

Solvent-free, triphase catalytic oxidation reactions  
over TS-1/H<sub>2</sub>O<sub>2</sub> system

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June, 2000

**SOLVENT-FREE, TRIPHASE CATALYTIC  
OXIDATION REACTIONS OVER TS-1/H<sub>2</sub>O<sub>2</sub>  
SYSTEM**

**A THESIS SUBMITTED TO THE UNIVERSITY OF PUNE FOR THE  
DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY**

**BY**

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**JUNE, 2000**

**.....TO MY BELOVED PARENTS**

## **CERTIFICATE**

Certified that the work incorporated in the thesis, " Solvent-free, triphase catalytic oxidation reactions over TS-1/H<sub>2</sub>O<sub>2</sub> system" submitted by Mr. Priyabrata Mukherjee, was carried out by the candidate under my supervision in the National Chemical Laboratory, Pune-411 008, India. Such materials, as has been obtained from other sources, have been duly acknowledged in the thesis.

**Rajiv Kumar**

**(Research supervisor)**

## ACKNOWLEDGEMENTS

*I am at a loss when I sit back to write something to acknowledge my research supervisor, Dr. Rajiv kumar. Nothing is sufficient to express my deep regards and sincere gratitude to him. He has been the source of my inspiration throughout my stay here in NCL, both in academic as well as in personnel level. He has cultivated in me to think in unorthodox manner. My deep regards and sincere gratitude to him for his constant encouragement throughout the course of this work and the inspiration and encouragement I am getting till today.*

*I'm thankful to my lab mates, Anirban, Deendayal, Chitta and Laha for their constant help and encouragement. I am also thankful to Sushama, Jaimol, Vandana, Venkatesh, Sharada, Karuna, Raja for the nice time I had with them. I am thankful to all my colleagues in the division. My special thanks to my distant friends Debi, Yesh, Cheeli, Nik for their constant support and the wonderful time I had and still having with them.*

*I am grateful to Dr. A. P. Singh, Dr. A. V. Ramaswamy, Dr. Gopinathan for their professional help and helpful discussion. I am grateful to Dr. Soni, Dr. Hegde, Dr. Jacob, Dr. Sainkar, Dr. behlekar, Dr. Agashe, Dr. Satyanarayan, Dr. Mirajkar and all other members in our division for their help in a way or the other.*

*I also thank the Council of Scientific and Industrial Research, New Delhi for the financial support and Director, National Chemical Laboratory, Pune, for allowing me to work here and submit the work in the form of a thesis.*

*Finally, my deepest regards to my parents and family members for the constant encouragement and support to pursue this work in their own special way.*

*Priyabrata Mukherjee*

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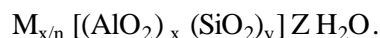


## **CHAPTER I: INTRODUCTION**

## I INTRODUCTION

### I.1 Definition and classification:

Zeolites are crystalline solid made up of silicon (Si), aluminium (Al) and oxygen (O) as the essential elements. They are joined tetrahedrally in such a fashion that both the Si and Al occupy the center of the tetrahedron and O shares the corner position. The tetrahedra are joined together by an oxygen bridge such that no two adjacent tetrahedrons can have the Al atom in the center. The general formula of any zeolite can be represented as<sup>1</sup>



This represents the crystallographic unit cell formulae of any zeolite where M is the cation from group I or II of valence n. M can also be organic cations. The ratio y/x may have any value from one to infinity. Z is the number of water molecules. The presence of one Al atom in the lattice develops one unit negative charge in the framework. The presence of silicon could lead to no such residual charge, as it is tetrapositive in nature. The negative charge, imposed by the presence of aluminium atom, is either compensated by group I or group II metals cations or by organic cation molecule in case of as synthesized zeolite material. The trivalent Al ion in the zeolite can either partly or completely be replaced by trivalent other ions like Ga<sup>+3</sup>, B<sup>+3</sup> Fe<sup>+3</sup>, etc or by tetravalent ions such as Ti<sup>+4</sup>, Zr<sup>+4</sup>, Sn<sup>+4</sup>, etc. These metallo-silicate analogs of the zeolite are commonly referred as molecular sieves.

There is no single classification by which all the properties of a particular zeolite can be explained. Therefore, various classifications of zeolites are there, like on the basis of pore opening, chemical composition, natural abundance etc.

All zeolites can be classified by the number of T atoms, where T = Si or Al, that define the pore opening. Zeolites containing these pore openings may also be referred to as small pore<sup>2</sup> with 8- member ring (MTN, NU-1 etc.), medium pore<sup>3</sup> having 10- member ring opening (MFI, MEL, etc.), large pore<sup>4, 5</sup> with 12- member ring opening (FAU, BEA, MTW

etc.) and ultra large pore<sup>6</sup> having 14- member ring opening (UTD-1). Recently, ordered mesoporous materials<sup>7</sup> (M41S) are also reported.

Zeolites are also classified on the basis of chemical composition. Irrespective of its chemical composition and distribution of T- atoms, IUPAC and IZA assigned 3 letters code to describe a known framework topology like LTA, MFI, UTD-1, etc, are given in the following table.

Type	Si / Al Ratio	Example
Low silica	1.5	LTA, FAU, LTL, etc
High silica	5-500	MFI, BEA, etc
All silica	$\infty$	Silicalite-1, Si-NCL-1, Si-UTD-1, etc

## I.2. Metallo-silicates:

Various metal ions have been successfully incorporated in framework structures of different morphologies and the resultant molecular sieves are termed as metallo-silicates. Various metal ions with varying charges have been used for the synthesis of metallo silicates. They are briefly summarized in the following table.

Metal ion	Example	Reference
M <sup>+3</sup>	B <sup>+3</sup> , Al <sup>+3</sup> , Fe <sup>+3</sup> , Cr <sup>+3</sup> , V <sup>+3</sup> , Ga <sup>+3</sup> , As <sup>+3</sup> , etc	8
M <sup>+4</sup>	Ti <sup>+4</sup> , Sn <sup>+4</sup> , Zr <sup>+4</sup> , Ge <sup>+4</sup> , V <sup>+4</sup> , etc	9
M <sup>+5</sup>	As <sup>+5</sup>	10

