CHAPTER III
THEORY

3.1 Nitric oxide pollution

Nitric oxide is a major atmospheric pollutant. It has the ability to generate secondary contaminants through its interaction with other primary pollutions (like carbonyl corresponding molecules, alcohol radicals, etc.) also resulting from the combustion of fossil fuels in stationary sources such as industrial boilers, power plants, waste incinerators, and gasifiers, engines, and gas turbines or from the decomposition of a large number of organic products by light or micro organisms.

Nitric oxide plays a major role in the photochemistry of the troposphere and the stratosphere. It reacts with photochemical pollutions such as ozone, formaldehyde, organic hydroperoxides and peroxyacryl nitrates that all are very reactive and have a very short lifetime. This is a very fast reaction which generates more nitrogen oxides and organic nitrates. In the presence of oxygen, nitric oxide is oxidized very quickly to NO_2 which is partly responsible for acid rain and the urban smog. They have very negative effects in agriculture, but may also predispose to respiratory diseases by weakening the ability of the bronchopulmonary structures to function properly [105].

3.2 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, cyanate and isocyanate compounds. This could be completely avoided in this case, except N_2O formation. Cu- zeolites are currently the best catalysts that involve in redox mechanism [106, 107].

3.3 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. 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 occur as a result of the nature of catalyst, 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 good stability over time, and are thus recommended for technical applications.

3.4 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 [5-8]. The reaction of NO with CO:

$$NO + CO \longrightarrow CO_2 + \frac{1}{2} N_2 \tag{3.1}$$

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:

$$NO + H_2 \longrightarrow N_2 (\text{or } NH_3, NO_2) + H_2O \tag{3.2}$$
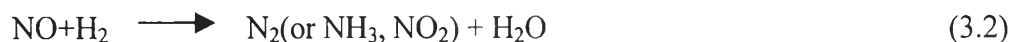
Neither the reduction of NO with CO nor that with hydrogen can be considered as selective because, in addition to nitrogen, other undesired compounds like N_2O or NH_3 (in the case of hydrogen) are generated. Oxygen is always presented in the exhaust gases. The oxygen excess achieved by lean carburization 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.

## 3.5 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 by Iwamoto et al. [59-61] and Held et al. [62] independently. They showed 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 [10] 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.

3.6 Zeolite crystallites

Zeolites are crystallites, hydrated aluminosilicates structurally based 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.

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

$$Mx/n[(AlO_2)_x(SiO_2)_y]wH_2O$$
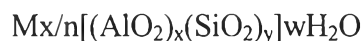
where M is the cation of valence n, w is the number of water molecules and the ratio y/x usually has values of 1-5 depending upon the structure. The sum (x+y) is the total number of tetrahedra in the unit cell [108]. The portion with $[(AlO_2)_x(SiO_2)_y]$ represents the framework composition.

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 approximately 0.55 nm in diameter in Figure 3.1a are able to access a network of intersecting pores within the crystal. The three dimensional structure of silicalite and ZSM-5 is illustrated in figure 3.1b [109].
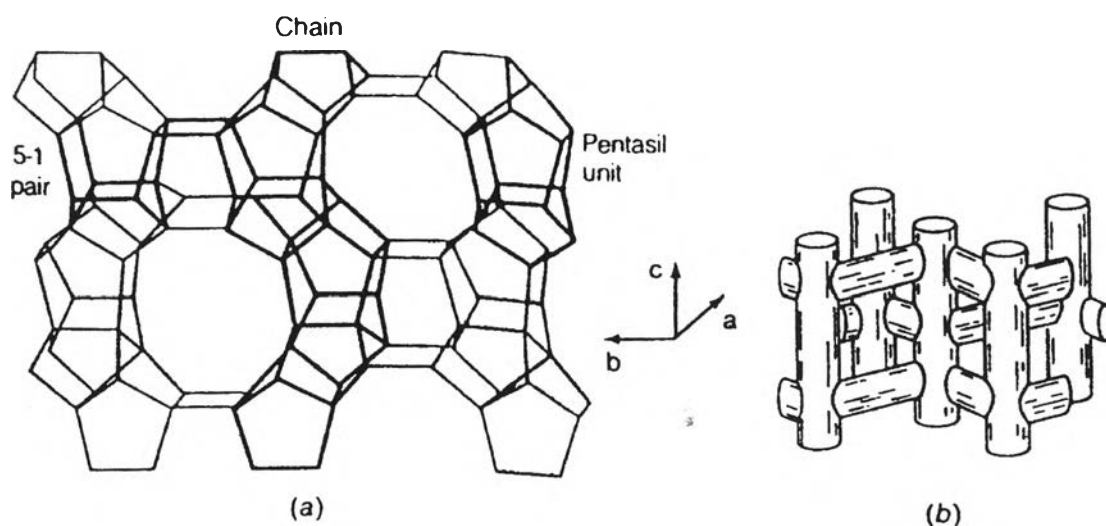

