CHAPTER III

THEORY

3.1 Feature of Zeolite

3.1.1 Molecular Sieves

The history of zeolites began in 1756 which the swedish mineralogist Cronstedt discovered the first zeolite mineral. The word " Zeolite" derived from two Greek words " zeo" and " lithos" meaning " to boil" and " a stone". Union carbide corporation discovered a number of commercially significant zeolites, type A, X and Y , during their research in 1948 to 1954. In 1967 - 1969, Mobil Oil reported the synthesis of high silica zeolite beta and ZSM-5. Zeolites and Molecular sieves are finding applications in many areas of catalysts. Zeolites exhibits appreciable acid activity with shape-selective features not available in the compositional equivalent amorphous catalysts. In addition, these materials can act as supports for numerous catalytically active metals. They also, generally , have ion-exchange properties which allow to perform all sorts of ion-exchanged reactions[110,111].

For crystallite molecular sieve, McBain proposed the term "molecular sieve" to describe a class of materials that exhibited selective adsorption properties in 1932. He proposed that for a material to be a molecular sieve, it must separate components of a mixture on the basis of molecular size and shape differences. Two classes of molecular sieves were known when McBain put forth his definition: the zeolites and certain microporous charcoals. The list now includes the silicates, the metallosilicates, metalloaluminates, the $AlPO_4$'s, and silico- and metalloaluminophosphates, as well as the zeolites. The different classes of molecular sieve materials are listed in figure 3.1. All are molecular sieves, as their regular framework structures will separate components of a mixture on the basis of size and shape. The difference lies not within the

structure of these materials, as many are structurally analogous, but in their elemental composition. Therefore, all are molecular sieves though none but the aluminosilicates should carry the classical name, zeolite [112].

3.1.2 ZSM-5 Zeolites

The crystalline solids of primary catalytic interest, called aluminosilicates, incorporate Al, Si, and O. Naturally occurring minerals and many solids prepared in the laboratory exemplify this class. Several of the more than 100 synthetic aluminosilicates find wide application as industrial catalysts. The zeolites are structurally unique in having cavities or pores with molecular dimensions as a part of their crystalline structures. These bear catalytic sites. Having microscopic cavities, the zeolites are comparable to enzymes which have catalytic group with molecular sieve and they are also suggestive of the donut shaped cyclodextrin. Because the zeolites have well-defined crystalline structures., the catalytic groups in them are relatively well understood.[113]

Zeolites are highly crystalline, hydrated aluminosilicates [111-115] that upon dehydration develop in the ideal crystal, an uniform pore structure having minimum channel diameter of from about 0.3 to 1.0 nm. The size depends primarily upon the type of zeolite and secondarily upon the cations present and the nature of treatments such as calcination and leaching. The zeolite provides high activity and unusual selectivity in a variety of acid-catalytic reactions. In many cases, but not all, the unusual selectivity is associated with the extremely fine pore structure, which permits only certain molecules to penetrate into the interior of the catalyst particles, or only certain products to escape from the interior. In some cases unusual selectivity seems to stem instead from constraints that the pore structure sets on allowable transition states.[114-115].
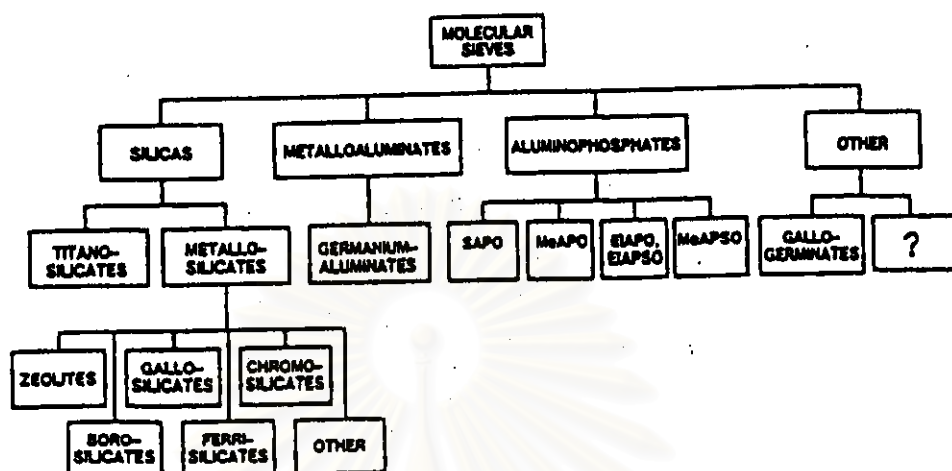
Figure 3.1   Classification of molecular sieve material indicating

extensive variation in composition[112].

The structure of zeolites consists of a three-dimensional framework of SiO_4 or AlO_4 tetrahedral, each of which contains a silicon or aluminum atom in the centre. The oxygen atoms are shared between adjoining tetrahedral, which can be present in various ratios and arranged in a variety of ways. The framework thus obtained contains pores, channels, and cages, or interconnected voids. [116]

Zeolites may be represented by the general formula:

$$M_{x/n} [(AlO_2)_x (SiO_2)_y] w H_2 O$$

where the term in brackets is the crystallographic unit cell. The metal cation of valence n is present to produce electrical neutrality since for each aluminum tetrahedron in the lattice there is an overall charge of -1 [115]. M is a cation which balance the charge of zeolite surface, w is the number of water molecules per unit cell, and x, y are the total number of tetrahedral per unit cell [110]. As catalysts, zeolites are unique in their ability to discriminate between reactant molecular size and shape [117].

The catalytically most significant are those having pore openings characterized by 8-, 10-, and 12- rings of oxygen atoms. Some typical pore geometry are shown in figure 3.2.

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

In zeolite group ZSM ,which stand for " Zeolite Socony-Mobil, the ZSM-5 zeolite is currently the most interesting in industrially field. Its structure is shown in figure 3.3 in which pores are shown as arrays of tubular channels. Two pore types exist, intersecting with each other, and both formed by 10 -membered oxygen rings. One pore type has straight but slightly elliptical openings, the other zig-zag and essentially circular openings. The intersection provides an opening that in effect can provide a type of cavity. In addition, A material that is nearly pure silica , termed silicalite, has essentially the same structure as zeolite ZSM-5.