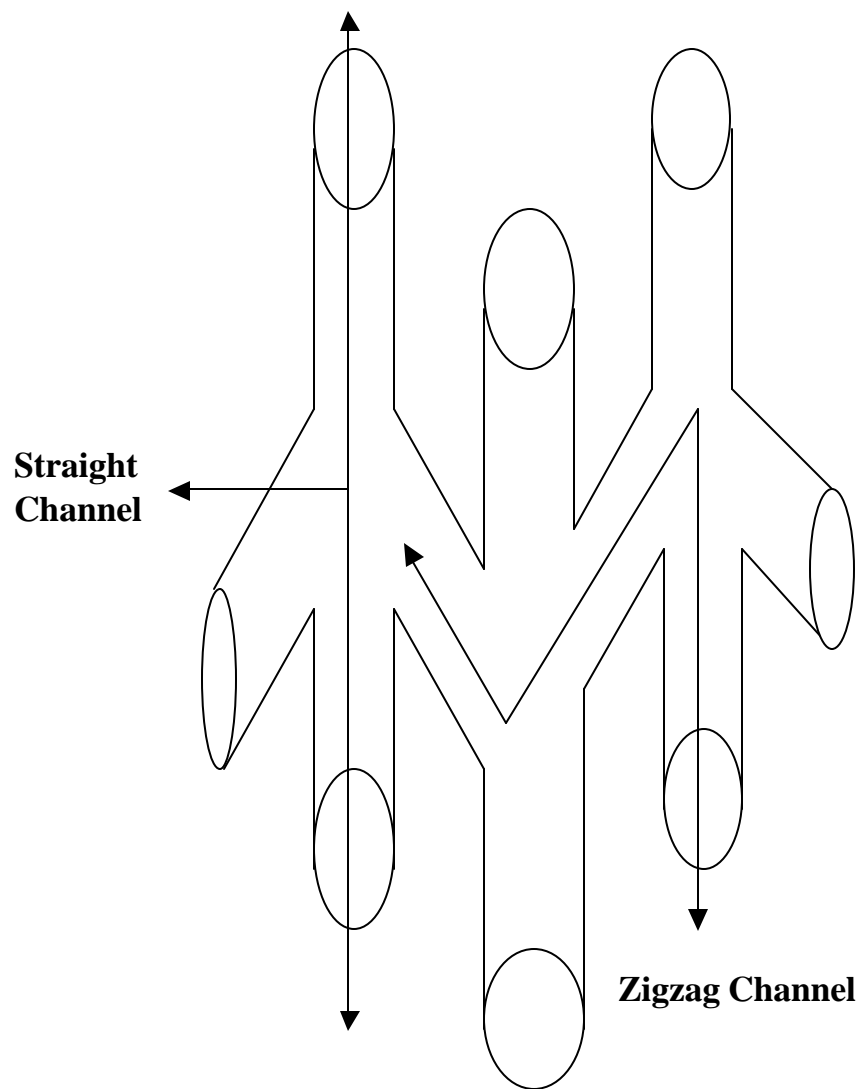
Depending on the charge of the metal ion incorporated, the resultant framework may be cationic or neutral. When a tetravalent metal ion like Fe<sup>+3</sup> is incorporated, the unit cell of the

framework gains a unit negative charge per  $\text{Fe}^{+3}$  ion incorporated. Similarly, incorporation of a tetravalent metal ion like  $\text{Ti}^{+4}$  does not create any charge imbalance in the framework. When a  $\text{B}^{+3}$  is introduced in the zeolite framework it is called boro-silicate, similarly for  $\text{Ga}^{+3}$ , it is called gallo-silicate and for  $\text{Ti}^{+4}$  it is called titano-silicate.

### **I.2.1 Titanosilicates:**

Titanosilicate results when a  $\text{Si}^{+4}$  from silicate matrix is replaced tetrahedrally in the framework position by  $\text{Ti}^{+4}$  ion. When the substitution is carried out in the silicalite-1<sup>11</sup>, pure siliceous analog of ZSM-5, the resultant titanosilicate is termed as TS-1. When the substitution is carried out on silicalite-2<sup>12</sup>, pure siliceous analog of ZSM-11, the resultant titanosilicate is known as TS-2. Similarly titanosilicates from other morphologies such as ZSM-48<sup>13</sup>, Beta<sup>14</sup>, MCM-41<sup>15</sup>, etc are also known.

Among all the titanosilicates, TS-1 and TS-2 have been used extensively in the catalytic reactions because of their unique pore architecture and higher catalytic activity. They have MFI and MEL structure respectively and both of them are members of the pentasil family<sup>16</sup>. Linking of chains of 5-membered ring secondary building units forms them. MFI topology are obtained when adjacent planes or sheets are related to one another by an inversion center and MEL types are obtained when the sheets are related by a mirror plane. This type of linking results in the formation of two intersecting channels in MFI with 10-membered ring openings. One is elliptical with cross section  $0.51 \text{ nm} \times 0.53 \text{ nm}$  and the other one is circular with a cross section of  $0.55 \text{ nm}$ . The cavities formed in ZSM-5 (MFI) by these intersecting channels are equivalent to a maximum diameter of  $0.9 \text{ nm}$  (shown in figure 1). The theoretical channel length in ZSM-5, obtained from crystallographic data, is  $8.8 \text{ nm}$ <sup>17,18</sup>.



**Fig. 1. Pore and channel structure of TS-1**

### **I.2.2. Synthesis of Titanosilicalite-1:**

The difficulty in the synthesis of metallo-silicates arises because of the formation of stable insoluble metal oxide / hydroxide precipitate, either during preparation of gel or during the crystallization of the metallo silicate<sup>19</sup>. The normal pHs of the gels for the synthesis of the metallo silicates are around 9-13. Under such alkaline conditions,  $Ti^{+4}$  has a strong tendency to form insoluble amorphous  $TiO_2$  species, unlike silicates or aluminates which dissolve under alkaline conditions.

The presence of extra-framework Ti-species has a strong influence in its catalytic activity. It may promote extensive homolytic side reactions including decomposition of hydrogen peroxide<sup>20</sup>.

To overcome the above difficulties in the synthesis of TS-1, several routes are tried to synthesize TS-1 with no amorphous extra-framework titanium species.

Kumar et al. had tried the synthesis of metallocilicate in presence of complexing agent such as oxalic acid, acetyl acetone. The use of this complexing agent may prevent the formation of metal oxide / hydroxide precipitate by complexing with the metal ion used in the synthesis. TS-1 has been synthesized successfully using acetylacetone as the complexing agent without formation of extra-framework  $TiO_2$  species<sup>19</sup>.

Padovan et al.<sup>21</sup> had tried synthesis of TS-1 by wetness impregnation method of  $SiO_2$ - $TiO_2$  co precipitate. The dried  $SiO_2$ - $TiO_2$  co-precipitate is impregnated with a required quantity of TPAOH solution similar to the pore volume of the solid and the subsequent treatment leads to the formation of TS-1 without the formation of  $TiO_2$  species.

Uguina et al.<sup>22</sup> has successfully synthesized TS-1 from  $SiO_2$ - $TiO_2$  co gel using modified Padovan's method.

Atom planting method was introduced by Kraushaar et al.<sup>23</sup> where highly siliceous zeolites are treated with titanium chloride vapor at high temperature. Ti-mordenite, which has



not been synthesized under hydrothermal conditions, synthesized by this atom planting method.

Gao et al.<sup>24</sup> synthesized TS-1 using aq. solution of  $\text{TiCl}_3$  as the titanium source and thereby avoiding the precipitation of  $\text{TiO}_2$ . After 2-5 days of autoclaving at 433 K, TS-1 was obtained without any trace of extra-framework titanium species.

