



## CHAPTER II

### BACKGROUND AND LITERATURE SURVEY

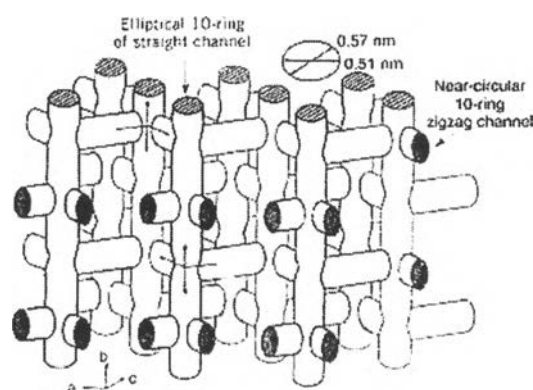
#### 2.1 Zeolite

Zeolite is an aluminosilicate material that forms as a framework. The zeolite framework is made up of  $\text{SiO}_4^{-4}$  and  $\text{AlO}_4^{-5}$  tetrahedral linked together by sharing the oxygen atom. A negative charge is produced when an alumina tetrahedral is present, so a cation must be present to balance the charge. The structures contain channels or interconnected voids that are occupied by the cations and water molecules. In most zeolite structures, the primary structural units, tetrahedral, are assembled into secondary building units, which may be a simple polyhedral, such as, cube, hexagonal prisms, or truncated octahedral. The polyhedral will connect to each other to form a unit cell. There are many ways for polyhedral to be connected, therefore there are many unit cells formed. The porosity is mostly generated only when the polyhedral are connected to form a unit cell. The pores can be classified as cages and channels. High aluminium content zeolites tend to be a cage structure framework while high silica content zeolites tend to be a channel structure framework. The window is a pore aperture of the framework structure. Classification of zeolites based on size of windows is shown in Table 2.1.

**Table 2.1** Classification of zeolites based on size of windows

Small	Medium	Large	Extra large		Mesoporous
4-5 °A	5-6 °A	7-8 °A	12 °A	13 °A	16-100 °A
8-T ring	10-T ring	12-T ring	18-T ring	20-T ring	Variable
Zeolite A	ZSM-5	Faujasite	VPI-5	Cloverite	MCM-41
Chabazite	Theta-1	Mordenite			MCM-48
ZK-5	Ferrierite	Offretite			
Rho	ZSM-48	Beta			
Erionite		Zeolite L			

Zeolites are high capacity and selective adsorbents capable of separating molecules, mainly based on the size and shape of the molecule relative to the size and geometry of the main apertures of the structure. Separation may be based on the molecular-sieve effect or may involve the preferential or selective adsorption of one molecular species over another. The separations are governed by several factors. The basic framework structure or topology of the zeolite determines the pore size and the void volume. The example of framework structure of ZSM-5 zeolite is shown in Figure 2.1. The exchange cations, in terms of their specific location in the structure, population density, charge and size, affect the molecular-sieve behavior and selectivity of the zeolite. By changing the cation type or number, the selectivity of the zeolite in a given separation can be tailored or modified within certain limits.



**Figure 2.1** Framework structure showing the topology of the ZSM-5 zeolite.

In zeolites, catalysis takes place preferentially within the intracrystalline voids. Aperture size and type of channel system affect catalytic reactions, through which reactants and products must diffuse. Modification techniques include ion exchange, variation of Si/Al ratio, hydrothermal treatment or stabilization can improve catalytic activity and selectivity. In addition, the zeolite framework structure determines shape-selective effects. Several types have been demonstrated including reactant selectivity, product selectivity, and restricted transition-state selectivity. Non-shape-selective surface activity is observed on very small crystals, and it may be desirable to poison these sites selectively, e.g. with bulky compounds unable to penetrate the channel apertures, or by surface silation.

## 2.2 Toluene Disproportionation

Toluene disproportionation over zeolite catalyst yields benzene and a mixture of xylenes. General zeolite used in this reaction is ZSM-5 to increase para-isomer content in the products compared with the thermodynamic equilibrium. Chemical modification of the zeolite causing the reduction of pore diameter produces catalysts that achieve high selectivity of para-xylene. This favorable result is explained by greatly reduced diffusivity of ortho- and meta-xylenes compared with that of the less bulky para-isomer.

The mechanism of toluene disproportionation over zeolite can be summarized in the following steps:

1. Toluene diffuses through the zeolite channels and reacts on the acid site giving benzene and xylenes mixture.
2. The initial product diffuses through the zeolite pore structure and simultaneously undergoes internal isomerization reactions, yielding the primary product, the first observable outside the zeolite channels. The proportion of para-xylene in the primary product is expected to increase due to the faster diffusion of this isomer.
3. The primary product undergoes a secondary isomerization, becoming the secondary product finally observed in the effluent.

