CHAPTER II

THEORY

This chapter explains about zeolite, TS-1 structure, hydrothermal method and reactions of alcohol.

2.1 Zeolite

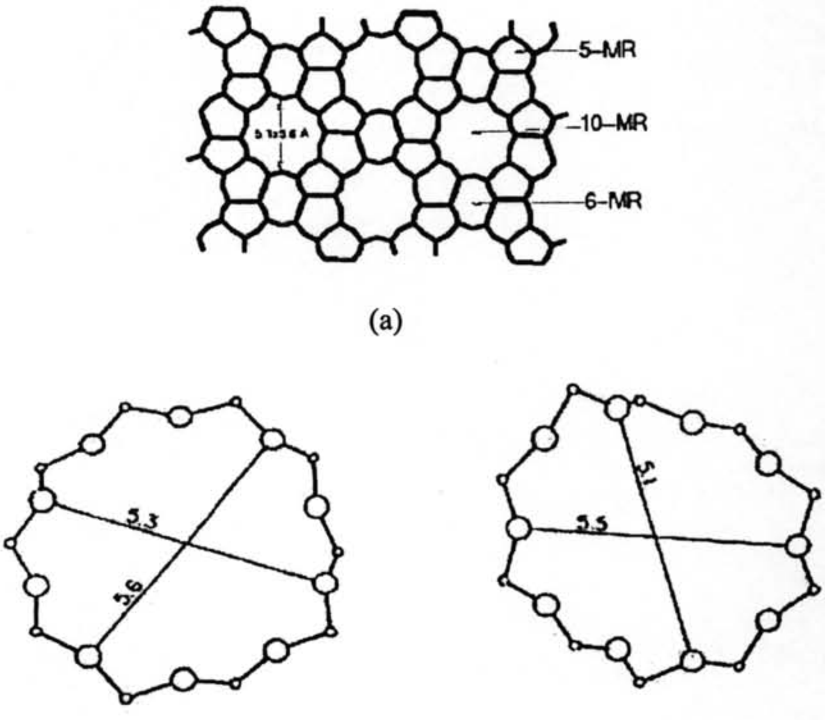
Zeolites are three-dimensional, microporous, crystalline solids with well-defined structures that contain aluminum, silicon, and oxygen in their regular framework; cations and water are located in the pores. The silicon and aluminum atoms are tetrahedrally coordinated with each other through shared oxygen atoms. Zeolites are natural minerals that are mined in many parts of the world; most zeolites used commercially are produced synthetically. Zeolites have void space (cavities or channels) that can host cations, water, or other molecules. Because of their regular and reproducible structure, they behave in a predictable fashion.

Zeolite based catalysts, which are commonly used in acid catalyzed reactions, are also used in oxidation reactions. There was zeolite catalyst development by titanium containing zeolite with MFI structure and it was called that titanium silicalite (TS-1).

2.2 TS-1 structure

Titanium silicalite, the first successful example was the isomorphic substitution of Si^{4+} with Ti^{4+} from a ZSM-5 silicalite framework which was reported by Taramasso et al. in 1983. Examples of titanium silicalite molecular sieves are TS-1 with MFI-type structure and TS-2 with MFI/MEL-type structure, both of which are in the pentasil family of zeolite structures.

The framework structure of TS-1 consists of corner shared oxygen ions of $[TiO_4]$ and $[SiO_4]$ tetrahedral as shown in Figure 2.2. As Ti^{4+} ions substitute isomorphously the Si^{4+} ions, TS-1 is electrically neutral and does not possess ion exchange property. TS-1 is member of the pentasil family, rings consisting of five O atoms, isomorphous with ZSM-5 and silicalite-1. Its pore system consists of ten-membered ring openings. These are important because they provide openings in the structure large enough for passage of even rather large molecules. TS-1 has elliptical straight channels having a diameter of 5.1 - 5.6 Å intersected perpendicularly by circular sinusoidal channels having a diameter of 5.4 Å. The framework structure of TS-1 as viewed from the *b* direction is shown in Figures 2.1a, 1b and 1c.