Van der Pol et al.<sup>25</sup> has studied the effects of various reaction parameters on the synthesis of TS-1 and had shown that those smaller crystallites are much more active than the larger crystallites. So attempts have been made to synthesize TS-1 with smaller crystal sizes.

Recently Kumar, et al.<sup>26</sup> has developed a new method for synthesizing TS-1 using phosphoric acid as promoter. This method gives particles in the size range 100 nm – 200 nm with almost uniform particle size distribution. G. Zhang et al.<sup>27</sup> synthesized discrete colloidal crystals of TS-1. W. Honglin et al.<sup>28</sup> synthesized nano structured TS-1 supported on  $\text{TiO}_2$ .

#### **I.2.2.1. Effect of template:**

These are organic molecules, generally, organic amines or organic quaternary ammonium salts. They usually contain a hydrophobic part (hydrocarbon chain) and a hydrophilic part (amine or quaternary ammonium moiety). The hydrophobic part of the template molecule polarizes the hydrophilic water envelope around the various building units and reorganizes them in a particular orientation<sup>29</sup>. These molecules are usually known as structure directing agents as well as void filler. Depending on the nature of the template, zeolites with different morphologies are obtained. Templates may help the formation of zeolite either by kinetically or thermodynamically or both. Chemically they help  $\text{TO}_4$  units to pack around themselves in a preferred orientation and thereby providing it with nucleus on which further nucleation followed by crystallization can occur<sup>30</sup>. Thermodynamically it may help by lowering the chemical potential of the lattice formed upon the inclusion of the templates during nucleation. Tetrapropylammonium cation in the form of hydroxide is the most

commonly employed template for the synthesis of TS-1. Although tetrapropylammonium hydroxide is most commonly used, tetrapropylammonium bromide is also used in presence of different amines such as ammonia, hexane diamine<sup>29</sup>, etc.

#### **I.2.2.2. Alkalinity**

Alkalinity of the solution plays a key role in the hydrothermal synthesis of zeolites. This is known as mineralizer or mobilizing agent. It solubilizes both silicon and aluminium sources and brings them in a homogeneous solution with sufficient number of soluble precursors for the zeolite synthesis. A supersaturated solution is reached which contains sufficient number of T-atoms in tetrahedral position with condensable ligands. Through condensation of these T atoms from the supersaturated solution, nucleus of the zeolite is formed which due to further nucleation leads to the formation of zeolite crystal<sup>1</sup>. However, the alkalinity of the solution has a marked influence on the crystal size as well as the solid yield of the TS-1. At high OH<sup>-</sup> concentration multiple nucleation takes place which leads to the formation of irregularly shaped crystals. The solubilization of different silicate precursors leads to a decrease in the yield of TS-1<sup>25</sup>.

#### **I.2.2.3. Temperature:**

The rate of nucleation increases with increase in temperature helping crystallization in zeolite synthesis. It can again determine the type of products that will crystallize from the solution. At high temperature, the water molecules, which normally fill up the pores of the porous solids, will be evaporated and dense packed structure is expected. Similarly if the pores are filled up with the high boiling liquid, then even at high temperature open porous structure is formed<sup>32</sup>. However, TS-1 synthesis is dependent on temperature. It has both a lower limit and an upper limit. Beyond these limiting values, formation of extra-framework titanium species is facilitated.

#### **I.2.2.4. Time:**

The crystallinity of a zeolitic material usually increases with time up to a certain extent, after that the phase transformation in zeolites follows the Ostwald rules of successive transformation. The least thermodynamic product will form first. This is then successively transformed to most stable product through meta-stable phase<sup>33</sup>. TS-1 also follows the general rule that with time the crystallinity of the sample increases.

#### **I.2.2.5. Dilution:**

Dilution also has an effect in the nucleation and crystallization process in the synthesis of TS-1. Increase in the water content leads to the dilution of the reactive zeolite precursors. Therefore, increased dilution prevents supersaturation and retards nucleation. Besides, increase in dilution forms a thicker sphere of hydration around both the silicate / titano-silicate species. Before these reactive species condense, they have to strip off their hydration sphere. So increased dilution may lead to an increase in nucleation time and may retard crystallization<sup>25</sup>.

#### **I.2.2.6. Inorganic cation:**

The presence of inorganic cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ , etc) has a tremendous role in the synthesis of TS-1. In general, inorganic cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ , etc) as well as organic ( $\text{TME}^+$ ,  $\text{TEA}^+$ ,  $\text{TPA}^+$ , etc) strongly perturb the hydrogen bonding among the water molecules and orient them in a particular pattern around them. The smaller the size of the cation, greater is the charge density, greater the perturbation of the hydrogen bonded water molecules. Depending on whether these cations can organize the water molecules or not, they are defined as structure breaking and structure making. The small cations such as  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , etc, are called structure making as they can reorganize the water molecules. Large cations like  $\text{Cs}^+$ ,  $\text{NH}_4^+$ , etc are called structure breaking, as because of their low charge density they are not able to reorganize the water molecules. However,  $\text{TEA}^+$ ,  $\text{TME}^+$ , are found to be structure

making as their hydrophobic part helps in the reorganization of the water molecule<sup>29</sup>. The silicate can replace these organized water molecules and aluminate species and cage like structure can be obtained<sup>34</sup>. However, alkali and alkaline earth metals have a negative effect on the synthesis of TS-1. The presence of alkali cation prevents the incorporation of the  $Ti^{4+}$  in the silicalite lattice and favors the formation of extra-framework titanium species<sup>35</sup>.

#### **I.2.2.7. Promoter:**

The addition of a small amount of certain oxyanions of group VA and VIIA (such as perchlorate, phosphate, arsenate, etc) to the synthesis mixture of zeolites significantly enhances the nucleation and crystallization process of silica based molecular sieves<sup>26</sup>. Various promoters reduce the synthesis time of different zeolites in a varying degree. The time taken to obtain the fully crystalline ZSM-5 with different promoters follow the order none (48 h)  $> ASO_4^{-3}$  (14h)  $> PO_4^{-3}$  (8h)  $\geq ClO_4^-$  (7h). A direct correlation was observed between the charge by radius ratio ( $Z/r$ ) of the central cation of the promoter and the synthesis time of ZSM-5 prepared with that promoter. As the polarizing ability of the central cation increases, the synthesis time decreases. This is applicable not only to microporous aluminosilicates, but also to metallosilicates and also for mesoporous materials<sup>26, 36, 37</sup>. In the synthesis of TS-1, phosphoric acid is used as promoter. Using phosphoric acid, TS-1 can be obtained within 6 h of the reaction at 433 K<sup>26</sup>.

#### **I.3. Physico-Chemical Characterization:**

There are several techniques for the characterization of different zeolites. Each technique is unique by itself and provides important information about the structure of a particular zeolite. The most commonly employed characterization techniques are power X-ray diffraction spectroscopy (PXRD), adsorption and surface area analysis, chemical analysis by energy dispersive X-ray (EDX), infrared spectroscopy (IR), ultraviolet-visible spectroscopy (UV-Vis), scanning electron microscopy (SEM).

