorptive, thermal , and catalytic.
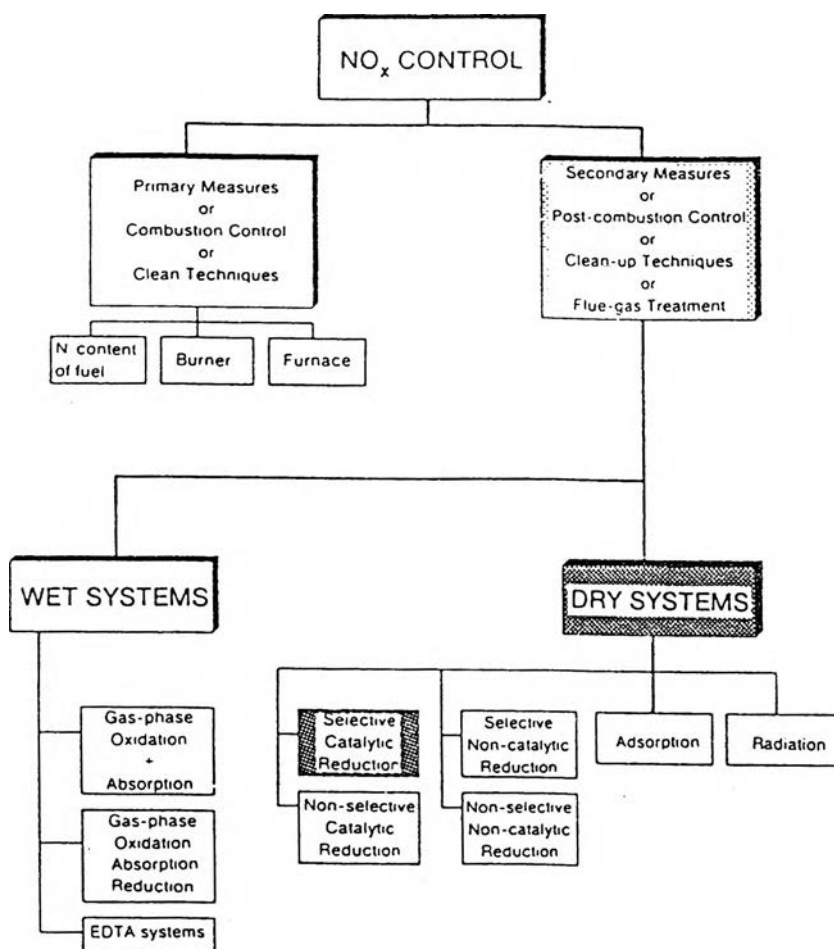

Figure 3.2 Available techniques to decrease emission of nitrogen oxides [Fritz and Pitchon (1997)].

Below are current and future solutions to removing nitrogen oxides.

3.1.3.1 Decomposition of NO

The decomposition of NO would represent the most attractive solution in emission control, because the reaction does not require that any reactant be added to NO exhaust gas and could potentially lead to the formation of only N_2 and O_2. Additional

reductants such as hydrocarbons, CO, H_2 or ammonia can lead to the production of secondary pollutants like oxygenated hydrocarbons, CO, CO_2, N_2O or ammonia or, even, as was often reported in the past, cyanate and isocyanate compounds. This could be completely avoided in this case, except N_2O formation. Up to now Cu- zeolites are the best catalysts that involve in redox mechanism [Valyon *et al.* (1993)].

3.1.3.2 Selective catalytic reduction (SCR) of NO with ammonia

The catalytic reduction of nitrogen oxides in effluent residual gases from various industries, mainly nitric acid plants, can be carried out selectively using ammonia or urea. This is the so-called selective catalytic reduction (SCR) process. SCR uses a catalyst to facilitate reactions between NO_x and ammonia in the presence of oxygen; although there are a number of reactions, it can best be represented by:

$$4NO + 4NH_3 + O_2 \longrightarrow 4N_2 + 6 H_2O \tag{3.1}$$
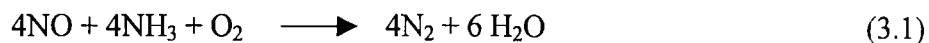
The reactions occur in a narrow temperature range; the main step is the reduction of NO or NO_2 to N_2. Generally, liquid ammonia is injected in the residual gas before the catalytic reaction takes place, using a sophisticated system of distribution.