The preliminary findings of toluene disproportionation over ZSM-5 catalysts were first patented by Kaeding (1977). At atmospheric pressure and a temperature range of 450°-600°C, he reported that the main products in the reaction were benzene and xylenes. The percentage conversion of toluene and the ratio of benzene to xylenes were found to increase with increasing temperature, and para-xylene present in the xylene mixture was always in equilibrium with its isomers.

Meshram *et al.* (1983) investigated the effect of catalytic parameters. They observed that benzene to xylene ratio was independent with pressure, while the percentage of toluene converted was dependent on pressure. In addition, they also found that the strong acid site of ZSM-5 zeolite promoted the dealkylation of toluene.

Mavrodinova *et al.* (1985) studied the toluene conversion over HZSM-5 zeolite and reported that the coke was formed only on the external surface of the zeolite.

The para-selectivity increased by modifying ZSM-5 with phosphorous. Increasing the temperatures also reduced the percentage of para-xylene products (Meshram *et al.*, 1987).

Bhaskar and Do (1990) showed that toluene in the presence of hydrogen over ZSM-5 catalysts underwent dealkylation and disproportionation reactions, but in the presence of nitrogen, only disproportionation reaction occurred. The amount of para-xylene in the xylene mixture was more than the equilibrium value for the large crystal catalysts only.

### 2.3 Zeolite Surface Modification

The effect of unmodified and modified ZSM-5 zeolites was studied by Uguina *et al.* (1993,b). When a ZSM-5 was modified with Si and Mg compounds, only the para-xylene isomer was just outside the channel system. The mechanism for the unmodified ZSM-5 model was based on the alkyl transfer mechanism. The kinetics of the reaction was better fitted with pseudo first order model. Further study on the roles of ZSM-5 modifier agents in selective toluene disproportionation was done in the same year. The results showed that modification of ZSM-5 with Si gave high para-selectivity and catalytic activity in toluene disproportionation. This modifier agent was located on the external surface of zeolite crystals. Due to its large molecular size it prevented secondary isomerization reaction at the outside crystal by reducing external acid site of the zeolite. Cs cation, having smaller size, could present within the channel system in order to partially block pores of zeolite, thus, low toluene conversion was obtained with this agent. In addition, the para-selectivity was mainly related to the deactivation degree of the external surface.

Kuneida *et al.* (1999) investigated the source of selectivity of para-xylene formation in the toluene disproportionation over ZSM-5 zeolites. The result was in agreement with Uguina *et al.* (1993,a), they found that the selectivity in disproportionation could be related with not only the diffusion rate but also the

external solid acidity, except for unusual species of zeolites. These unusual properties might be correlated with non-homogeneous distribution of cation Al or Si in the zeolite. Therefore, the source of selectivity strongly depended on the physical and chemical properties of the zeolite.

Fang *et al.* (1999) found that the selective coking during toluene disproportionation over HZSM-5 zeolite could enhance para-selectivity. In the presence of N<sub>2</sub> carrier gas, light volatile soft coke preferred to deposit within the intracrystalline channels of the zeolite, and was responsible for a decrease in toluene conversion. This internal coke could be removed by H<sub>2</sub>. Coke that tended to deposit on the external surface of zeolite was mostly bulky hard coke. This external coke effectively modified the surface acid properties of the zeolite crystallines, which in turn cut off the secondary isomerization pathways of para-xylene, thus enhancing the para-selectivity.

The mild hydrothermal treatment for the H-ZSM-5 and Pt incorporation ZSM-5 had greatly reduced both of hydrodealkylation and disproportionation activities, but enhanced para-xylene selectivity (Aboul-Gheit *et al.*, 2001). The reason is that steaming had removed strong acid sites, whereas Pt had covered a portion of these strong acid sites. Moreover, the thermal hydrotreatment before Pt incorporation improved bifunctionality (acid and metal function) and increased the selectivity of para-xylene. However, hydrothermal treatment after Pt incorporation seemed to reduce the bifunctionality.

The enhancement of shape selectivity of ZSM-5 by chemical vapor deposition (CVD) by bulky organic silicon compounds is one of the important modification methods. The shape and product selectivity mechanisms were based on the difference in the diffusion rates of xylene isomers and the amount of external acid sites. Therefore, CVD technique changed neither the channel size nor acidity by depositing silica at the external surface of zeolite, and at the same time narrowed down the pore opening size due to coating inert silica on the external surface (Halgeri and Das, 2002).