### **I.3.1. Powder X-ray diffraction (PXRD):**

When a solid is isolated from a synthesis mixture, it is first analyzed by PXRD. The outcome of the PXRD of the material is the following<sup>38, 39</sup>

- Uniqueness of structure
- Presence of single phase or mixture of phases
- Incorporation of other elements
- Level of crystallinity

The normal scan range in zeolite and microporous molecular sieves is in  $5^{\circ} 2\theta$  to  $40^{\circ} 2\theta$  as most important peaks are obtained in this range. Comparing with the standard PXRD pattern, the material can be identified. But for mesoporous solids, the scan angle is between  $1^{\circ} 2\theta$  to  $10^{\circ} 2\theta$  as most intense peaks are obtained in this range. From the unit cell volume expansion it is possible to predict about the incorporation of the metal in the framework. The incorporation of the larger titanium atoms will change the unit cell lattice parameter. Thus in TS-1, a, b and c values are 20.111 Å, 19.997 Å and 13.385 Å compared to 20.101, 19.887 and 13.365 Å respectively for monoclinic silicalite-1<sup>38</sup>.

### **I.3.2. Infrared Spectroscopy:**

This is another experimental technique, which offers structural details of zeolite structure through different vibrational modes. Besides, it helps in measuring the acidity of the materials as well as for detection of isomorphous substitution in the framework. There are several techniques for recording IR spectra such as dilution with KBr, nujol mull, and self-supported wafer<sup>40</sup>. The KBr dilution method is the most commonly employed method. The lattice vibrations of zeolites, normally, occur in the range  $300-1300\text{ cm}^{-1}$ . The assignment that can be done from IR is given below,

#### **Internal tetrahedra:**

Asymmetric Stretching:  $1250 - 950\text{ cm}^{-1}$

Symmetric stretching: 720 – 650 cm<sup>-1</sup>

T-O Bending: 420 – 500 cm<sup>-1</sup>

**External linkages:**

Double ring: 650 – 550 cm<sup>-1</sup>

Pore opening: 300 – 420 cm<sup>-1</sup>

Symmetric Stretching: 750 – 820 cm<sup>-1</sup>

Asymmetric Stretching: 1050 – 1150 cm<sup>-1</sup>

Acid strength of zeolites can also be determined by FTIR spectroscopy in the absorption range 3600 – 3700 cm<sup>-1</sup> (Brönstead acid sites) by using ammonia, pyridine<sup>41</sup>, triphenyl phosphine, etc as probe molecules. Incorporation of metals also can be determined as an additional band at 960 cm<sup>-1</sup> appears because of M-O-Si linkages (M = Metal)<sup>42, 43</sup>. In the case of TS-1, it has two important regions in the IR spectrum. One the OH region and the other below 1000 cm<sup>-1</sup>. In the region of OH vibrations it has got two major peaks. The first one at 3540 cm<sup>-1</sup> is broad and the other one at 3728 cm<sup>-1</sup> is sharp. However, these peaks can not be differentiated as to whether they are because of the titanol group or due to silanol group<sup>44</sup>.

In the other region below 1000 cm<sup>-1</sup> lattice structure bands appears at 805 and 555 cm<sup>-1</sup>. All the titanium silicates exhibit one common feature in this region, a band at about 960-970 cm<sup>-1</sup>. Such a band is also found in the case of other metallo silicates where metal is in the framework position. Though there are lot of discrepancies regarding the assignment of this band, but it is generally accepted that this band is due to stretching vibration of Si-O bond perturbed by a neighboring Ti (IV) in the lattices position<sup>45</sup>.

**I.3.3. UV- Vis Spectroscopy:**

This is particularly useful for metal incorporated zeolites i.e., metallosilicates. The absorption in the UV-Vis range arises because of the ligand to metal charge transfer. It helps to determine the co-ordination number of the metal in the zeolite. Thus for TS-1, the absorption at 215 nm is due to the transfer of charge from  $O^{-2}$  to tetrahedrally coordinated<sup>46</sup>  $Ti^{+4}$ . With increase in co-ordination number, the charge-transfer band shifted to longer wave -length. TS-1 exhibits a charge transfer band at 205-220 nm due to the presence of isolated  $[TiO_4]$  or  $[TiO_3OH]$  moieties. This charge transfer occurs due to electron transfer from ligand oxygen to the vacant orbital of titanium ions in the framework. Therefore, it is directly related with the titanium incorporation in the framework position. So a change in the band position is directly related with the change in coordination state of Ti (IV) in the framework.

Hence the presence of the band at ca. 210 nm is accepted as evidence for the presence of isolated Ti (IV) species whereas the band at 280-330, if present, is taken as the presence of extra-framework titanium species<sup>47</sup>.

#### **I.3.4. Scanning Electron Microscopy:**

This is another important tool for characterization of the zeolite catalyst. The micrograph shows the morphology of the particle formed (e.g., cubic, circular, etc) as well as the presence of amorphous phase in the samples<sup>48</sup>.

#### **I.3.5. NMR Spectroscopy:**

Nuclear magnetic resonance spectroscopy, both in the liquid state and in the solid state, is very important for determining the active species in the molecular level during synthesis of zeolites from aluminosilicate gels. Lippamaa et al has shown that  $^{29}Si$  MAS NMR is highly sensitive to the nature and chemical environments of the atoms<sup>49</sup>. Considerable knowledge regarding the structure of the alumino-silicate has been gained through  $^{27}Al$  and  $^{29}Si$  MAS NMR<sup>50-56</sup>.

### **I.3.6. Adsorption Measurement:**

To determine the pore size distribution, pore volume and surface area, the adsorption of nitrogen is usually carried out over zeolites and related molecular sieves at low pressure ( $10^{-6}$  Torr) and low temperature (77K). The sieving property of a zeolite depends on its pore size, pore volume as well as surface area. The analysis of adsorption isotherm helps in determining the micropore volume and pore size distribution of the molecular sieves<sup>57, 58</sup>.

### **I.4. Catalysis:**

The catalytic activity in zeolite and porous materials is governed, mainly, by diffusion process. The main processes governing the catalytic activity are<sup>59</sup>,

- Transport of the reactant to the zeolite surface followed by diffusion of the reactant to an active site inside the pore / channel.
- Adsorption of the reactant to an active site.
- Chemical reaction of the adsorbed reactant to form adsorbed product(s).
- Desorption of the adsorbed product(s).
- Diffusion of the adsorbed products from interior active site to the outer surface of the catalyst.
- Transfer of the product(s) away from the zeolite surface.