Unwanted secondary reactions can happen as a result of the catalyst nature, the oxygen content, the temperature or the presence of acid gases. The products occurred from the reaction between NH_3 and O_2 may be NO, NO_2, and N_2O. And if SO_2, CO_2 or HCl presence in the system the corrosive products such as NH_4HSO_4, $(NH_4)_2SO_4$, NH_4Cl, and $(NH_4)_2CO_3$ can be produced, Vanadia-titania catalysts exhibit a very good stability over time, and are thus recommended for technical applications.

3.1.3.3 Catalytic reduction of NO in the presence of CO or H_2

The use of CO or H_2 for catalytic reduction was one of the first possibilities investigated in view of eliminating NO from automotive exhaust gas [Teraoka *et al.* (1984), Funabiki and Yamada (1991), Sato *et al.* (1991) and Iwamoto *et al.* (1997)].

The reaction of NO with CO:

$$NO + CO \longrightarrow CO_2 + \frac{1}{2} N_2 \qquad (3.2)$$
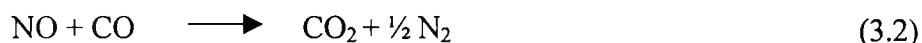
The reaction of NO with CO is one of the most important reactions occurring in automotive catalytic converters, where both reactants are undesirable pollutions. because of the presence of some hydrogen in the exhaust gases, the following reaction also occurs:

$$NO + H_2 \longrightarrow N_2 (or\ NH_3, NO_2) + H_2O \qquad (3.3)$$

Neither the reduction of NO with CO nor that with hydrogen can be considered as selective because, in addition to nitrogen, other undesired compounds like N_2O or NH_3 (in the case of hydrogen) are generated. Oxygen is always presented in the exhaust gases. The oxygen excess achieved by lean carburization or addition of air in the exhaust stream prevents the reduction of NO and causes the concomitant oxidation of CO or H_2 by O_2 and NO.

In spite of the considerable research work carried out on these important reactions, the existence of these important reactions, the existence of these side reactions and the difficulty to achieve long-term stability of the catalysts in the presence of H_2O, SO_2 and heavy metals make that only few systems can be used in practice.

3.1.3.4 Selective catalytic reduction (SCR) of NO in the presence of hydrocarbons

The SCR of NO by hydrocarbons is believed to be the most promising way to eliminate nitrogen oxide. The main advantage of the corresponding reaction is the use of a gas mixture very similar to that found in exhausts.

This catalytic process was first experimented on copper ion-exchanged zeolites. It found that the catalytic activity of Cu-ZSM-5 could be greatly enhanced by small

amounts of hydrocarbons in the presence of excess oxygen. These initial results opened new possibilities for the catalytic elimination of NO from exhaust gases, and nowadays the types of catalyst mentioned and the possible reductants are extremely varied. The enormous amount of interest of the scientific community for this topic is reflected both by the number of contributions in different journals [Iwamoto et al.(1992)] and by the published an excellent review study of the patent literature on catalysts used in the removal of NO_x, indicating that over 200 patents have already been published, most of them after 1990.

3.2 Zeolites

3.2.1 Structure of Zeolites

Zeolites are highly crystalline, hydrated aluminosilicates structurally base on infinitely extending three dimensional network of AlO_4 and SiO_4. These networks are linked to each other by sharing all of the oxygens [Breck (1984) and Satterfield (1980)].

The structural formula of a zeolite is best expressed for the crystallographic unit cell as:

$$Mx/n[(AlO_2)_x(SiO_2)_y]wH_2O$$
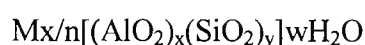
where M is the cation of valence n, w is the number of water molecules and the ratio y/x has usually values of 1-5 depending upon the structure. The sum (x+y) is the total number of tetrahedra in the unit cell [Flanigen (1991)]. The portion with $[(AlO_2)_x(SiO_2)_y]$ represents the framework composition.