The tetrahedral of ZSM-5 are linked to form the chain-type building block. The chains can be connected to form a layer (fig.3.3). Rings consisting of five O atoms are evident in this structure; the name pentasil is therefore used to describe it. Also evident in figure 3.5 are rings consisting of 10 oxygen atoms; these are important because they provide openings in the structure large enough for passage of even rather large molecules. The layers can be linked in two ways, the neighbouring layers being related either by the operation of a mirror or an inversion. The former pertains to the zeolite ZSM-11, the latter to silicalite or ZSM-5; intermediate structures constitute the pentasil series.
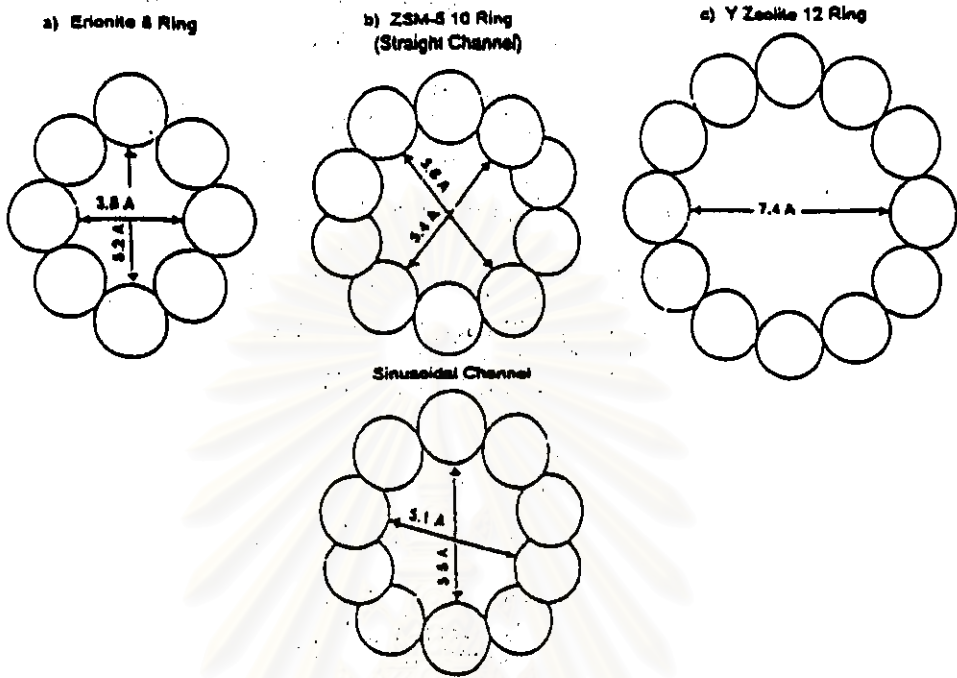
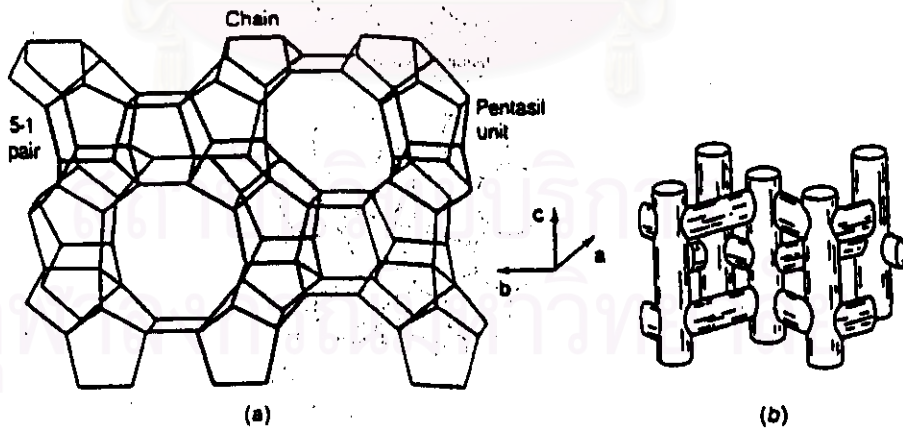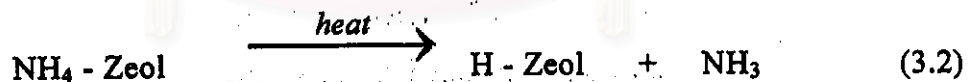Figure 3.2 Typical zeolite pore geometry [112]

Figure 3.3 Three-dimensional structure of silicalite (ZSM-5) [113].

(a) Structure formed by stacking of sequences of layers.

(b) Channel network.

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 T atoms (framework metal atoms). Therefore, structural information is important in understanding the absorptive and catalytic properties of zeolites [118].

3.2 Ion-exchange Reaction in Zeolites

The cation exchange property of zeolite minerals was first observed 100 years ago. 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, however, is found that ion - exchanged is the simplest and most important for modifying the properties of zeolite. Zeolites are normally prepared in the Na form , and this can be changed to NH4 form and also following by heat treatment to produce H-form zeolite. The equations of these ion-exchange are

$$Na - Zeol \quad + \quad NH_4^+ \quad \longrightarrow \quad NH_4 - Zeol \quad\quad (3.1)$$

$$NH_4 - Zeol \quad \xrightarrow{\ heat\ } \quad H - Zeol \quad + \quad NH_3 \quad\quad (3.2)$$

The transition metal exchanged zeolites could be prepared as well. The procedure which is certainly the most suitable in introduce cation into the zeolite-frame work , 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 shown in figure 3.4 and the equation below :[118]
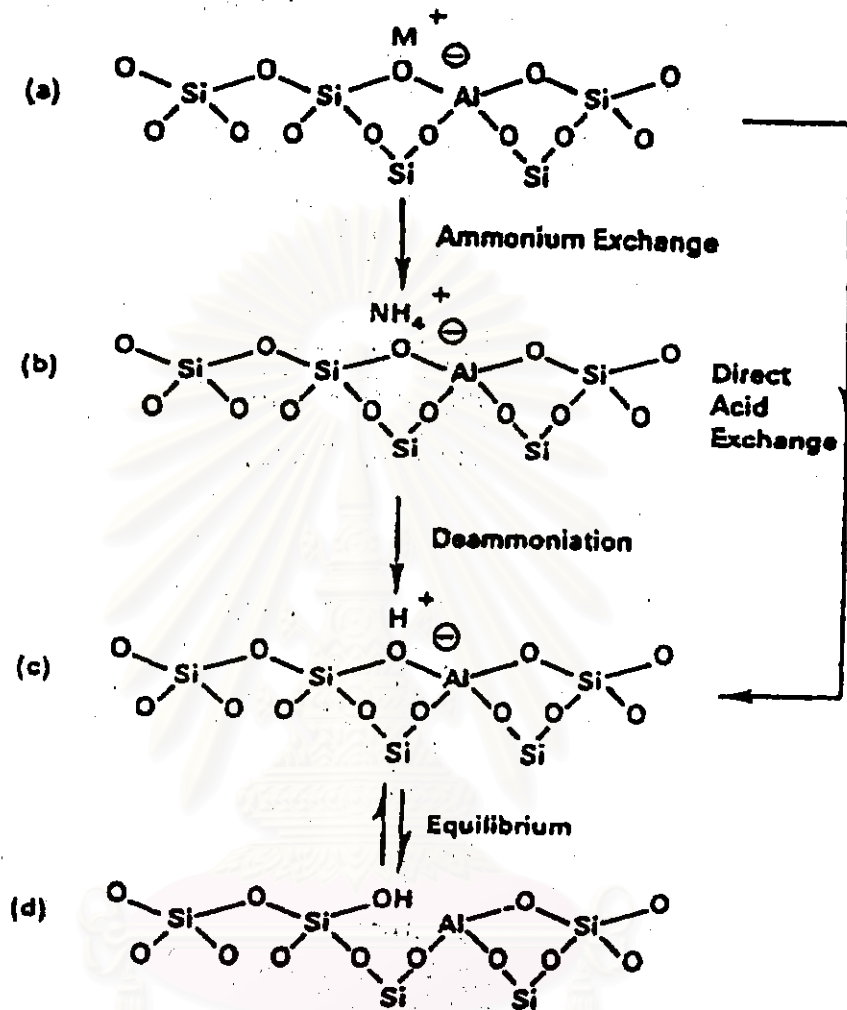
$$(Na)^+_n\text{-Zeol} + Me^{n+}(H_2O)x \longrightarrow Me^{n+}(H_2O)\text{-Zeol} + nNa^+ \quad\quad (3.3)$$
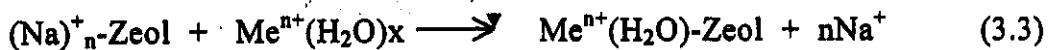
Figure 3.4 Diagram of the surface of a zeolite framework [112].