#### **I.4.1. Shape selectivity:**

One of the interesting features of the heterogeneous solid catalysts is the shape selectivity of the reactions. Three types of shape selectivity are mainly observed in zeolite catalysis<sup>60</sup>. The reactant shape selectivity, product shape selectivity and restricted transition-state shape selectivity. The reactant shape selectivity arises because of the different dimensions of reactant molecules. When more than one reactant is involved in a reaction, that reactant, the molecular dimension of which fits the pore diameter/channel dimension of the zeolite, can enter and react. This is known as reactant shape selectivity. This type of shape



selectivity is utilized in petrochemical chemistry where linear alkanes are cracked preferentially leaving aside the branched alkanes<sup>61, 62</sup>. When a number of products are formed inside the pores/channels of a zeolite, those products will diffuse out whose sizes are within the range of the pore diameter/channel dimension of the zeolite. The remaining heavy products will either break down to smaller molecules and will come out or they will deactivate the catalyst<sup>63-65</sup>. This is known as product shape selectivity. Not all transition states are allowed to form inside the zeolite pore/channel. Only those transition states whose molecular dimension is within the dimension of the zeolite pore channel will be selectively formed. This is exhibited in the subsequent product distribution pattern<sup>66</sup>. This is known as transition state shape selectivity.

#### **I.4.2. Applications of TS -1:**

Since its discovery in early 80's TS-1 has been studied, mainly, as oxidation catalyst for a variety of reactions in presence of aqueous H<sub>2</sub>O<sub>2</sub> as oxidant. Examples of TS-1 as oxidation catalysts are manifested in the following reactions,

- Oxyfunctionalization of alkanes<sup>67</sup>.
- Hydroxylation of aromatics<sup>68</sup>.
- Epoxidation of alkenes<sup>69</sup>.
- Oxidation of alcohols<sup>70</sup>.
- Oxidation of ethers<sup>71</sup>.
- Ammoximation of carbonyl compounds<sup>72</sup>.
- Oxidation of amines<sup>73</sup>.
- In Bayer-Villiger oxidation to form lactones<sup>74</sup>.

Other than its use as oxidation catalyst, it is also used in C-C bond formation and also used in diastereo-selective epoxidation of allylic alcohols<sup>75</sup>.

Recently TS-1 has been used in presence of promoter like Pd to enhance its catalytic activity and selectivity<sup>69</sup>. Sometimes TS-1 is used for N<sub>2</sub>O decomposition<sup>76</sup>. Selective oxidation of propylene to propylene oxide is done over Au supported on TS-1 in presence of H<sub>2</sub> and O<sub>2</sub><sup>77</sup>.

#### **I.4.3. Biphase and triphase catalysis:**

A large number of reactions are found not to occur or end up with very low reaction when the reactants are in different phase and the contact among the reactions are inhibited because of phase separation. This leads to poor mass transfer from one phase to the other, which results in very poor reaction. The collision among the reactant molecules is an essential requirement for a bimolecular reaction to occur. However, as early as 1951, Jarrousse<sup>78</sup> found that alkylation of cyclohexanol and phenyl acetonitrile can be carried out in different phases in the presence of quaternary ammonium salts. Maekar<sup>79</sup> et al (1961) have found that the sodium salts of fatty acids can be alkylated more readily by epichlorohydrin in presence of benzyl trimethyl ammonium chloride. In 1965 Gibson and Hoskin<sup>80</sup> discovered the triphenylarsonium permanganate for organic oxidation reactions. Starks<sup>81</sup>, in 1971, found that the reaction between n-octylbromide (organic phase) and sodium cyanide (aq. Phase) did not proceed even after 2 weeks of reaction. However the reaction was found to occur when a quaternary ammonium salt was used. He then coined the term “phase transfer catalyst” for that salt and the process “phase transfer catalysis” (PTC). The problem of phase separation was classically overcome by using a solvent, which has both lyophilic and as well as hydrophilic character. However, the use of the solvents makes work up procedure difficult and they are detrimental to nature too. The phase transfer catalysts have got several advantages over the common solvents. The reaction, using PTC, occurs under milder conditions and only catalytic amount of PTC is required for the reaction to occur. However, the removal of the PTC from the reaction mixture is again the problem. This problem

regarding the separation of soluble PTC from the reaction mixture leads to the development of immobilized PTC on solid insoluble support, insoluble PTC. In 1975 Reger<sup>82</sup> coined the term triphase catalysis in cyanide displacement reaction using quaternary ammonium salts immobilized on insoluble resins.

Three general types of triphase catalysis are most commonly observed<sup>83</sup>.

(i) Liquid – Liquid – Solid (ii) Solid – Liquid – Solid and (iii) Gas – Liquid – Solid.

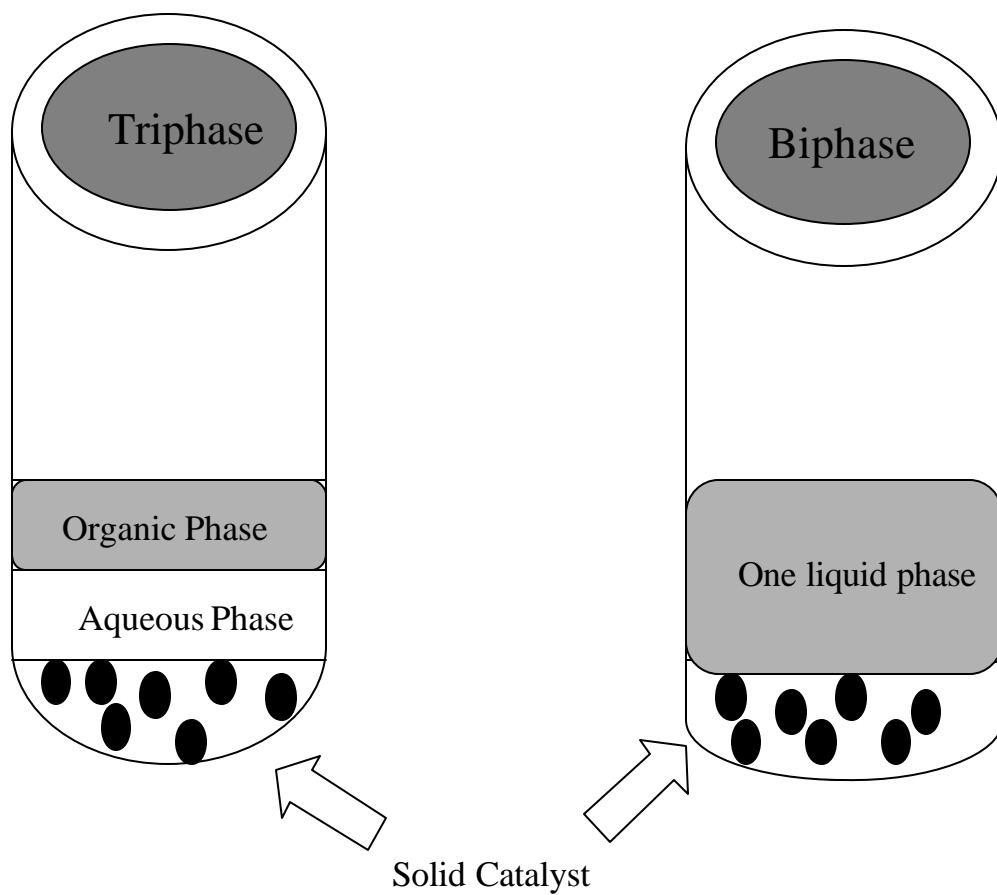
In the liquid – liquid – solid (L-L-S) system, the inorganic reagent is present in the aqueous phase. In the solid-liquid-solid (S-L-S) type the inorganic reagent is present in the solid form. In the gas-liquid-solid (G-L-S) type, the inorganic reagent in the gaseous form is bubbled through the reactor. Since the essential requirement for a reaction to occur is the collision among the reactants, therefore the diffusion of the reactants is an extremely important phenomenon in the catalysis. A series of steps may be involved in the triphase catalysis of L-L-S type over polymer supported resins.