Figure 3.1 Three-dimensional structure of silicalite (MFI) (Gate 1992 [109])

  (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 3.1b; 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.

The zeolite ZSM-5 structure was originally prepared by Argauer and Landott in 1972 in the presence of the organic tetrapropylammonium (TPA) cation with a range of

SiO_2/Al_2O_3 claimed between 15 and 100. Soon afterwards, the catalysts that incorporate transition elements other than Al into the framework of MFI structure, metallosililcates, were synthesized [110, 111]. The elements were usually introduced by adding metal salts as one of the starting materials for the synthesis of the metallosilicate. A variety of metallosilicates containing different kinds of transition elements were prepared by adopting the rapid crystallization method exhibiting very high thermal stability that is effective in practical use.
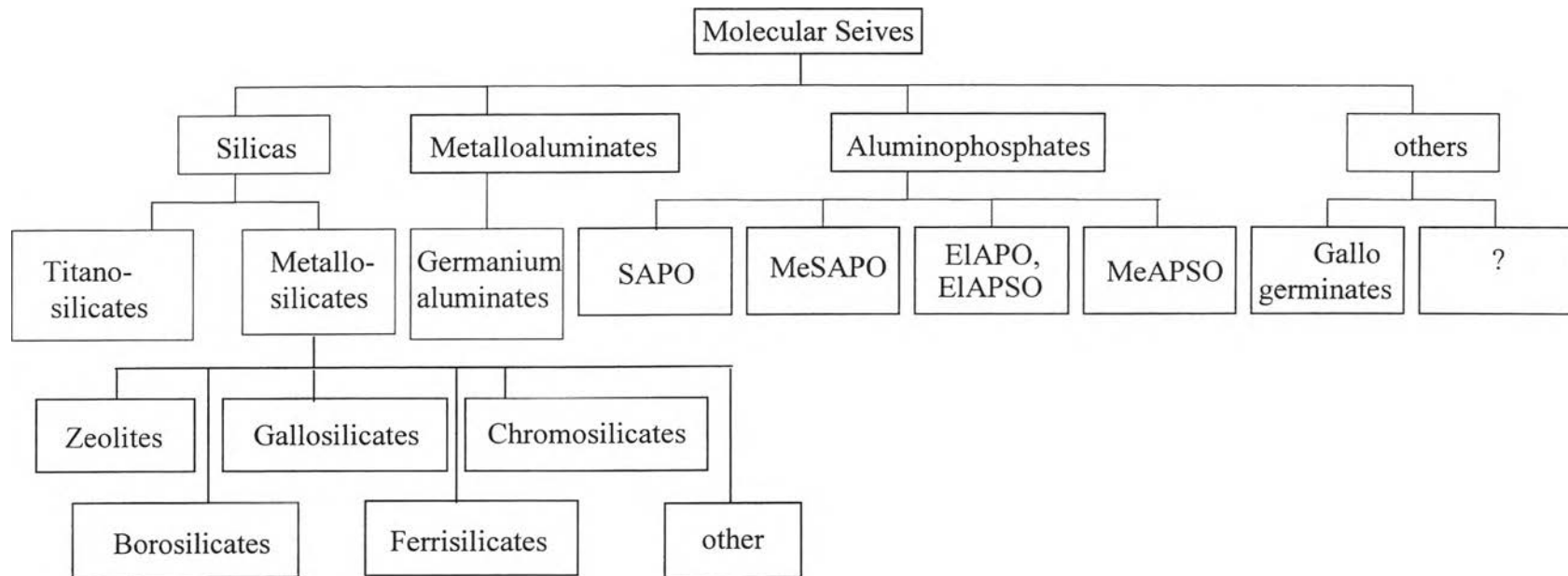
Table 3.1 Classification of molecular seive materials indicating extensive variation in composition. The zeolites occupy a subcategory of the metallosilicates (Flaginen 1991[108]).