(b) (c)

Figure 2.1 The framework structure of TS-1 viewed from the *b* direction

(a) ten-membered rings viewed cross-sectional straight channels

(b) ten-membered rings viewed along [010] straight channel

(c) ten-membered rings viewed along [100] sinusoidal channel

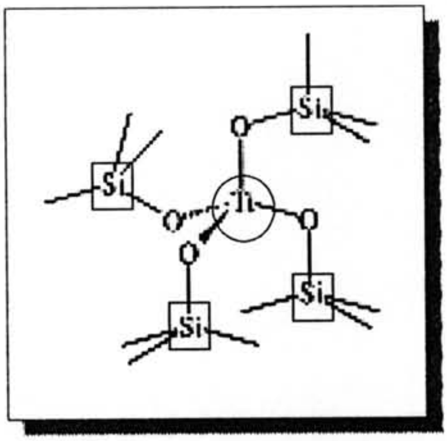
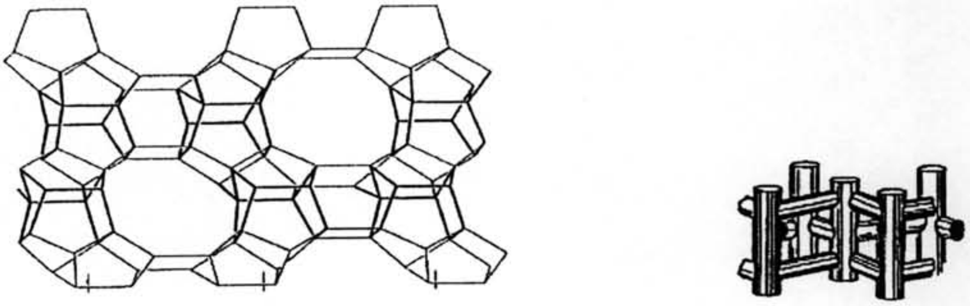


Figure 2.2 Isomorphous substitution of Si with Ti atoms in zeolite framework of TS-1

The three–dimensional structure of silicalite (MFI type catalysts) is represented in Figure 2.3a. The ten-membered rings provide access to a network of intersecting pores within the crystal. The pore structure consists of two intersecting channel systems as shown in Figure 2.3b: one straight and the other sinusoidal and perpendicular to the former. Many molecules are small enough to penetrate into this intracrystalline pore structure, where they may be catalytically converted.



(a) (b)

Figure 2.3 Three-dimensional structure of silicate (MFI type)

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

(b) Channel network

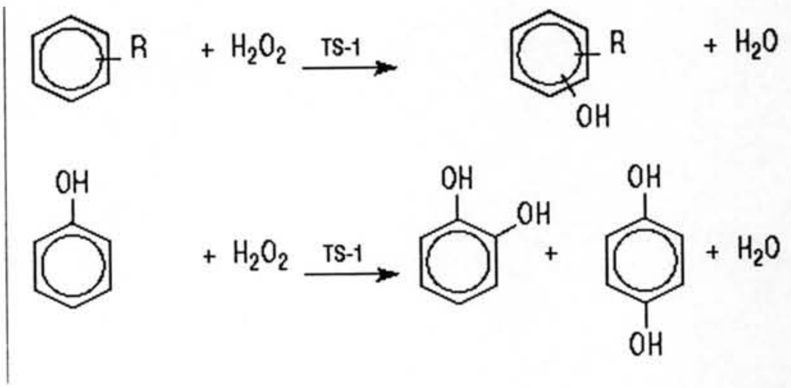
The interpretation of the catalytic activity of TS-1 must take into consideration the role played by these few Ti^{4+}: in fact pure silicalite is totally inactive, and other phases containing Ti have not been identified. Due to the fact that TS-1 crystallizes from a homogeneous solution, it is reasonable to assume that the distribution of Ti^{4+} in the crystal lattice is at random; since the Si/Ti ratio is in the range 40-90 in typical preparation, most Ti^{4+} must be isolated from each other by long sequences of -O-Si-O-Si-O-.

The amount of Ti positioned within the framework of the molecular sieve is believed to be important and beneficial in many reactions. However, it is also widely believed that non-framework Ti-species, on the exterior or interior surfaces of crystals may decrease the catalytic effectiveness of titanium silicalite molecular sieves.

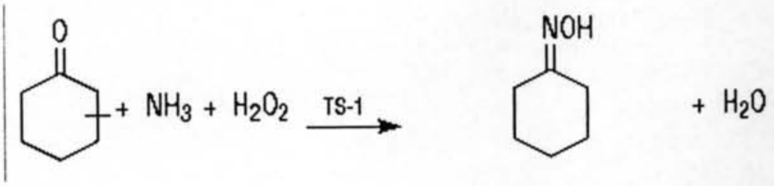
2.3 Applications of TS-1 catalyst

TS-1 catalyst can exhibit unique activity and selectivity in several oxidation reactions of organic substrates carried out with dilute hydrogen peroxide at mild reaction conditions, with water as a major byproduct. Catalytic activity on TS-1 catalyst is shown below.

