CHAPTER II

TITANIUM SILICALITE -1

Titanium silicalite molecular sieve (TS-1 zeolite) was discovered in 1983 by Taramasso et al. and since then it has gradually been acknowledged as one milestone in heterogeneous catalysis. With hydrogen peroxide (H_2O_2) as the oxidant, the TS-1 zeolite shows excellent performances to many types of selective oxidation processes such as hydrocarbons, alkenes and etc [7].

TS-1 is microporos solid materials made of SiO2 and TiO2 that have silicalite structure and it has the ZSM-5 structure presented in Figure 2.1.
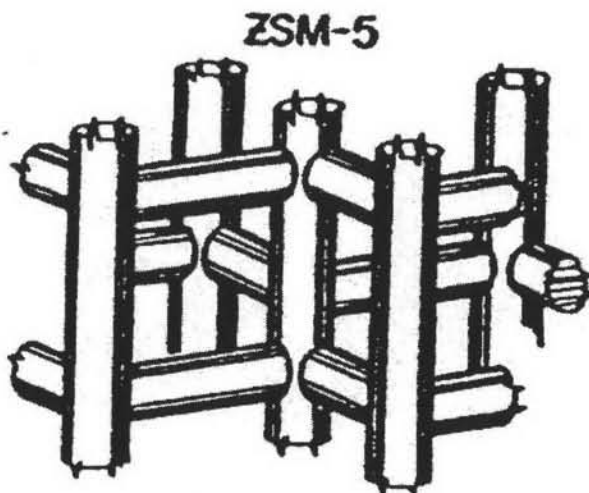

Figure 2.1 The characteristic of ZSM-5 [8].

Titaniun 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 TiIV compounds immediately shows that TiIV 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 TiIV 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 TiIV,

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 SiIV with TiIV it seems justified to represent TS-1 as a silicalite in which few TiIV have taken the place of SiIV. The interpretation of the catalytic activity of TS-1 must take into consideration the role played by these few TiIV: 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 TiIV in the crystal lattice is at random; since the Si/Ti ratio is in the range 40 - 90 in typical preparations, most TiIV must be isolated from each other by long sequences of -O-Si-O-Si-O-. If TiIV replaces a SiIV 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 streching 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 TiIV are occupied by SiIV 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
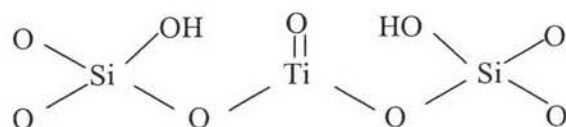
Other more elaborated and detailed representations could be given, should the present model prove inadequate to interpret all experimental facts. TiIV in TS-1 maintains the strong affinity of soluble TiIV salts for H_2O_2 and in fact the addition of H_2O_2 gives rise to a strong yellow colour which can be attributed to the formation of surface titaniunperoxo compounds which can be in the hydrated or dehydrated form and which constitutes the actual oxidants [9].
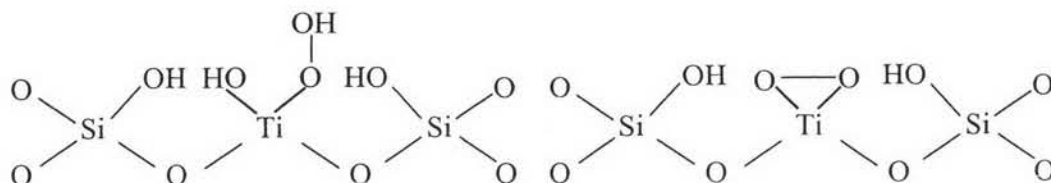
Work carried out on Mo(VI) and W(VI) peroxocompounds has demonstrated that peroxocompounds can act as oxidants in stoichiometric epoxidations involving a nucleophilic attack of the substrate to the peroxidic oxygen: in the presence of excess H_2O_2 the peroxo compound is regenerated and this accounts for the catalytic nature of the reaction. It seems reasonable to assume that a similar mechanism operates in the case of Ti(IV) peroxocompounds [10]. The relevance of isolated TiIV and the connection with catalytic performances appears to hold also for the TiO_2/SiO_2 catalyst. In fact high epoxide selectivities are obtained when TiO_2 is distributed on high surface area SiO_2 and its concentration is limited to 2%. It is very likely that at this low concentration TiIV are isolated and surrounded by SiIV. Furthermore, SiO_2 or TiO_2 alone, or physical mixtures of SiO_2 and TiO_2 or various metal titanates exhibit no significant activity. Similarly, supporting TiO_2 on carriers different from SiO_2 like Al_2O_3, MgO or ZrO_2 leads to catalysts whose activity is lower or nil. One piece of evidence seems very convincing: when the TiO_2 concentration on the catalyst is reduced from 4% to 0.4%, all other conditions being equal, an increase in epoxide selectivity is obtained. The only effect that a reduction in the concentration of TiO_2 can have is an increase in the degree of dispersion of each TiIV: chances for each TiIV of having SiIV as near neighbours increase, as does the selectivity of the catalyst. The correlation between the isolated TiIV and selectivity of the catalyst in epoxidation could be due to the fact that on TiIV having other TiIV as near neighbours, a mechanism proceeding through a bimolecular interaction of surface peroxo species could be operating which would give rise to a high decomposition rate of H_2O_2 or hydroperoxides to O_2. This mechanism could not operate on perfectly isolated TiIV.