a) In the as-synthesized from M^+ is either an organic cation or an alkalimetal 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 a tricoordinate aluminum.

The cation exchange behaviour of zeolites depends upon

1) the nature of the 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 work has been done in organic solvents)

6) the structural characteristics 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 a basis for interpreting the variable cation exchange behaviour of zeolites.

Cation exchange in zeolite is accompanied by dramatic alteration of stability, adsorption behaviour and selectivity, catalytic activity and other important physical properties. Since many of these properties depend upon controlled cation exchange with particular cation species, detailed information on the cation exchange equilibria is important. Extensive studies of the ion exchange processes in some of the more important mineral and synthetic zeolites have been conducted [111].

3.3 Acidic Characteristic of Zeolite

### 3.3.1 Generation and Feature of Acidic Property of Zeolite

In the case of zeolite catalyst, the source of acidity may be rationalized in term of a theory developed largely by linuis Pauling, if an aluminum ion , which is trivalent , is substituted isomorphously for silicon ion, which is quadrivalent , in a silica lattice comprising sillica tetrahedral, the net negative

charge must be stabilized by a nearby positive ion[114]. Classical Brønsted and Lewis acid models of acidity have been used to classify the active sites on zeolites. Brønsted acidity is proton donor acidity; this occurs in zeolites when cations balancing the framework anionic change are protons(H^+). Lewis acidity is electron acceptor acidity; a trigonally co-ordinated alumina atom is an electron deficient and can accept an electron pair, therefore behaves as a Lewis acid [117, 119].

Protonic acid centres of zeolite are generated in various ways. Figure 3.4 depicts the thermal decomposition of ammonium exchanged zeolites yielding the hydrogen form [112].

The Brønsted acidity due to water ionization on polyvalent cations, described below, is depicted in figure 3.5 [115].

$$M^{n+} + xH_2O \longrightarrow M(OH)_x^{(n-x)+} + xH^+ \qquad (3.4)$$
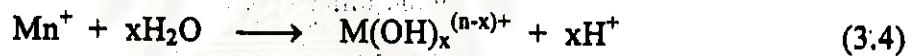
The exchange of monovalent ions by polyvalent cations could improve the catalytic property. Those highly charged cations create very acidic centres by hydrolysis phenomena.

Brønsted acid sites are also generated by the reduction of transition metal cations. The concentration of OH groups of zeolite containing transition metals was noted to increase by reduction with hydrogen at 250-450 °C and increase with the rise of the reduction temperature [115].

$$Cu^{2+} + H_2 \longrightarrow Cu^0 + 2H^+ \qquad (3.5)$$

$$Ag^+ + 1/2H_2 \longrightarrow Ag^0 + H^+ \qquad (3.6)$$
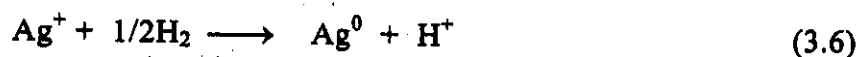
The formation of Lewis acidity from Brønsted sites is depicted in figure 3.6 [115]. The dehydration reaction decreases the number of protons and increases that of Lewis sites.

3.3.2 Measurement of Acidic Properties

The acid strength of a solid is defined as the ability of the surface to convert an adsorbed neutral base into its conjugate acid. For the amount of acid on a solid, it is usually expresses as the number or mmol of acid sites per unit weight or per unit surface area of the solid, and is obtained by measuring the amount of a base which reacts with the solid acid. This is also sometimes loosely called " acidity" . Temperature programmed desorption (TPD) of basic molecules such as ammonia, pyridine, etc. is frequency used to characterize the acid strength as well as acid amount on solid surface. Figure 3.7 shows a diagram of TPD of ammonia adsorbed on cation-exchanged ZSM-5. Two distinct peaks were observed for H-ZSM-5 , indicating the existence of strong(a peak at 723 K) and weak (a peak at 463 K) acid sites. The acid strength of cation-exchanged ZSM- 5 follows the order H > Li > MgO/Li > Na, The acid amount being shown by respective peak intensity.

