CHAPTER II

THEORY

2.1 Framework substitution

The synthesis of molecular sieves occurs in hydrothermal conditions (temperatures in the 150-200 °C range) starting from an aqueous gel, containing a source of framework building elements (Al, Si) and the structure directing agent (template; usually an amine or a tetraalkylammonium salt). Instead of an aluminium source as for classical zeolites, trivalent (e.g., Fe^{3+}), or tetravalent (e.g., Ti^{4+}) salts can be added to the synthesis gel to obtain isomorphous substitution of Al or Si by the metal ion, whereby the latter occupies TO_4 tetrahedra. Isomorphous substitution is feasible when the atomic radius ratio of cation/oxygen is between 0.225 and 0.414. However, during calcinations of the as-synthesized material to remove the template, the transition metal can change its oxidation state and be expelled from the framework. Titanium and other active metals, e.g., V, Cr, Mn, Fe, Co, Cu, Zr and Sn have reportedly been incorporated in a variety of molecular sieve structures (silicalites, zeolites, AlPOs, SAPOs) by hydrothermal synthesis, although there is not always clear proof of there incorporation.

2.2 Titanium silicalite – 1

Titanium silicalite is the most interesting material obtained by isomorphic substitution of trivalent metals or tetravalent metals in the framework of crystalline aluminosilicates or silicates. Titanium silicalites with MFI (TS-1) and MFI/MEL (TS-2) structures have been used in several oxidation reactions with H_2O_2 as the oxidizing agent.

Titanium has a stable valence of 4 and in an oxidizing medium it is very likely that this valence is maintained. An examination of the chemistry of Ti^{4+} compounds immediately shows that Ti^{4+} has a strong tendency to assume a high coordination number: with oxygen, six groups in octahedral coordination form a stable and very

frequently observed configuration, but to do this Ti^{4+} must have near neighbours capable of increasing their coordination number to satisfy at the same time titanium valency of four and coordination of six. When bulky groups are linked to Ti^{4+}, tetrahedral coordination is also observed. Coordination of seven in a pentagonal pyramidal arrangement like in peroxo compounds and of eight like in $Ti(NO_3)_4$ are also observed.

From the crystalline structure and the regular change in unit cell parameters which are consistent with isomorphous substitution of Si^{4+} with Ti^{4+} it seems justified to represent TS-1 as a silicalite in which few Ti^{4+} have taken the place of Si^{4+}. 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 silicon/titanium ratio is in the range 40 - 90 in typical preparations, most Ti^{4+} must be isolated from each other by long sequences of -O-Si-O-Si-O-. If Ti^{4+} replaces a Si^{4+} it should be tetrahedrally coordinated by $O^=$ however, the presence of a band at 980 cm^{-1} closely corresponds to the band observed in other titanium compounds containing the $>Ti = O$ group, whose stretching frequency is 975 cm^{-1} with bond distances of 1.66 – 1.79 Å; furthermore, hydroxyl groups are present at the surface as shown by the increase in selectivity which is obtained upon silylation.

Finally, near neighbour positions of Ti^{4+} are occupied by Si^{4+} which in a field of $O^=$ is stable only in tetrahedral coordination. A simple representation of the sites where substitution has occurred which takes into consideration the various pieces of experimental evidence could be
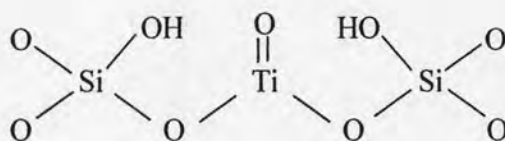
The amount of titanium positioned within the framework of the molecular sieve is believed to be important and beneficial in many reactions. However, it is also widely believed that non-framework Ti-species, on the exterior or interior surfaces of crystals may decrease the catalytic effectiveness of titanium-silicate molecular sieves. Similar deleterious effects may be caused by other contaminants such as aluminum and alkali elements. In particular, extra-framework massive Ti-oxides as well as other contaminants cause undesirable side reactions and as a consequence losses of activity and selectivity of the catalyst.

2.3 Hydrothermal method

Hydrothermal methods utilize water under pressure and at temperatures above its normal boiling point as a means of speeding up the reaction between solids. The water performs two roles. The water as liquid or vapor serves as the pressure transmitting medium. In addition, some or all of the reactants are partially soluble in water under pressure and this enables reactions to take place in, or with the aid of, liquid and/or vapor 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 synthesis of phases that are unstable at higher temperatures. It is also a useful technique for growth of single crystals; by arranging 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 2.1. The critical temperature of water is 374 °C. Below 374 °C, two fluid phases, liquid and vapor can coexist. Above 374 °C only one fluid phase, supercritical water, ever exists. Curve AB presents the saturated stream curve. At pressures below this curve liquid water is absent and the vapor phase is not saturated with respect to steam; on the curve the vapor is composed of saturated stream which is in equilibrium with liquid water; above the curve, liquid water is effectively under compression and the vapor phase is absent.