$+ O_2 + 2H_2O$
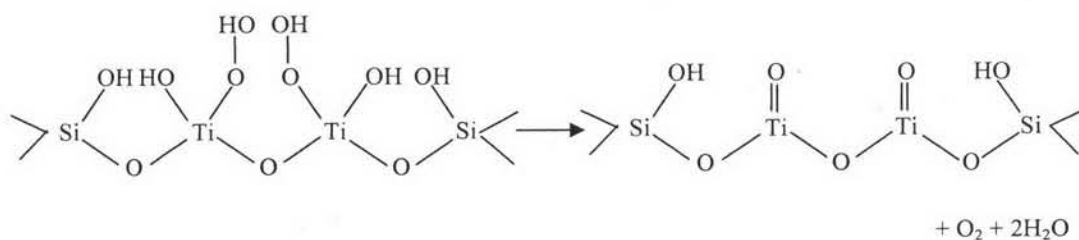
Low decomposition of H_2O_2 (or hydroperoxides as well) means greater stability of titanium peroxo compound whose reduction can only be carried out by the organic substrate with increased yields of useful oxidized products. When the different results between TS-1 and TiO_2/SiO_2 in the hydroxylation of phenol are analyzed the

existence of a "restricted transition state selectivity" must be assumed to explain the small amount of tars formed [11].

2.1 TS-1 catalyzed reactions

The wide scope of reactions are illustrated in Figure 2.2. The conversions include olefin and diolefins to epoxides, aromatic compound to phenols, ketone to oximes, primary alcohol to aldehydes and then to acids, secondary alcohol to ketones, and alkanes to secondary and tertiary alcohols and ketones.
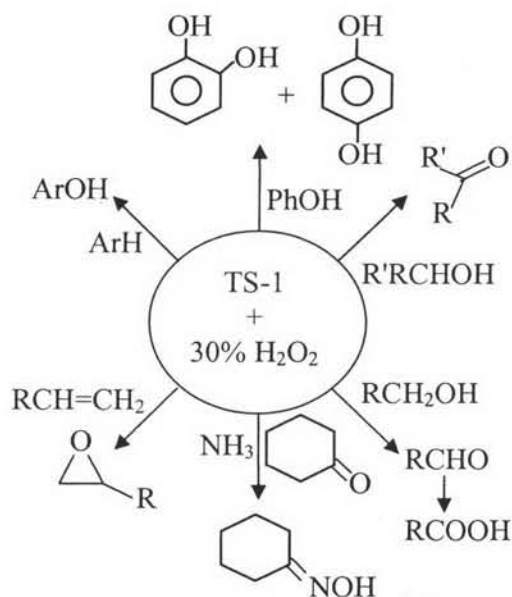

Figure 2.2 General scope of reactions catalyzed by TS-1

For case of alkyl-substituted benzenes are oxidized both on the benzene ring and on the side chain. Additionally, some dimerization occurs. Alkyl benzene containing linear alkyl groups are oxidized preferentially at the side chain nearest the benzene ring, for example ethyl benzene oxidizes first to 1-phenyl ethanol and then to acetophenone [11].