Infrared spectroscopic studied of such species adsorbed from the vapour phase are perhaps the most conclusive in distinguishing between Brønsted and Lewis sites, since the spectrum of ,e.g., co-ordinately bonded pyridine is much different from that of the pyridinium ion formed by proton transfer from a Brønsted acid. In addition, Hashimoto proposed a method of distinguishing between Brønsted and Lewis acid sites by adsorption studies with 2-6 dimethylpyridine, postulates to poison only Brønsted acid sites, and NH_3, assumed to poison both types of sites[113].
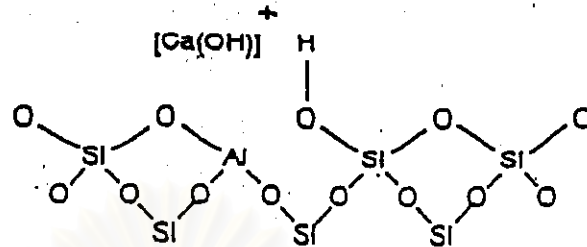
Figure 3.5 Water molecules coordinated to polyvalent cation are dissociated by heat treatment yielding Brønsted acidity [115].
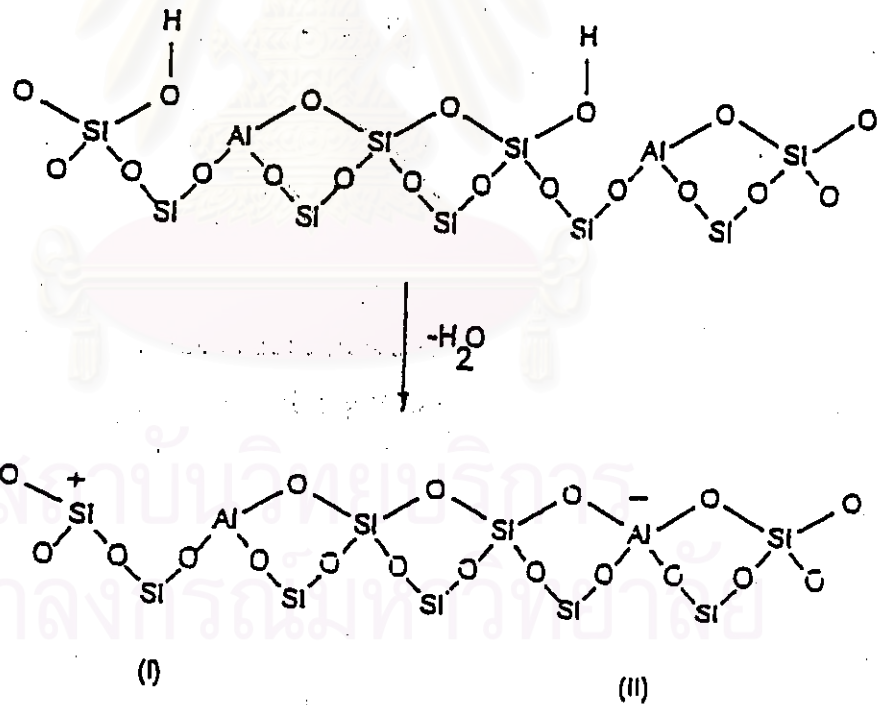

Figure 3.6 Lewis acid site developed by dehydroxylation of Brønsted acid site [115].
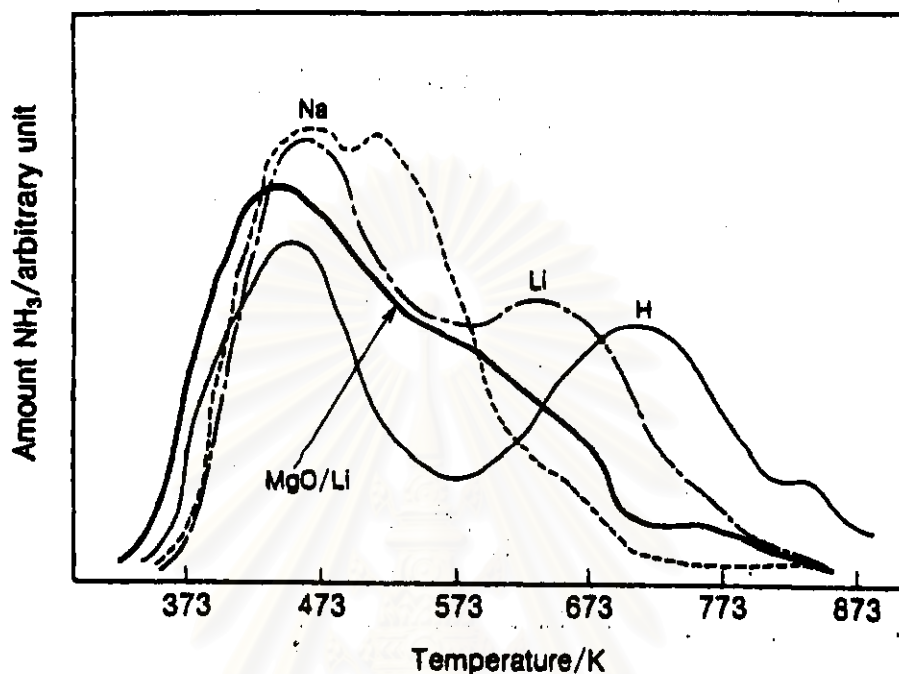
Figure 3.7 TPD spectra of NH_3 on cation - exchanged ZSM-5 zeolites
(Si/Al = 44)[113]

3.3.3 Factors of Acidic Properties of Zeolites

In general, the increase in Si/Al ratio will decrease number of acid site but increase acidic strength and thermal stability of zeolite [120]. Since the number of acidic OH groups depend on the number of aluminum in zeolite's framework, decrease in Al content is expected to reduce acid site of zeolite.

Based on electrostatic consideration, the charge density at a cation site increases with increasing Si/Al ratio. It was conceived that these phenomena are related to reduction of electrostatic interaction between framework sites, and possibly to difference in the order of aluminum in zeolite crystal-the location of Al in crystal structure [119].

Recently, it has been reported that the mean charge on the proton was shifted regularly towards higher values as the Al content decreased [117]. Simultaneously the total number of acidic hydroxyls, governed by the Al atoms, were decreased. This evidence emphasised that the entire acid strength distribution (weak, medium, strong) was shifted towards stronger values. That is, weaker acid sites become stronger with the decrease in Al content.

Brønsted (OH) and Lewis (-Al-) sites can be present simultaneously in the structure of zeolite at high temperature. Dehydroxylation is thought to occur in ZSM-5 zeolite above 500 °C and calcination at 800 to 900 °C produces irreversible dehydroxylation which causes defection in crystal structure of zeolite.

Dealumination is believed to occur during dehydroxylation which 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 3.8. The extent of dealumination monotonously increases with the partial pressure of steam.
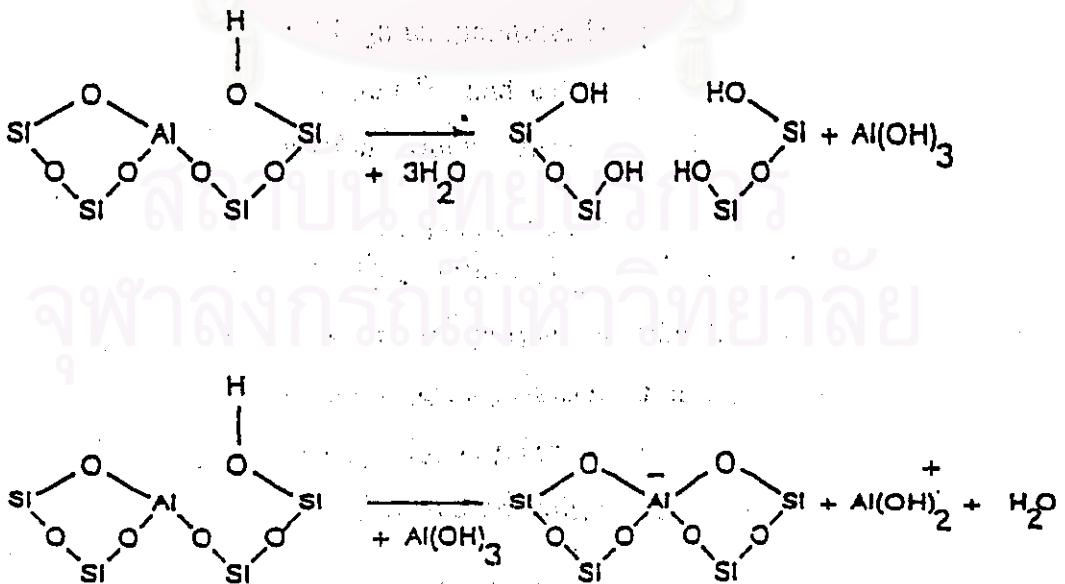

Figure 3.8 Steam dealumination process in zeolite [115].