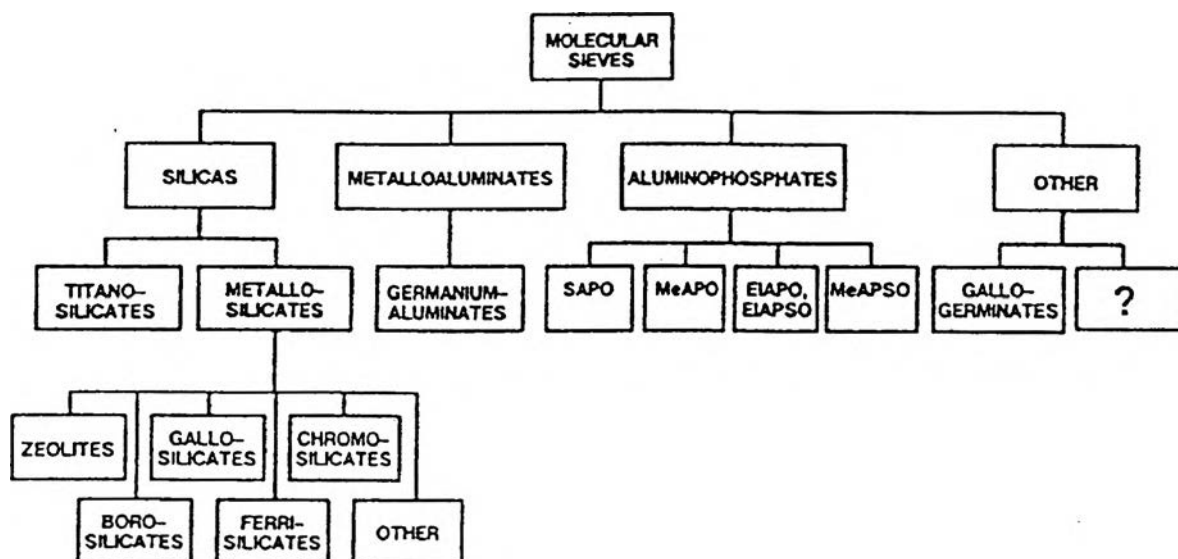

Figure 3.3 Classification of molecular sieve materials indicating extensive variation in composition [Flanigen (1991)].

ZSM-5 and silicalite have achieved commercial significance. Comparing the properties of the low and intermediate zeolites with those of the high silica zeolites and silica molecular sieves, their resulting properties allow the low and intermediate zeolites to remove water from organic and to carry out separations and catalysis on dry streams. In contrast, the hydrophobic high silica zeolites and silica molecular sieves can remove and recover organic from water streams and carry out separations and catalysis in the presence of water. Therefore, high silica zeolites showed the higher stability of the framework against the water vapor than low silica zeolites.

The ten membered rings with the ca. 0.55 nm in diameter in figure 3.4 (a) are enable to access to a network of interesting pores within the crystal. The three dimensional structure of silicalite and ZSM-5 is illustrated in figure 3.4 (b) [Gate (1992)].
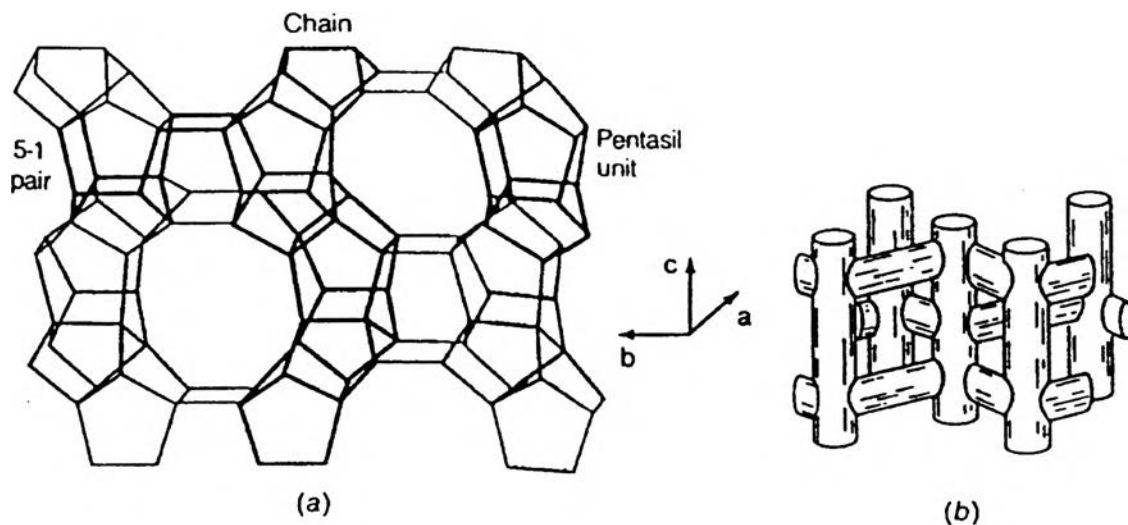
Figure 3.4 Three-dimensional structure of silicalite (MFI) [Gate (1992)]

    (a) Structure formed by stacking of sequences of layers

    (b) Channel network

The pore structure consists of two intersecting channel systems as shown in figure 3.4 (b); one straight and the other sinusoidal and perpendicular to the former. Small molecules can penetrate into this intracrystalline pore structure, where they may be catalytically converted.