2.2 Application of TS-1

Since, early 80's TS-1 has been mainly studied as oxidation catalyst for a variety of reactions in presence of aqueous H_2O_2 as oxidant. Examples of TS-1 as oxidation catalysts are manifested in the follwing reactions:

- Oxyfunctionnalization of alkanes.
- Hydroxylation of aromatics.
- Epoxidation of alkenes.
- Oxidation of alcohols.
- Oxidation of ethers.
- Ammoximation of carbonyl compound.
- Oxidation of amines.
- In Bayer-Villiger oxidation to from lactones.

Other than its use as oxidation catalyst, it is also used in C-C bond formation and also used in diastereo-selective epoxidation of allyalcohols [12].

2.3 Metal modified and pretreated TS-1

Production active used TS-1 as a matrix with Al, V, Fe, Co, and Ru introduced at the stage of hydrothermal synthesis. Both of the modified and unmodified TS-1 were tested in oxidation of benzene to phenol by N_2O. Due to the earlier studied zeolite system. Fe introduction into the TS-1 matrix produced α-sites that catalyzed the oxidation of benzene to phenol with high activity and selectivity. In all cases, the chemical composition of the initial gel was calculated to provide 1 wt% of metal in TS-1. This condition was satisfied for Al and Ru (1 and 0.88 %wt respectively). For Co and Cr concentration was higher but V was lower than calculated value. The properties of Metal-TS-1 samples were inert and not even trace amounts of phenol were produced in their presence. Only The Al-containing sample exhibited a detectable but very low activity. However, this could hardly be interpreted as an intrinsic catalytic activity of Al species [13].

The TS-1/diatomite catalyst was prepared for the hydroxylation of phenol with H_2O_2 in fixed bed reactor and the effect of pretreatment on the properties of TS-1/diatomic. This indicated, pretreatment with HNO_3, KAc, NaAc and NH_4Ac aqueous solution, the framework structure of TS-1 was not destroy and titanium in framework was not removed. But the extra-framework TiO_2 was removed partly, which leaded to the slight increase of the crystallinity of catalyst and the decrease of acid concentration on the surface of the TS-1/distomite catalyst. As a result, the activity, selectivity and utilization of H_2O_2 for hydroxylation of phenol were improved. About the surface area of catalyst had no obvious change compared with that of the untreated catalyst. For the TS-1/diatomic catalyst was pretreated by $NH_3 \cdot H_2O$, Na_2CO_3 and Na_3PO_4 solution, its framework silicon decreased and the concentration of acid sites on the surface of catalyst increased slightly. As a result, the catalytic activity of the TS-1/ diatomite catalyst for hydroxylation of phenol descended [14].

The catalytic activity of TS-1 catalysts modified by Fe Al Co and V were synthesized, characterized and tested in the hydroxylation of benzene by hydrogen peroxide and the effects of pretreatment with nitric acid aqueous solution on the catalytic activity of catalysts. The result of reaction demonstrated this metal incorporate in TS-1 frame work promoted the catalytic activity higher than TS-1. Especially, TS-1 was modified with Co which had the highest catalytic activity. After the catalysts were pretreated by nitric acid aqueous solution, the framework structure of catalyst was not destroyed and titanium in the framework was not removed. But, the extra-framework was removed partly. As a result, the activity of the pretreated catalysts was improved. The catalytic activity of the investigated catalyst was in the following order Co-TS-1 > V-TS-1 > Fe-TS-1 > Al-TS-1 > TS-1. For Co-TS-1 is found to be the best one due to it cause the lowest H_2O_2 decomposition and has the least phenol product deposite on the surface[3].