The enhancement of the acid strength of OH groups is recently proposed to be pertinent to their interaction with those aluminum species sites are tentatively shown in figure 3.9. Partial dealumination might, therefore, yield a catalyst of higher activity while severe steaming reduces the catalytic activity.
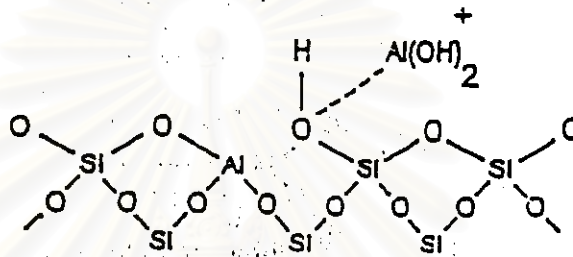

Figure 3.9 The enhancement of the acid strength of OH groups by their interaction with dislodged aluminum species [115].

3.4 Nitric Oxides Removal Processes

At present, one of the most significant problem in air pollution is removal of nitric oxides, which are the prevailing by products of high temperature combustion. Their removal from the burnt gases is requires in most advanced societies in stationary installations, power plants factories and in mobile sources--automotive vehicles. Sources of NOx and the history through progress in its removal technologies are summarised below.

3.4.1 Sources of Nitrogen Oxides

The main sources of NOx in the lower atmosphere are the combustion of fossil fuels and the burning of biomass. Other sources are nitrogen fixation by light, volcanic activity, the oxidation of ammonia in the troposphere, the inflow of NO from the stratosphere, and ammonia oxidation from the

decomposition of proteins. In fact, road and air traffic as well as other industrial and domestic burning of fuels, are the most important sources of oxides of nitrogen[2]. Figure 3.10 illustrates the various chemical transformations of nitric oxide in atmosphere that lead to air pollution problems. Note that NO is the key starting point for all of the other oxides on nitrogen. Nitric NO is not only produced by the burning of fossil fuels, but also by lightning, microbial decomposition of proteins in the soil, and volcanic activity. Once produced, nitric oxide is rapidly oxidized by ozone, OH, or HO_2 radicals form the higher oxides of nitrogen, such as NO_2, HNO_2, and HO_2NO_2. Thus, if NO is prevented from entering the atmosphere, most of the downstream effects of NOx pollution can be eliminated[121].

3.4.2 Control Technology for NOx

Figure 3.11 shows the types of control technology which are currently available: two main groups can be seen: (I) primary measures, or combustion control, also called clean techniques; and (II) secondary measures, or post-combustion control, also termed clean-up techniques or flue-gas treatment. Possible primary measures are the control of the nitrogen content of the fuel, modification of the burner and modification of the process, which seems to be somewhat more logical than a subdivision into catalytic and non-catalytic process[2].

3.4.3 NO Decomposition

The direct decomposition of nitric oxide to its elements has been a significant challenge for scientists for decades especially since no added reductant is necessary.
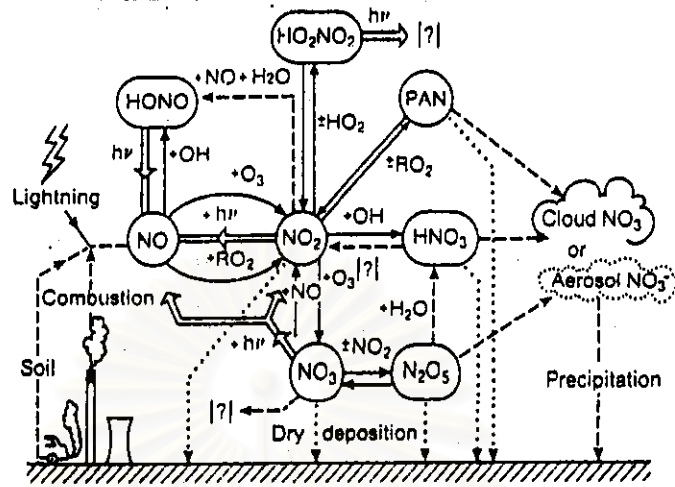
$$NO(g) \rightarrow 1/2N_2 + 1/2O_2 \qquad (3.7)$$

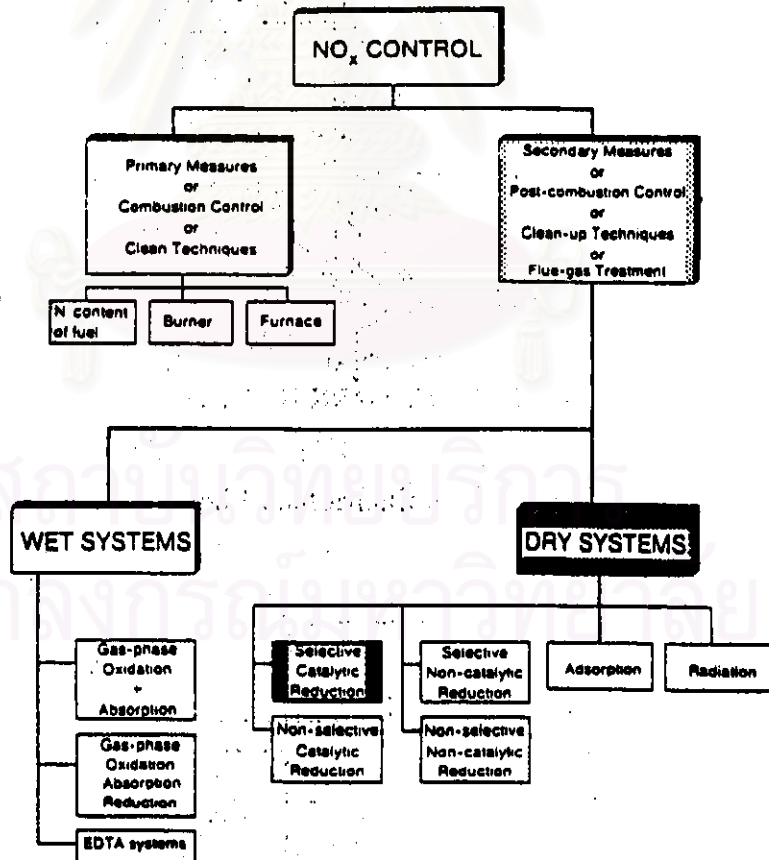Figure 3.10 Chemical transformations of atmospheric NOx[2]