Zeolites are often prepared in the sodium form, and this can be replaced by ion exchange with various other cation including ammonium, or by hydrogen ion, or even by transition metal in order to achieve high activity in specify reaction.

The properties of a zeolite are depended on the structure of zeolite, the size of the free channels, the location, charge and size of the cation within the framework, the presence of faults and occluded material, and the ordering of the T atoms (framework metal atoms) Therefore, structural information is important in understanding the absorptive and catalytic properties of zeolite [Kokotailo (1984)].
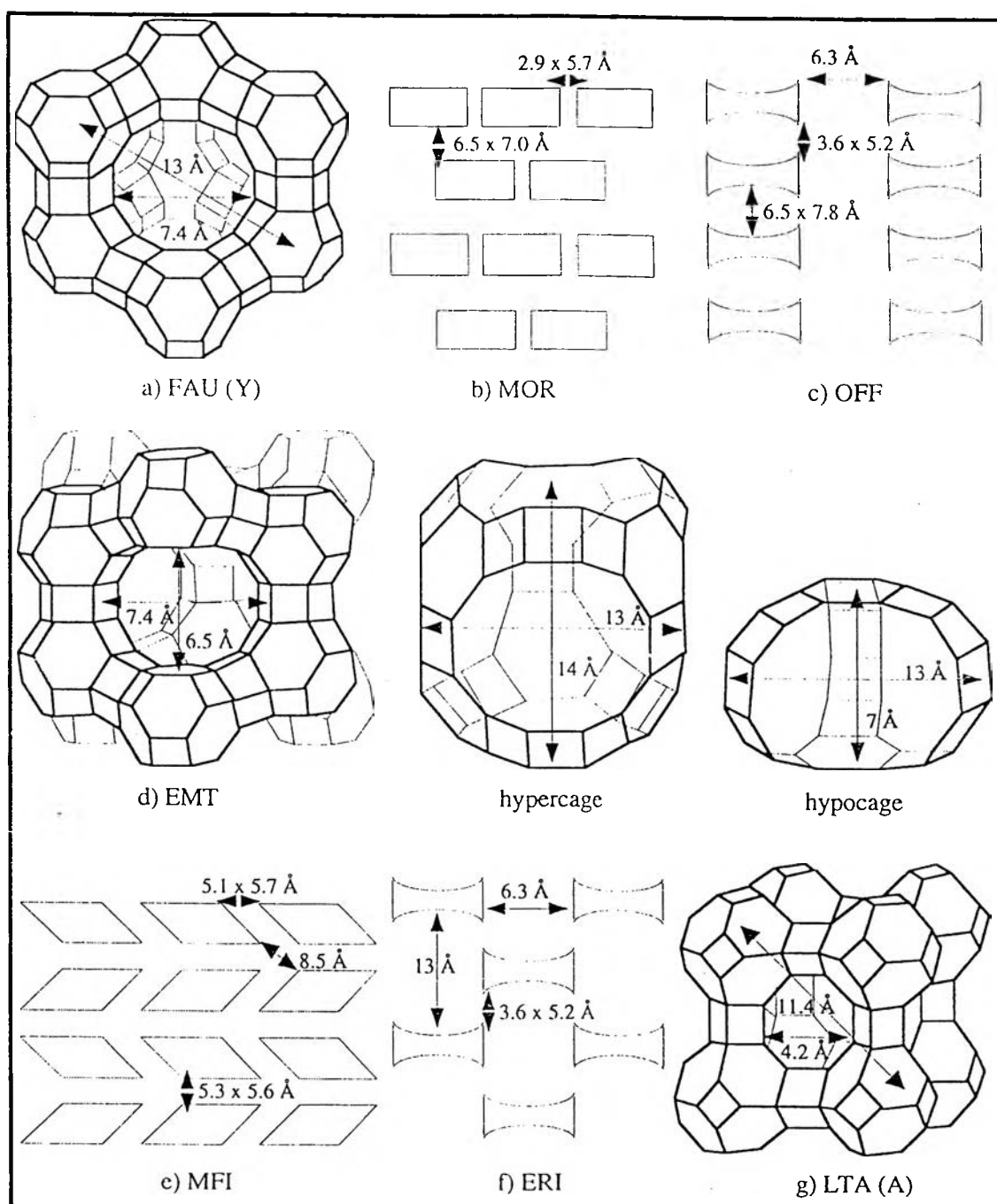
Figure 3.5 Schematic representation of the pore structure of various zeolite with large pore apertures : FAU (Y), MOR, OFF, EMT, with average pore apertures: MFI (ZSM-5), with small pore apertures : ERI, LTA (A) [Guisnet *et al.*(1997)].