The dashed curves in Figure 2.1 maybe 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 percent full of water: at, for example, 600 °C, a pressure of 800 bar is generated inside the closed vessel. Although Figure 2.1 applies strictly to pure water, the curves are modified little, provided the solubility of solids present in the reaction vessel is small.
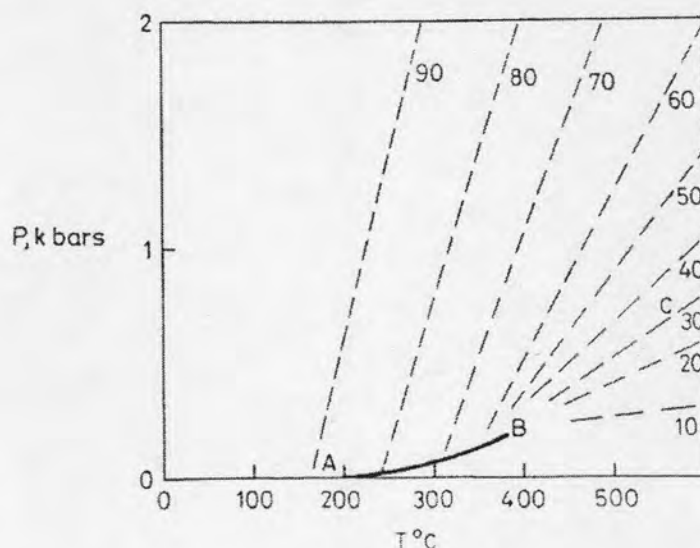

Figure 2.1 Pressure-temperature relations of water at constant volume. Dashed curves represent pressures developed inside a closed vessel; numbers represent percentage degree of filling of the vessel by water at ordinary pressure (P)and temperature (T).

The design of hydrothermal equipment is basically a tube, usually of steel closed at one end. The other end has a screw cap with a gasket of soft copper to provide a seal. Alternately, the bomb may be connected directly to an independent pressure source, such as a hydraulic ram; this is known as the cold seal method. The reaction mixture and an appropriate amount of water are placed inside the bomb which is then sealed and placed inside an oven at the required temperature.

2.4 The basic catalyst characterization methods

In this study, the basic characterization methods used to characterize physical and chemical properties of the investigated catalyst are listed in Table 2.1.

Table 2.1 Characterization methods and their purposes in this study

Characterization method	Measured properties
X-ray fluorescence spectroscopy (XRF)	Chemical compositions
Scanning electron microscopy (SEM)	Morphology
X-ray diffraction technique (XRD)	Phase structure and crystallinity
Multipoint BET techniques (BET)	Surface area and pore volume
Infrared spectroscopy (IR)	Orthorhombic silicalite defection
Electron spin resonance (ESR)	Transition metal state in catalyst framework
Temperature program desorption (TPD)	Acid site and acid strength

2.5 Criteria for test reaction selection

Performance (e.g. activity, selectivity) of a catalyst can be evaluated by using the suitable test reaction. The criteria for selecting a proper test reaction are discussed as follow:

1. The homogenous reactions of the reactants should be kept as minimum as possible in order to prevent the interference of the undesired reaction on result interpretation.

2. The reactant should not too inert to cause the tested catalysts behave like an inactive catalyst.

3. The reactant should not extremely reactive in order that the results of performance comparison between different catalysts will be clear.

4. To help in tracing the reaction pathway, the reactant should have only one active functional group and selected reaction should not produce many intermediate agents in the system.

5. The reactant should not cause catalyst deactivation such as poising and coking.

In practice, the reaction corresponding to all the listed criteria above may not available.

For criteria about functional group and reactivity, alcohol is therefore one of the best choice to use as reactant in our study. Alcohol is an organic chemical containing –OH group as its functional group. In addition, alcohol is also reactive for gas phase oxidation which is used as test reaction in this study.

2.6 Reaction of alcohol

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.

2.6.1 Oxidation

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.

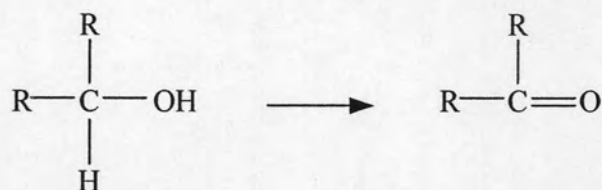A primary alcohol contains two α-hydrogens, and can either lose one of them to form an aldehyde,

$$R-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-OH \longrightarrow R-\overset{\overset{H}{|}}{C}=O$$

A 1°alcohol   An aldehyde

or both of them to form a carboxylic acid.

$$R-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-OH \longrightarrow R-\overset{\overset{OH}{|}}{C}=O$$

A 1° alcohol   A carboxylic acid

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

$$R-\underset{\underset{H}{|}}{\overset{\overset{R}{|}}{C}}-OH \longrightarrow R-\overset{\overset{R}{|}}{C}=O$$

A 2° alcohol   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).

$$R-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{C}}-OH \longrightarrow \text{no oxidation}$$

A 3° alcohol

2.6.2 Dehydration

Dehydration requires the presence of an acid and the application of heat. It is generally carried out in either of two ways: (a) by heating the alcohol with sulfuric or phosphoric acid; or (b) by passing the alcohol vapor over a catalyst, commonly alumina (Al_2O_3), at high temperature. An alcohol is converted into an alkene by dehydration (elimination of a molecule of water).

| Alcohol | Alkene | Water |
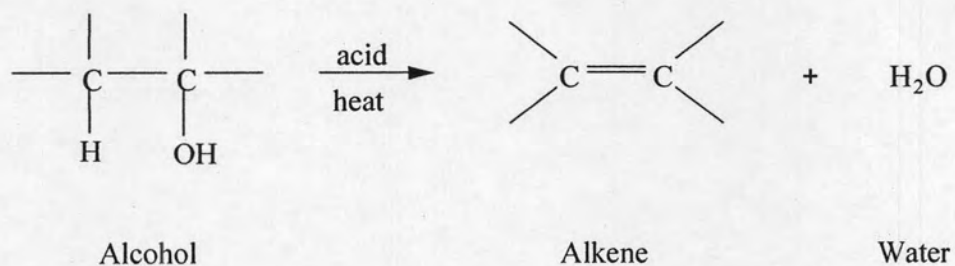
The various classes of alcohols differ widely in ease of dehydration, the order of reactivity being.

Ease of dehydration of alcohol $3° > 2° > 1°$