Figure 3.11 Available techniques to decrease emission of NOx[2]

The NO decomposition reaction as shown in equation 3.7, although thermodynamically favourable by > 20 kcal/mol at 25 °C[121], it has not been demonstrated any substantial yield until recently by Iwamoto et al.[4,5,122]. His work ultimately led to the breakthrough that Cu-ZSM-5 is capable of decompostioning nitric oxide into its elements at 500 °C. Their early work reported incomplete, yet substantial, conversion of nitric oxide to oxygen(60%) and nitrogen(85%) and it was suggested that nitrogen dioxide was produced. This work represented a step out improvement over what others had tried for decades to achieve. To date Cu-ZSM-5 is unique. This breakthrough in catalytic technology offers a new alternative for the removal of nitric oxide from flue gas while generating the compounds of air. Further, this direct decomposition of NO to its elements is achieved without the addition of a reductant such as ammonia to remove nitric oxide from exhaust emission.

Incomplete NO decomposition with corresponding to the nitrogen dioxide formation in the catalytic process is due to unreacted nitric oxide which is inturn reacting with the product oxygen from the decomposition reaction. From review of Iwamoto [123], he noticed that the mechanism of NO decomposition possibly involved in either(1) redox cycles of Cu ions during the decomposition or (2) Cu^{2+} isolated ions. However, this process is quite new, thus the more detail of this reaction is necessary to further study.

3.4.4 Reactions with H_2 and CO

There are several catalysts which use hydrogen to remove NOx , however, these have not seen widespread commercialisation. A great deal of work was reported in the 70's on the use of various metals and oxides for the reduction of nitric oxide by carbon monoxide or hydrogen. These approaches are ineffective in the presence of air, hence non-oxidising conditions are requires. For hydrogen, the activity on alumina varies as follows: Pd > Pt > Rh > Ru. However, platinum was found to have highest intrinsic activity, while palladium was more selective to nitrogen. Nitrous oxide formation was an intermediate during the reduction.

Unlike hydrogen as a reductant, carbon monoxide can inhibit nitric oxide reduction over platinum, palladium, and rhodium, while carbon monoxide accelerates reduction over ruthenium. The difficulty is that in the presence of air, the carbon monoxide is generally oxidized first, therefore, these processes must operate under reducing atmosphere[121].

3.4.5 Three-way Catalytic Reaction

The spark-ignited combustion engine has been developed to provide the power to operate the automobile. The emissions and operation varied with the Air/Fuel ratio as shown in figure 3.12.

When the engine is operated rich of stoichiometric, the CO and HC emissions are highest while the NO_x emissions are depressed. This is because complete burning of the gasoline is prevented by the deficiency in O_2. The level of NO_x is reduced because the adiabatic flame temperature is reduced. On the lean side of stoichiometric, the CO and HC are reduced because nearly complete combustion dominates. Again, the NO_x is reduced because the operating temperature is decreased. Just lean of stoichiometric operation, the NO_x is at maximum, since the adiabatic flame temperature is the highest. At stoichiometric, the adiabatic flame temperature is lowered because of the heat of vaporization of the liquid fuel gasoline. The actual operating region of combustion for the spark-ignited engine is defined by the and rich flame stability, beyond which the combustion is too unstable[9].

At stoichiometric, the catalytic converter can control hydrocarbon and carbon monoxide in oxidizing condition where oxygen is added to the exhaust constituents. In addition, catalytic converter can also control nitrogen oxides in reducing condition in the exhaust where oxygen is removed from harmful compound as well. Thus, it can all three emissions simultaneously. The catalytic converter which carry out this task is called " Three-way Catalyst"[124].

The converter, generally, composes of five major component parts : substrate, support, stabilisers, base metal promoters and platinum group metals. The conventional catalyst is Pt, Rh/Al_2O_3. However, this catalytic converter

must be operated in very narrow range around stoichiometric air/fuel which is able to apply only in rich burn region operation associate with gasoline engine. Effect of exhuast gas stoichiometry on the conversion is expressed in figure 3.13.

3.4.6 Selective Catalytic Reduction by Ammonia

Selective catalytic reduction (SCR) of NOx using ammonia was first discovered in 1957. It was found that NH_3 can react selectively with NOx, producing elemental N_2 over a Pt catalyst in excess of oxygen. The major desired reaction are :

$$4NH_3 + 4NO + O_2 \longrightarrow 4N_2 + 6H_2O \qquad (3.8)$$

$$4NH_3 + 2NO_2 + O_2 \longrightarrow 3N_2 + 6H_2O \qquad (3.9)$$

One undesirable product, N_2O, which given its strong infrared absorptivity, is considered to be a powerful greenhouse gas:

$$2NH_3 + 2O_2 \longrightarrow 3N_2O + 3H_2O \qquad (3.10)$$

At temperature about 100 - 200 °C, NH_3 can also react with the NO_2 present in the process gas producing explosive NH_4NO_3 as in the reaction below:

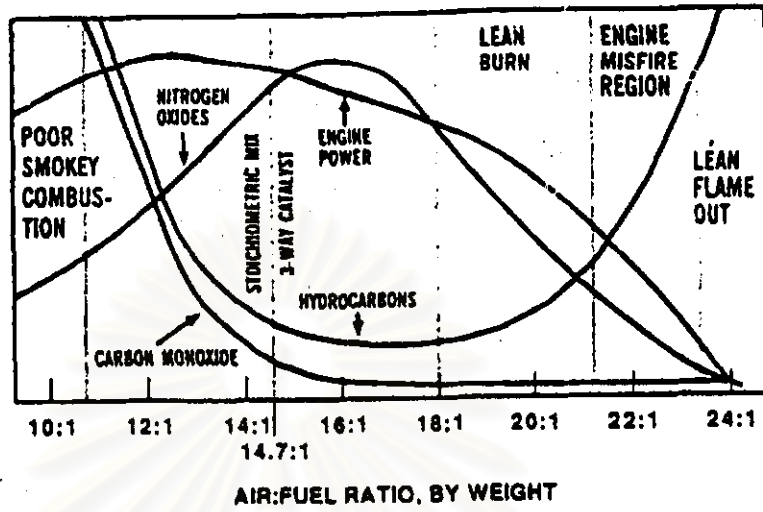$$2NH_3 + 2NO_2 + H_2O \longrightarrow NH_4NO_3 + NH_4NO_2 \qquad (3.11)$$