- (1) Diffusion of the inorganic reagent from the bulk to the surface of the catalyst particle.
- (2) Diffusion of the organic phase dispersed in the bulk inorganic phase into the catalyst.
- (3) Diffusion of the organic reagent from the dispersed phase onto the catalyst surface.
- (4) Intraparticle diffusion of the reactants into the pores of the catalyst support.
- (5) Reaction of inorganic reagent with the catalyst molecule inside the pores of the support.
- (6) Reaction of the organic reagent with the catalyst molecule with extracted anion.
- (7) Diffusion of the products from the interphase to the bulk of the liquid phase.

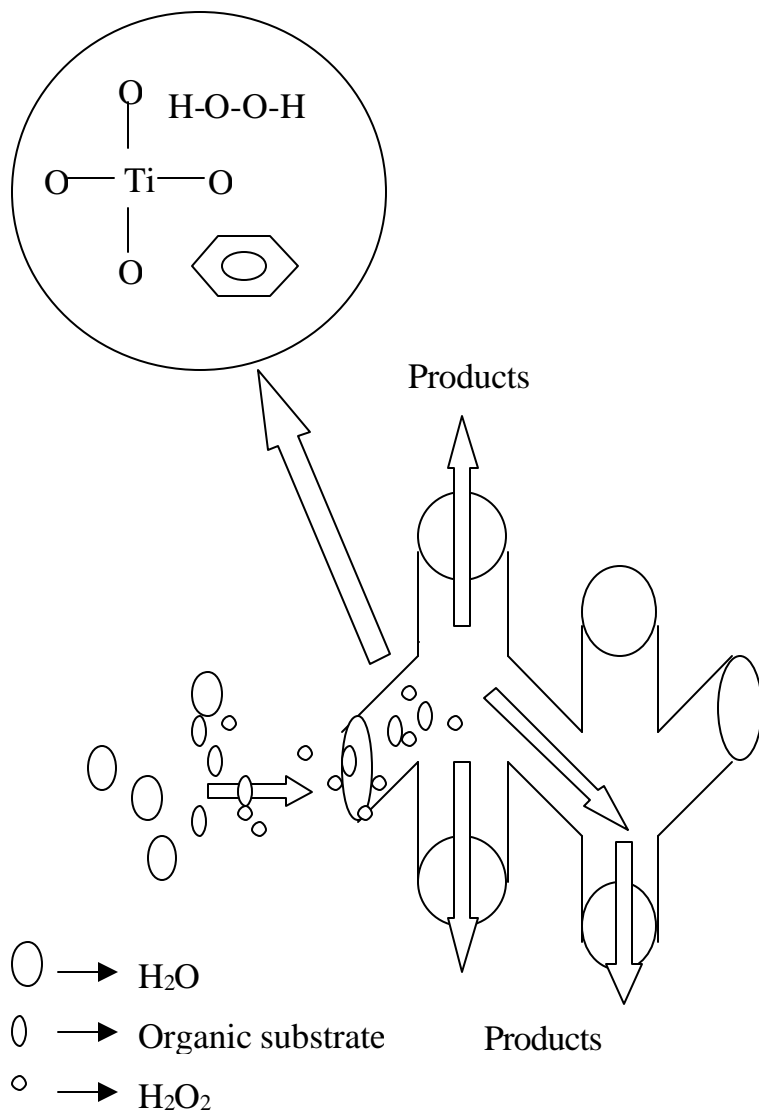
Similar types of steps can also be thought of for the reaction using microporous solid as catalyst where the active sites reside inside the pores of the catalyst. In that case the steps 6 and 7 differ a bit in that the reactants has to react with the active site inside the pores to form the product and diffusion of the product from the pores to the bulk of the liquid phase.

Recently, it has been observed that triphasic catalysis can also be made possible by suitable selection of the molecular sieves. When direct hydroxylation of simple aromatic compounds such as benzene, toluene, etc (liquid organic phase) was carried out with aqueous  $H_2O_2$  as oxidant in the presence of excess amount of water (liquid aqueous phase, L) using solid microporous TS-1 as catalyst (solid catalyst phase, S), a L-L-S system, a significant enhancement in both the reaction rates as well as product selectivity was observed. However, when an organic solvent such as methanol or acetone was used to homogenize the two immiscible liquid phases (solid – liquid phase, S-L type), the reaction was found to be very low<sup>84</sup>. Schematically these phases are shown in figure 2.

Although the similar types of diffusion reaction problems in the case of polymer supported resins can also be considered here, but unlike the former, here the competitive diffusion of the organic substrates compared to the water inside the relatively hydrophobic TS-1 should be considered. In this respect the TS-1 catalyzed triphase reaction differs from the former in that it's the competitive diffusion of the organic substrates compared to water to the hydrophobic TS-1 channel is the controlling factor of the reaction. The same diffusion problems can also be considered in the case of biphasic (L-S) system also. Here the solvent, because of its smaller size, competes favorably than the organic substrates to diffuse into the hydrophobic channel of TS-1. A schematic diagram of diffusion inside TS-1 channel is shown below (Fig. 3).