They can be classified into three categories depending on the number of oxygen atoms (or of Al+Si) in the pore apertures [Guisnet *et al.*(1997)]. Small pore zeolite (openings of 3.5-4.5 Å formed by rings of 8 oxygen atoms) such as A zeolite (LTA) and erionite (ERI) can sorb only linear aliphatic molecules. Those with average pore size (4.5-6.0 Å, 10 oxygen atoms) such as ZSM-5 (MFI) can .sorb branched aliphatic compounds and alkyl monoaromatics while those with large pores (6.0-8.0 Å, 12 oxygen atoms) such as zeolite Y (FAU) and EMT can accept very bulky compounds. Zeolites with more than one pore system are classfied according to the aperture of the largest pore e.g. offretite (OFF) is classified as a large pore zeolite.

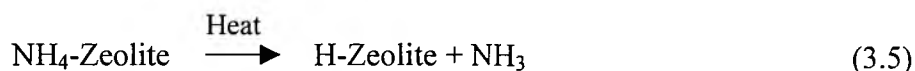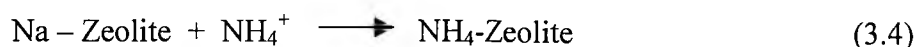Other structural parameters can play an important role in catalytic reactions:

a) The existence of cages or channel intersections (in which the acid sites are located) and their size and shape. See for instance in figure 3.5 the supercages of Y zeolites, the hypercages and hypocages of EMT zeolites, the large cages of ERI, and the channel intersections of MFI.

b) The dimensionality of the pore system accessible to a given molecule. The pore system of Y zeolites is tridimensional, that of MOR is monodimensional for organic molecules (they can access only to the large channels) and bidimensional for nitrogen and ammonia which have access to the large and small channels,

c) The existence of secondary porosity such as mesopores created during the dealumination of zeolites. Thus mesopores created in the crystallites of mordinites can render tridirectional the circulation of organic molecules.

3.2.2 Ion Exchange Reaction in Zeolite

The ease of cation exchange in zeolites and other minerals led to an early interest in ion exchange materials for use as water softening agents. Nowadays, it is found that ion exchanged is the simplest and most important for modifying the properties of zeolite. Zeolite are normally prepared in the Na form, and this can be change to NH_4 form and also following by heat treatment to produce H-form zeolite. The equations of this ion exchange are

$$Na - Zeolite + NH_4^+ \longrightarrow NH_4\text{-Zeolite} \qquad (3.4)$$

$$NH_4\text{-Zeolite} \xrightarrow{\text{Heat}} H\text{-Zeolite} + NH_3 \qquad (3.5)$$

The transition metal exchanged zeolite could be prepared as well. The procedure which is certainly the most suitable in introduce cation into the zeolite framework, consist of exchanging the primary cation, such as Na^+ or NH_4^+ and so on, with a solution of the metal salt, through conventional ion exchange technique as show in figure 3.6 and equation below: [Kokotialo (1984)]

$$(Na)_n^+\text{-Zeolite} + Me^{n+}(H_2O) \longrightarrow Me^{n+}(H_2O)\text{-Zeolite} + nNa^+ \qquad (3.6)$$

The cation exchange behaviour of zeolites depends upon

    1) the nature of cation species, the cation size, both anhydrous and hydrated, and cation charge

    2) the temperature

    3) the concentration of the cation species in solution

    4) the anion species associated with the cation in solution

    5) the solvent (most exchange has been carried out in aqueous solutions, although some has been done in organic solvents)