Figure 3.12 Spark-ignited gasoline engine emmission as a function of Air/Fuel ratio[9].
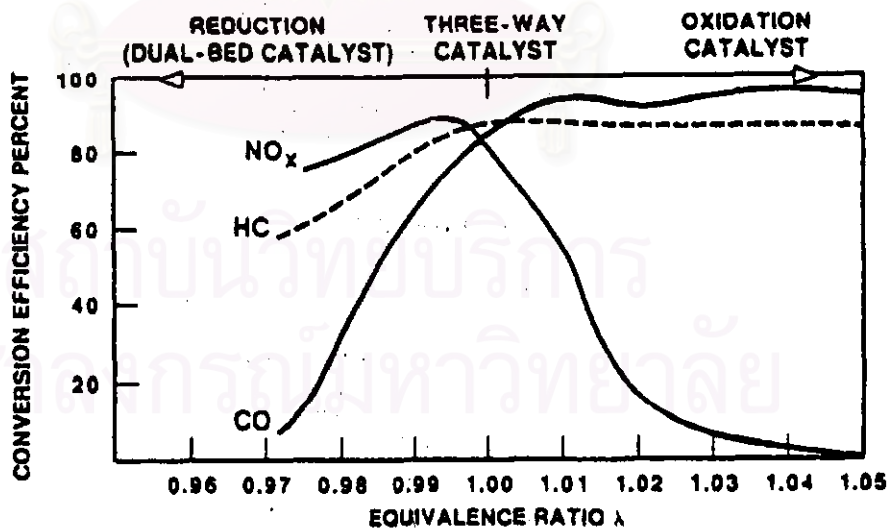

Figure 3.13 The effect of exhaust gas stoichiometry on the conversion efficiency of a rhodium/platinum catalyst[121].

The reaction can be avoided by never allowing the temperature to fall below about 200 °C. The tendency for formation of NH_4NO_3 can also be minimized by metering into the gas stream less than the precise amount NH_3 necessary to react stoichiometrically with the NO_x (1 to 1 mole ratio) By doing so, there is little excess NH_3 that can slip out of the reactor

It is apparent that NH_3/NO_x ratios much greater that 1 result insignificant NH_3 slip. In all applications, there is always a specification on permits NH_3 slip. Frequently,this is < 5 - 10 vppm. The major reactions involved in SCR NOx reduction are depicted schematically in figure 3.14.

Few Applications of the SCR NOx catalysts existed until the early 1970s, when reductions of the emission of NOx became an important control issue for stationary power source in Japan. The Pt technology was not applicable in this exhaust temperature region(i..e. > 250 °C) because of its poor selectivity for NOx reduction at these higher temperatures. Thus, it was during this period that the base metal catalysts were invented. Figure 3.15 shows a comparison of the operating temperature range for the various catalyst technologies available for SCR NOx. Note that the Pt catalysts lose selectivity above 250 °C. At > 250° C, V_2O_5/Al_2O_3 was used first. However, it was restricted to sulfer-free exhaust gases because the alumina reacted with SO_3 to from $Al_2(SO_4)_3$ and deactivated the catalyst. This problem led to another development, the use of a nonsulfating TiO_2 carrier for the V_2O_5 which then became the catalyst of choice. These catalysts functions at higher temperatures and over a broader range than Pt.
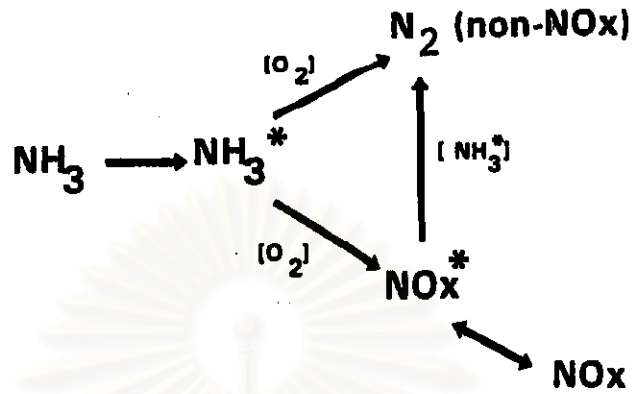
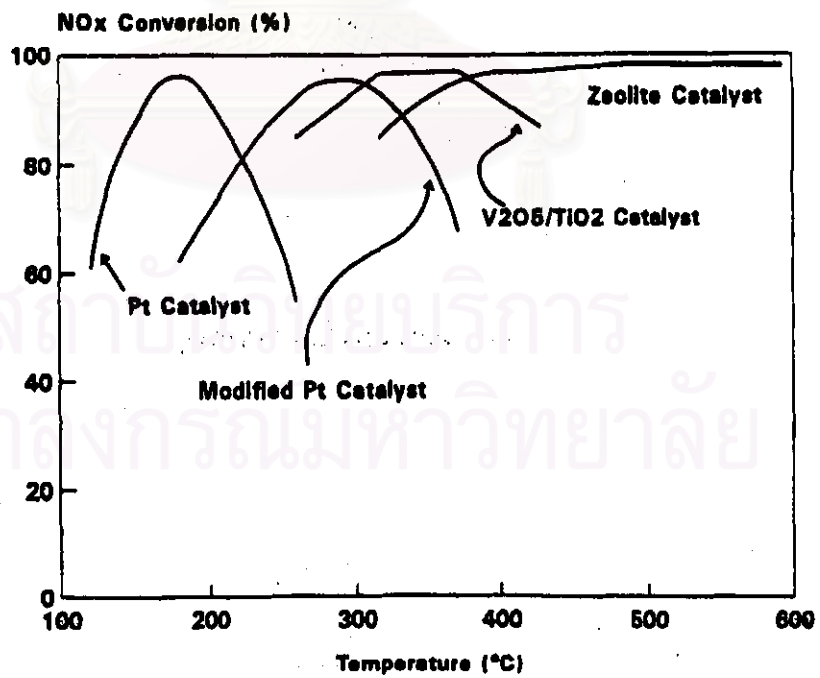Figure 3.14 Reaction network-catalytic reaction scheme of NH_3, NO_x and O_2 [9]

Figure 3.15 Operation temperature windows for different catalysts for the SCR by NH_3[9].

3.4.7 Selective Catalytic Reduction by Hydrocarbon

Recently, increased attention has been given to the catalytic reduction of nitric oxide under lean (net oxidizing) conditions. Such lean catalysts, if successful, could find application for NO_x emission control for diesel-fueled engines and for lean-burn gasoline-fueled engines, which provide improved fuel economy but which present new challenges for emission control. New regulations for trucks equipped with diesel engines will require lower NO_x emissions. Exhaust after treatment of NO_x is being pursued for both of these applications.