**Fig. 2 Pictorial description of triphase and biphase**



**Fig. 3. Diffusion reaction problem in triphase catalysis over TS - 1**

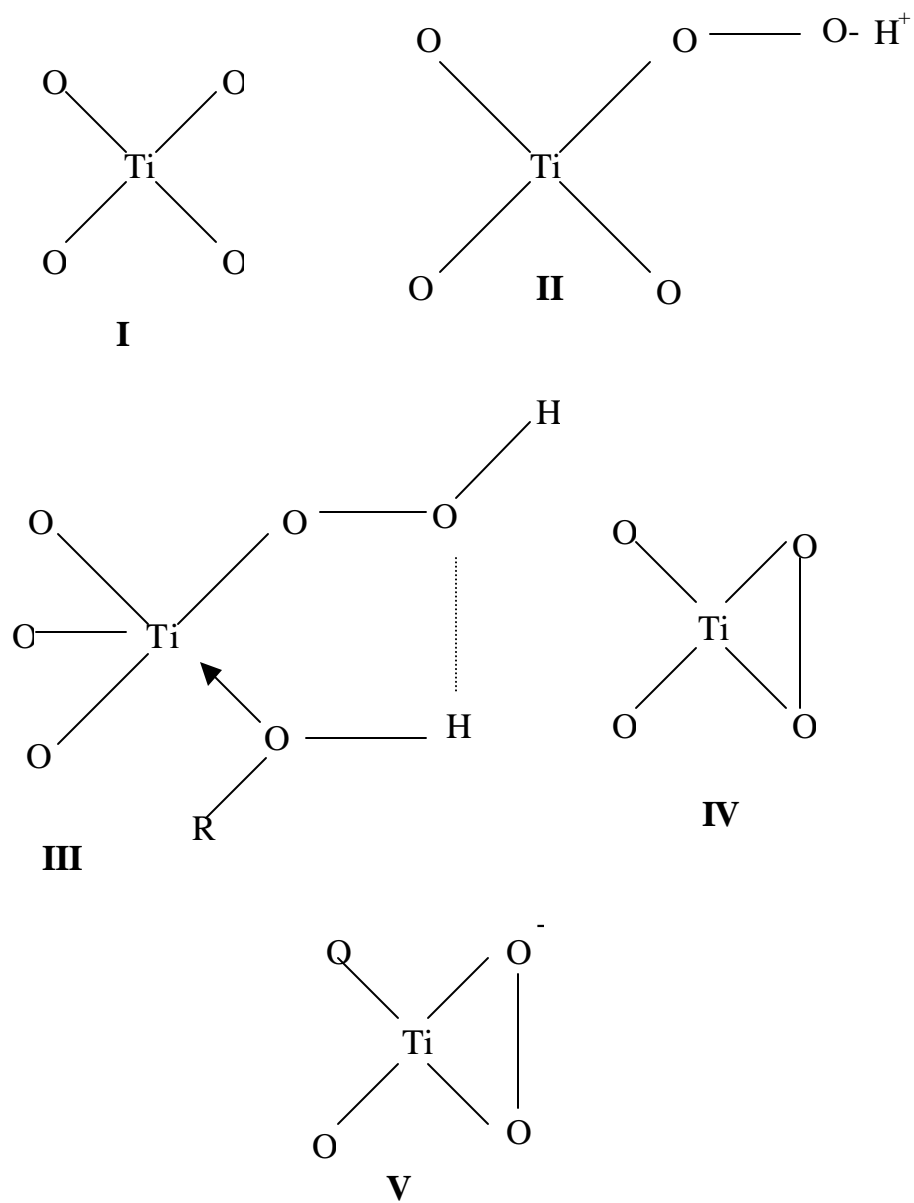
#### I.4.4. Catalytic sites in TS-1:

TS-1 behaves as a unique oxidation catalyst in the presence of aqueous hydrogen peroxide in a variety of reactions. Therefore, naturally, the emphasis on is to find out the reactive species in variety of oxidation processes involving TS-1 and aqueous  $\text{H}_2\text{O}_2$ . By different characterization techniques it was proved that Ti<sup>+</sup> ion, in TS-1, was in +4 oxidation state and is in tetrahedral environment. There are several evidences that Ti<sup>4+</sup> in the Td site in the framework is responsible for catalytic oxidation. But, however, the nature of the tetrahedral titanium species as well as the nature of the active species involved in the oxidation, still, has been the matter of discussion and debate. Recently Zecchina et al. have shown with the help of the EXAFS studies that there are at least two different kinds of tetrahedral framework titanium species in TS-1<sup>85</sup>.

Several changes were observed when TS-1 is treated with aqueous  $\text{H}_2\text{O}_2$ .

- The white color of TS-1 turned yellow upon addition of aq.  $\text{H}_2\text{O}_2$ .
- There is a dramatic change in the UV-Vis absorption of the TS-1 samples. The band at 212 nm decreases and 3 additional band appear at 305, 385 and 425 nm<sup>85, 86</sup>.
- A change in the IR spectrum is also observed. The intensity of the 960  $\text{cm}^{-1}$  decreases and a new band at 870-800  $\text{cm}^{-1}$  is formed. An anisotropic signal with  $g_{zz} = 2.0238$ ,  $g_y = 2.0099$  and  $g_x = 2.0030$  is found in the E.P.R. spectra of the samples<sup>87, 88, 89</sup>.

All these changes are completely reversible as heating or drying of the samples leads to the generation of the original samples. On the basis of all the above experimental results the following active species for TS-1 in presence of aq.  $\text{H}_2\text{O}_2$  have been envisaged (Fig. 4).



**Fig. 4. Different Potential Active Ti-Species**



### **I.5. Scope of the thesis:**

A common problem associated with the heterophase reactions is that they are ended up with very poor reaction and low yield. This is due to the poor mass transfer from one phase to the other or because of the presence of at least one component with very low concentration. The mass transfer problem is usually overcome by using common co-solvents like methanol, acetone, etc, or sometimes by using phase transfer catalysts. However, they suffer from the draw back of complex work up procedure.

Microporous titanium-silicate, TS-1 has been used extensively in the synthesis of fine chemicals involving oxidation of various organic substrates with aq.  $\text{H}_2\text{O}_2$  in the presence of co-solvent like methanol, acetonitrile, and acetone. However, TS-1 can be used as catalyst under solvent-free triphase conditions in the oxidation of water immiscible organic substrates with enhanced activity and selectivity. In the case of substituted benzenes, like toluene, anisole, etc, the triphasic condition leads to the formation of p- selective product in major amount with enhanced reactivity.

The objective of the thesis is to study, in detail, the effect of various reaction parameters on conversion and selectivity under triphase condition in the hydroxylation of  $\text{C}_6$ - $\text{C}_8$  aromatic hydrocarbons, benzene, toluene, p- xylene, ethylbenzene and anisole. Further, other objective of the thesis is to explore the reason of enhanced activity and p- selectivity in the hydroxylation of such aromatic compounds under solvent free triphase condition.

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## **CHAPTER II: EXPERIMENTAL**

## II. Experimental:

### II.1. Introduction

Titanium silicalite-1 (TS-1) has been extensively used as oxidation catalyst in the presence of aqueous  $\text{H}_2\text{O}_2$  as oxidant in a variety of organic reactions<sup>1-4</sup>. The catalytic activity of TS-1 depends on various factors such as the size of the crystallites, presence of defect sites, presence of extra framework titanium species, loading of  $\text{Ti}^{+4}$  in the framework, etc. Large crystallites as well as the presence of extra framework Ti- species reduce the catalytic activity to a large extent<sup>5</sup>. Therefore, synthesis method plays an important role on the physical and chemical properties of TS-1. Different synthesis methods produce TS-1 with different catalytic properties. Van der Pol et al<sup>6</sup>. have studied the effect of various reaction parameters in the synthesis of TS-1. Recently, it was found that the use of phosphoric acid as a promoter reduces the synthesis time to a great extent with the formation of smaller crystals with almost uniform particle size distribution<sup>7</sup>. Relatively higher loading of  $\text{Ti}^{+4}$  in the framework can be obtained using the Thangaraj's method<sup>8</sup>. For the synthesis of TS-1 we have used the promoter-induced methodology modifying Thangaraj's procedure for the synthesis of TS-1. The flow sheet for the synthesis of TS-1 is given in the Fig. 1.