    6) the structural characteristic of the particular zeolite

Cation selectivities in zeolites do not follow the typical rules that are evidenced by other inorganic and organic exchangers. Zeolite structures have unique features that lead to unusual types of cation selectively and sieving. The recent structural analyses of zeolites form basis for interpreting the variable cation exchange behavior of zeolite.
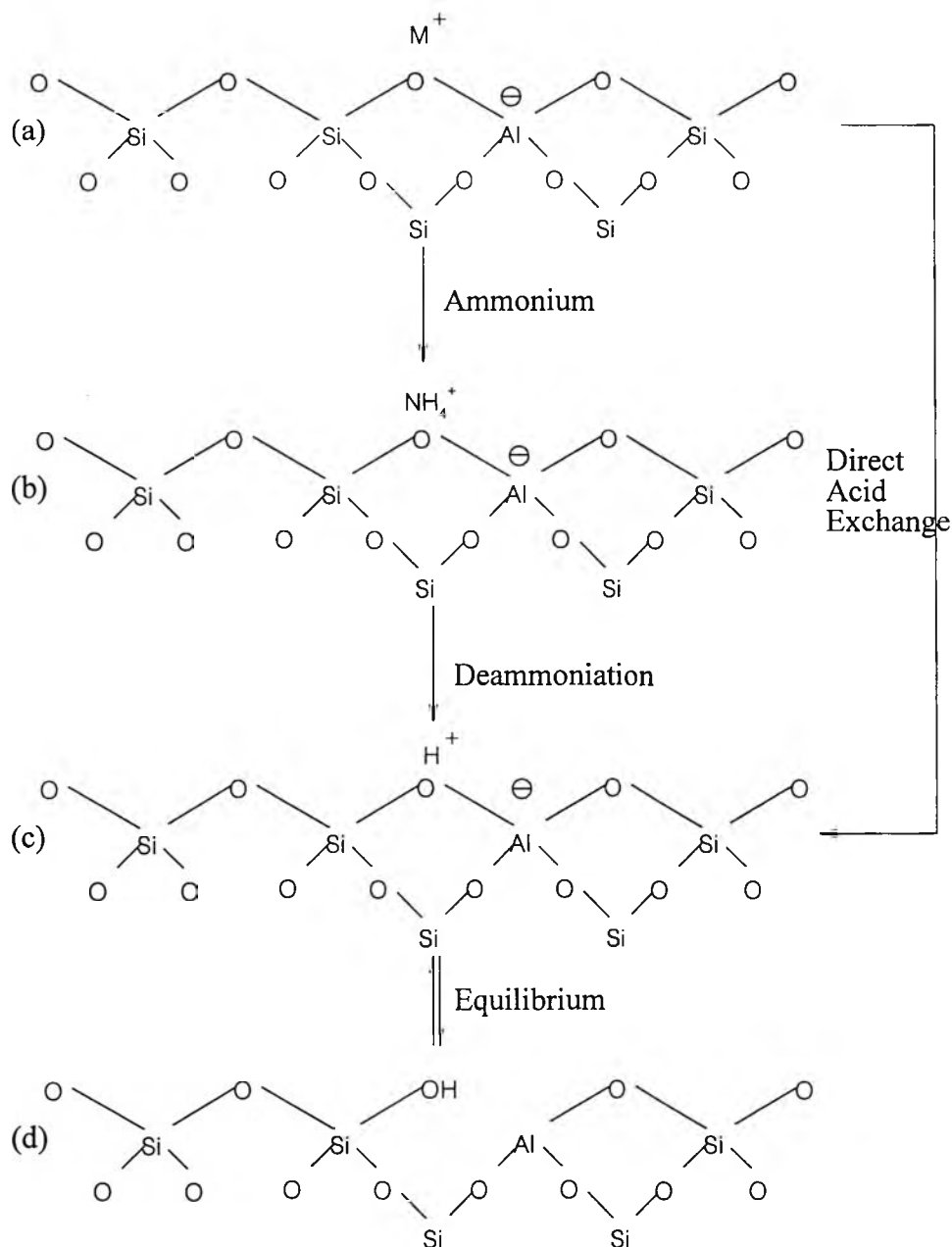
Figure 3.6 Diagram of the surface of a zeolite framework [Breck (1984)].

a) In the as-synthesis form M^+ is either an organic cation or an alkali metal cation.

b) Ammonium in exchange produces the NH_4^+ exchanged form.

c) Thermal treatment is used to remove ammonia, producing the H^+, acid form.

d) The acid form in (c) is in equilibrium with the form shown in (d), where there is a silanol group adjacent to tricoodinate aluminum.