1. Aromatic hydroxylation



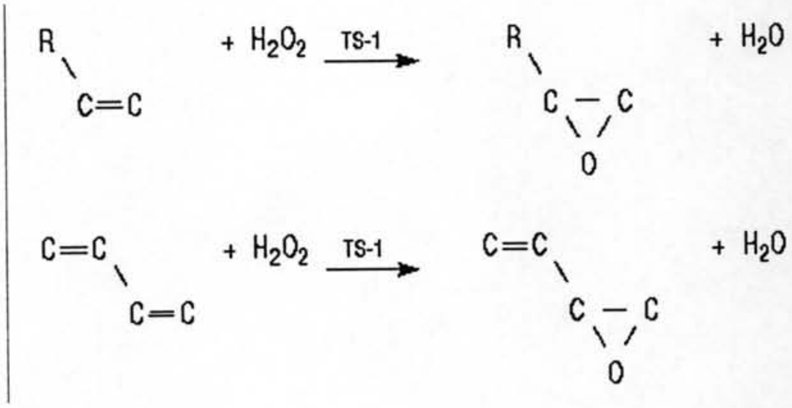
2. Ammoximation of cyclohexanone to the oxime



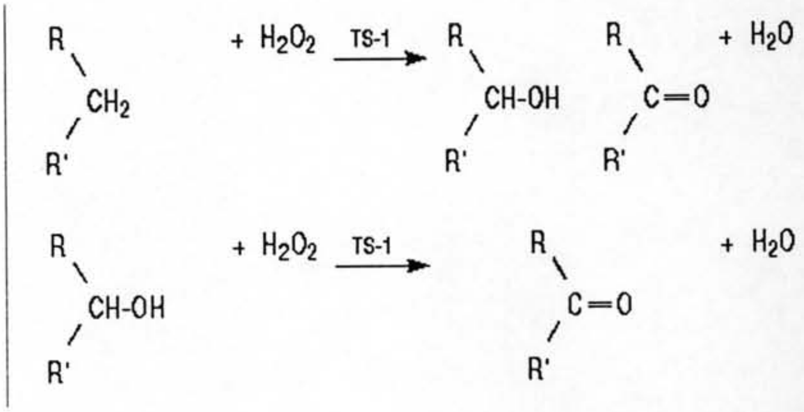
3. Primary alcohols oxidation to aldehydes

$$R{-}CH_2{-}OH + H_2O_2 \xrightarrow{TS\text{-}1} R{-}CHO + H_2O$$

4. Olefin epoxidation



5. Alkane oxidation



2.4 Hydrothermal method

Hydrothermal method utilizes water under pressure and at temperatures above its normal boiling point as a means of speeding up the reactions between solids. The water performs two roles. The water - as liquid or vapour - serves as the pressure transmitting medium. In addition, some or all of the reactants are partially soluble in the water under pressure and this enables reactions to take place in, or with the aid of, liquid and/or vapour phases. Under these conditions, reactions may occur that, in the absence of water, would occur only at much higher temperatures. The method is therefore particularly suited for the synthesis of phases that are unstable at higher temperatures. It is also a useful technique for growth of single crystals; by arrange for a suiTable temperature gradient to be present in the reaction vessel, dissolution of the starting material may occur at the hot end and reprecipitation at the cooler end.

Since hydrothermal reactions must be carried out in closed vessels, the pressure-temperature relations of water at constant volume are important. These are shown in Figure 2.4. The critical temperature of water is 374°C. Below 374°C, two fluid phases, liquid and vapour, can coexist. Above 374°C only one fluid phase, supercritical water, ever exists. Curve AB represents the saturated steam curve. At pressure below this curve liquid water is absent and the vapour phase is not saturated with respect to steam; on the curve the vapour is composed of saturated steam which is in equilibrium with liquid water; above the curve, liquid water is effectively under compression and the vapour phase is absent.

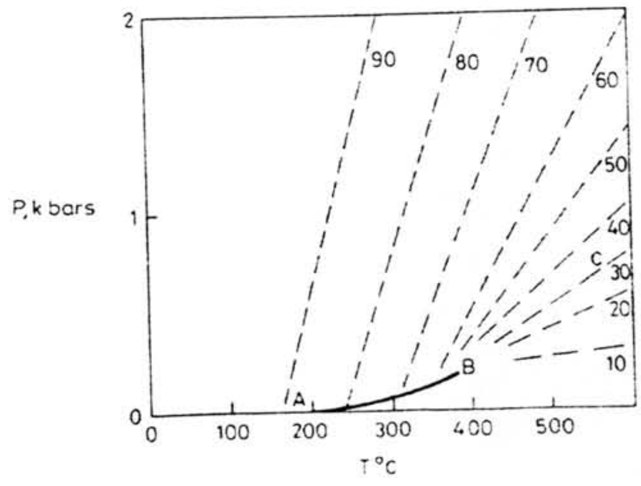


Figure 2.4 Pressure-temperature relations for water at constant volume. Dashed curves represent pressures developed inside a closed vessel; numbers represent the percentage degree of filling of the vessel by water at ordinary P, T. (West, Antony R., 1984)

The dashed curves in Figure 2.4 may be used to calculate the pressure that is developed inside a vessel after it has been partially filled with water, closed and heated to a certain temperature. Thus, curve BC corresponds to a vessel that is initially 30 per cent full of water: at, for example, 600°C, a pressure of 800 bar is generated inside the closed vessel. Although Figure 2.4 applies strictly to pure water, the curves are modified little, provided the solubility of solids present in the reaction vessel is small.