The diesel and lean-burn engines operate at air/fuel ratios of greater than 17:1. While NO_x emissions from the engine are considerably lower at these high air/fuel ratios, typical 3-way catalysts do not promote NO_x reduction, except in narrow temperature window in the vicinity of catalyst light-off. Catalyst are being explored which have a wider temperature range for NO_x reduction and exhibit higher lean NO_x conversion than the Pt-Rh 3-way catalyst [8].

In addition, it could be installed in the exhaust as a passive device, requiring no major engine modifications. A less attractive but feasible fallback approach is to catalytically reduce the NOx using on-board hydrocarbons(HC) according to process [9] below:

$$HC + NOx + O_2 \longrightarrow N_2 + H_2O + CO_2 \qquad (3.12)$$

There are many types of catalysts which proposed for the catalytic reduction of NO by hydrocarbon. However, among all, Cu/ZSM-5 was suggested the most activity.

Metal-doped ZSM-5 catalysts are active in promoting the conversion of nitric oxide to molecular nitrogen under oxidizing conditions, both by direct decomposition by selective catalytic reduction with hydrocarbons. The

sensitivity of the catalysts to poisoning by water vapour and sulfer dioxide precludes their use in the direct decomposition route.

Reduction by hydrocarbons occurs readily in the range 300-500 °C, and is favoured by high NO and hydrocarbon concentrations. For Cu-ZSM-5 a copper exchange level of ~ 100% is optimal. The reaction proceeds via an intermediate between adsorbed NO_2 and hydrocarbon formed on the surface. Oxygen is required to oxidize the NO to NO_2, but also attacks the hydrocarbon and the intermediate [125].

3.5 Transient Response Methods

3.5.1 Feature of Transient Experiment

The steady-state flow method has been widely used in the kinetic study of heterogeneous catalysis Under the conditions of steady study state, all elementary steps in series are progressing at the same rate and hence the measured rates hardly tell the precise kinetic structure, of mechanism, of catalytic reactions which usually consist of several elementary steps including adsorption of reactants, surface reaction, and desorption of products. In the kinetic analyses of any given reactions, it is a common practice for the investigator to postulate a number of suspected rate models and then to assess these models to verify a optimal one which best fits observed rate data. Usually, however, there are quite a large number of plausible rate models even for a rather simple reaction, and it is not easy to determine the most adequate model among others even with the help of mathematical model identification techniques with a electronic computer. This method is based on the assumption that there is a best model which reflects the true mechanism of the reaction sequences among the postulated models. But there is no certification which justifies this assumption. Therefore, even when a rate model is found to fit the rate data very well, the value of parameters appearing in the rate model should be further assessed in regards to their physical significance.

To meet requirements for establishing sound rate models transient response methods furnish more definite and first hand information relative to the true mechanism than do steady state experiments. When some perturbations are imposed on a reaction system under steady state, the transient response of the system as it approaches a new steady state exhibits a characteristic behavior reflecting the nature of the sequence of steps which underlie observed kinetics but cannot be unveiled by the steady state experiments.

This method provides quantitative information relative to the amounts and the rates of adsorption and desorption of adsorbed species, which consequently serve to reveal the mechanism of the reaction in question. The models thus established, therefore, sequence of events on the catalyst surface than do the models discriminated merely mathematically among many postulated models.

A further of this method is that it can provide suitable experimental data which serve in characterizing individual elementary steps so that one can determine the kinetic parameter or each elementary step by using these data for analysis. If there are any kinetic parameters which cannot be directly determined by making use of the response data of individual steps, these are to be determined by the ordinary parameter estimation technique by utilizing specified response data with the help of high speed electronic computers[126].

Effects due to transport resistance must be carefully avoided in work at atmospheric pressure, so that chemical effects having response times less than about a second cannot be followed. These limitations are avoided at low pressure[127].

3.5.2 Operations

Abrupt addition or removal of a reactant probably can only be realized via either in situ production of the reactant (via, e.g., a photochemical reaction) or via an experiment such as that described previously, i.e., with the catalyst present in a stationary phase and the reactants and products present predominantly in a fluid phase. Such an experiment may even allow study of

problems currently addressed in homogeneous catalysis. We mention systems involving transition metal complexes anchored to solids and systems with the catalyst dissolved in a highly dispersed, supported liquid phase.

The ability to determine via transient kinetic methods high values of k (and correspondingly low values of intermediate concentrations) depends on the amount of resolution in time available in the monitored transients. Practical limitations on time resolution are probably set by the following:

1. turbulence, causing mixing of fluid phases with different (isotopic) constitutions;

2. the trade-off between response time and sensitivity of the analytical techniques utilized in monitoring the transients:

3. rates of mass transfer between the immobile phase holding the catalyst and the fluid phase holding the reactants and products. We estimate that, with the exception of rarefied fluid phases, the first factor steps a practical lower limit of the order of 1 s to the attainable time resolution. This would limit transient kinetic information to reaction steps occurring with an absolute rate constant k of 1 s^{-1} or less[128].

Since the aim of the perturbing method is to acquire useful information on kinetics and the mechanism of reactions from the resultant response of a reaction system which is shifted from its steady state or equilibrium state, any kind of variables that defines the chemical kinetic state of the system may be used for this purpose, i.e., concentration, temperature, pressure, and flow rate. Unimposing perturbation of any one of these variable , a well-defined forcing function must be used for the sake of simplicity of the analysis of the response. The possible functions will be rectangular step functions, rectangular pluses, damped harmonic oscillations, and ramp functions.

The most common variable used to induce equilibrium shift in the study of homogeneous reactions in temperature, and the simplest of the forcing functions is the rectangular step function. It is the so-called temperature-jump

method which always used for homogeneous gas phase reactions[126]. However, There are some modes of operation which would be mentioned below:

Steps and Pulses. Supporting that the proper equipment can be devised for measuring gas-phase and in some cases--surface transients, the question arises as to what kind of forcing function should be used. An important class of experiments involves temperature as the perturbing variable. Temperature programmed desorption or reaction and flash desorption are widely used. Following transients induced by temperature change by mass spectrometric analysis of the gas phase has been highly developed.

Cycled Feed. The qualitative interpretation of response to steps and pulses is often possible, but the quantitative exploitation of the data requires the numerical integration of nonlinear differential equations incorporated into a program for the search for the best parameters. A sinusoidal variation of a feed component concentration around a steady state value can be analyzed by the well developed methods of linear analysis if the relative amplitudes of the responses are under about 0.1.

Self-sustained Oscillations. Under certain conditions, isothermal limit cycles in gaseous concentrations over catalysts are observed. These are probably caused by interaction of steps on the surface. Sometimes heat and mass transfer effects intervene, leading to temperature oscillations also[127].