Dehydroxylation is thought to occur in ZSM-5 zeolite above 500°C and calcination at 800 to 900 °C produces irreversible dehydroxylation which cause defection in crystal structure of zeolite.

Dealumination is believed to occur during dehydroxylation whish may result from the steam generation within the sample. The dealumination is indicated by an increase in the surface concentration of aluminum on the crystal. The dealumination process is expressed in figure 3.7. The extent of dealumination monotonously increases with the partial pressure of steam.
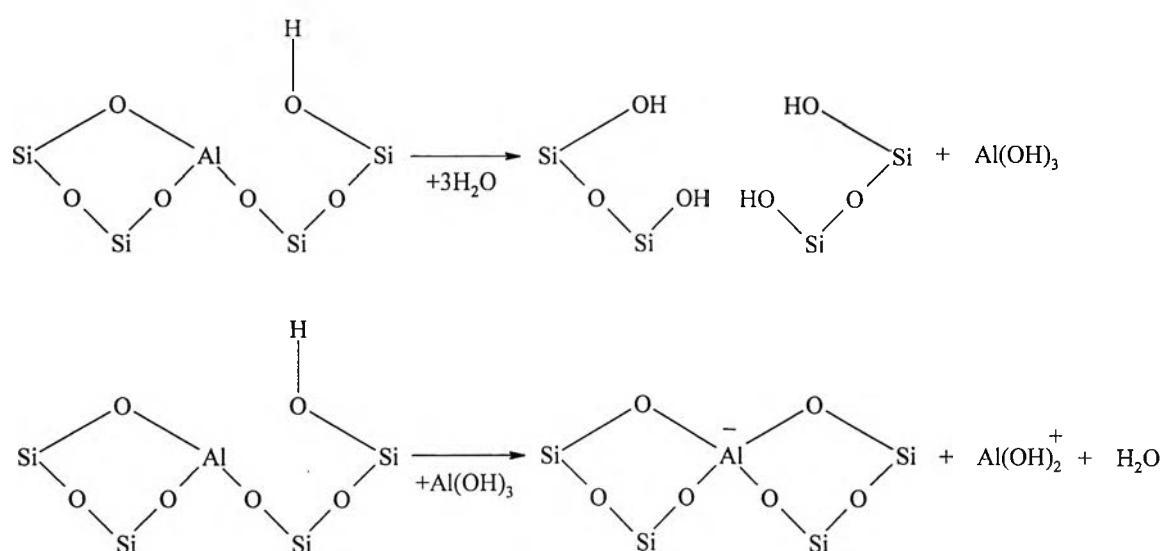

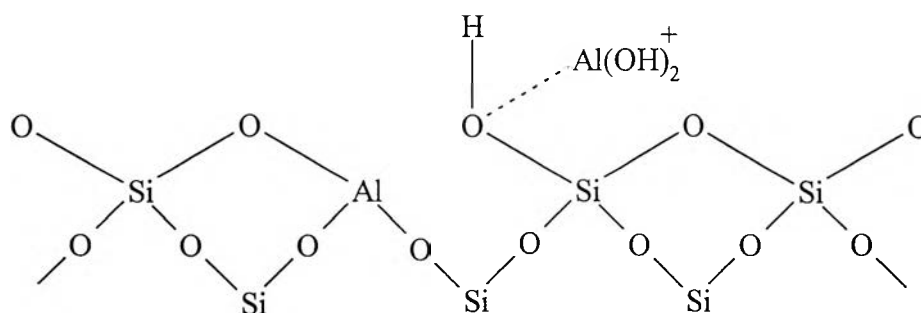**Figure 3.7** Steam dealumination process in zeolite [Satterfield (1980)].

Figure 3.8 The enhancement of the acid strength of OH groups by their interaction with dislodged aluminum species [Satterfield (1980)].

The enhancement of the acid strength of OH groups is recently proposed to be pertinent to their interaction with those aluminum species sites tentatively expressed in figure 3.8. Partial dealumination might therefore yield a catalyst of higher activity while severe steaming reduces the catalytic activity.