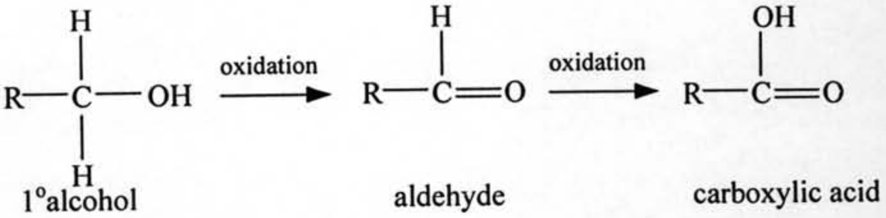
2.5 Reactions of alcohols

Reactions of an alcohol can involve the breaking of either of two bonds: the C-OH bond, with removal of the –OH group; or the O-H bond, with removal of –H bond. Either kind of reaction can involve substitution, in which a group replaces the –OH or-H, or elimination, in which a double bond is formed.

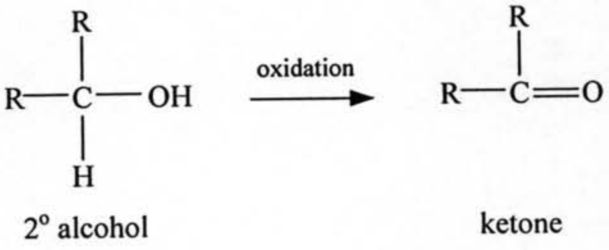
2.5.1 Oxidation reaction

The oxidation of an alcohol involves the loss of one or more hydrogens (α-hydrogens) from the carbon bearing the -OH group. The kind of product that is formed depends upon how many of this α-hydrogens the alcohol contains, that is, upon whether the alcohol is primary, secondary, or tertiary.

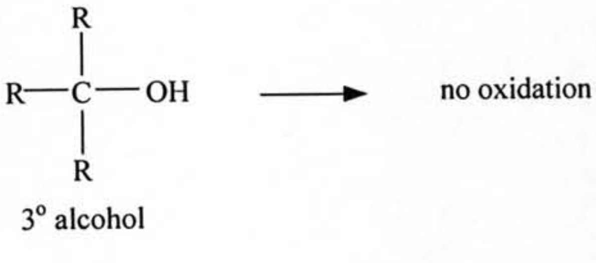
A primary alcohol contains two α-hydrogens, and can either lose one of them to form an aldehyde. Consequently, a formed aldehyde can be oxidized to a carboxylic acid.



A secondary alcohol can lose its only α-hydrogen to form a ketone.

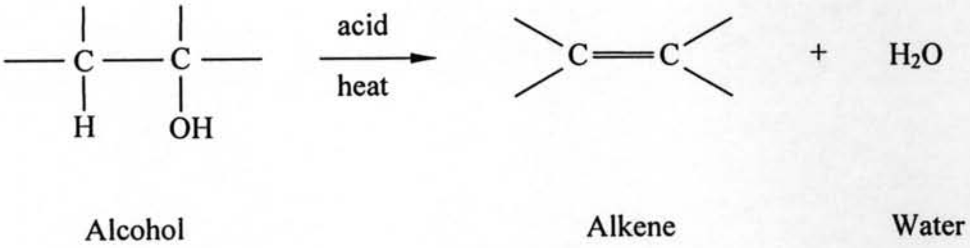


A tertiary alcohol contains no α-hydrogen and is not oxidized. (An acidic oxidizing agent can, however, dehydrate the alcohol to an alkene and then oxidized this)



2.5.2 Dehydration reaction

Dehydration can occur in the system involving the presence of an acid and the application of heat. An alkene is produced from elimination of a molecule of water in an alcohol.



The various classes of alcohols differ widely in ease of dehydration, the order of reactivity being

Ease of dehydration of alcohol $3^\circ > 2^\circ > 1^\circ$

As stated above, we found that oxidation of secondary alcohol does not produce intermediate agent unlike oxidation of primary alcohol. Therefore, it is advantage to evaluate tested catalysts with oxidation of secondary alcohol. In addition, because of any convenience and safety to prepare reactant in gas phase, 2-propanol is therefore selected to use as reactant in our test reaction.