### II.2 Materials used for the synthesis of TS-1:

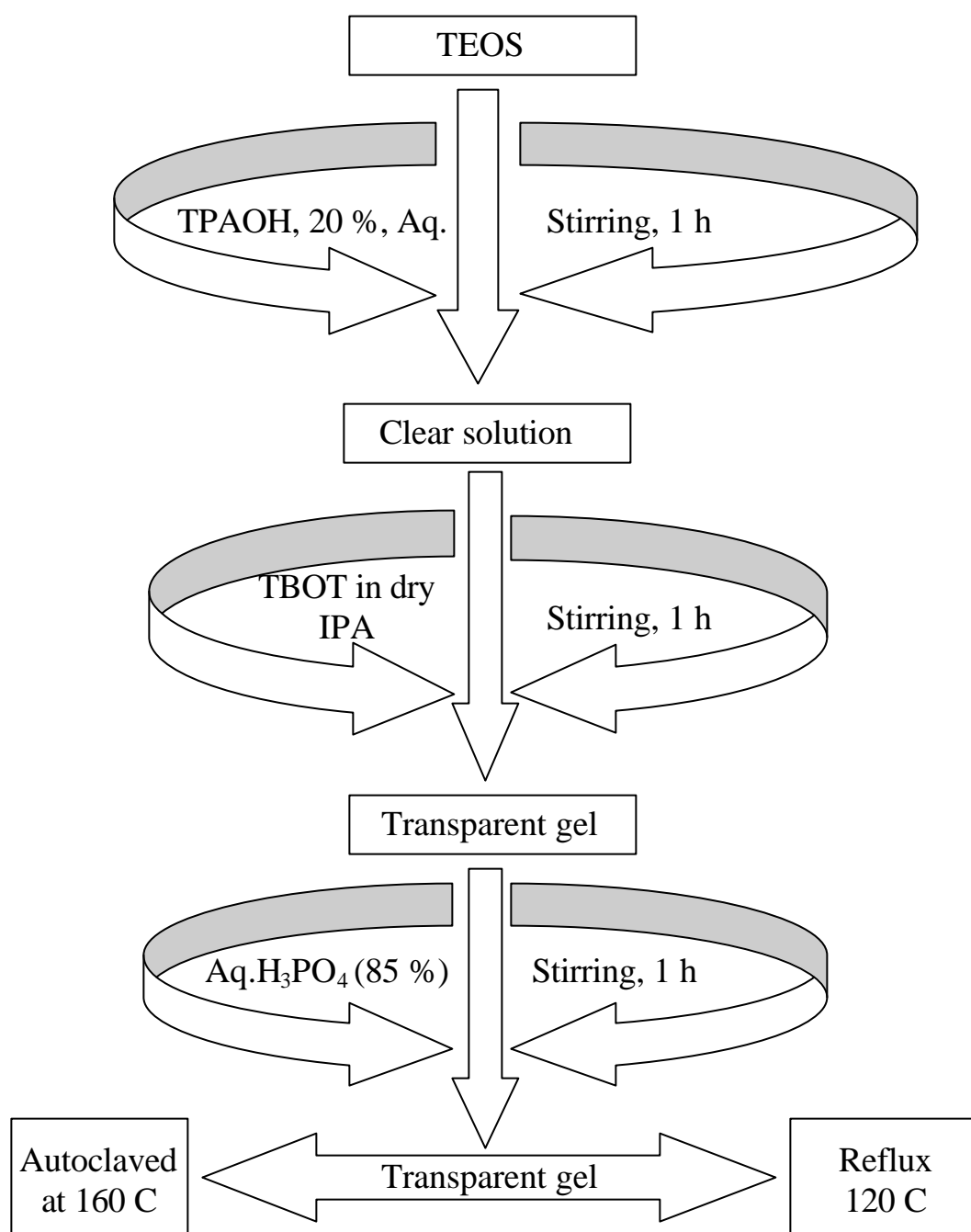
**Silica Source:** Tertaethylorthosilicate, TEOS [ $\text{Si}(\text{OC}_2\text{H}_5)_4$ ] (98 %, Aldrich)

**Ti- Source:** Tetra-n-butyl titanate, TNBT [ $\text{Ti}(\text{OC}_4\text{H}_9)_4$ ] (99 % , Aldrich)

**Promoter Source:** o-Phosphoric acid [ $\text{H}_3\text{PO}_4$ ] (85 % aqueous, sd fine. Chem. India)

**Template:** Tetrapropyl ammonium hydroxide solution (20 % wt aq., Aldrich)

**Fig.1: Flowsheet of TS-1 synthesis**



## II.3 Synthesis:

Three samples with different Si/Ti molar ratios (sample A, [Si /Ti = 33], sample B, [Si / Ti = 58] and sample C, [Si / Ti = 80]) were synthesized hydrothermally at high temperature (433 K). In a typical synthesis of sample A, as an example, 21.0 g TEOS (tetraethyl orthosilicate, Aldrich, 98.5 %) was added under stirring to 40.6 g TPAOH (20 % aq. Aldrich) and the stirring was continued for 1 h. Then 1.13 g TNBT (tetra-n-butyl titanate) in 5.0 g dry IPA (isopropyl alcohol) was added slowly to the above reaction mixture and again allowed to stir for 1 h. Finally 0.77 g H<sub>3</sub>PO<sub>4</sub> (phosphoric acid, 85 % aq. sd. fine. chem. India) in 19.7 g of water was added to the above mixture slowly and allowed to stir for one more hour. The solution thus obtained was autoclaved at 433 K for 6 h. The pH of the solution was measured before putting it into the autoclave.

For sample B and sample C, 0.60 g TNBT in 5 g IPA, and 0.42 g TNBT in 5 g IPA, respectively, were taken, keeping all other ingredients same. For low temperature (378 K) synthesis of TS-1 (sample D), the same gel composition of sample A was taken. After the stirring is over the clear gel was taken in a stainless steel autoclave and put in the oven at 378 K for 36 h. Two more samples were synthesized using the initial gel composition of the reaction mixture of samples A and changing the crystallization conditions. Sample D was synthesized in a sealed autoclave at 378 K for 36 H. Sample E was prepared under reflux conditions at atmospheric pressure. For the synthesis under reflux condition, the clear liquid was put in a 500 ml RB and refluxed at 383 K for 48 h. After the crystallization was over, the solid sample was separated from the mother liquor by centrifugation, pH of the mother liquor was measured again, washed thoroughly with distilled water, dried and calcined at 813 K for 16 h in air. Another sample was prepared at high temperature (433 K) but without the addition of promoter (sample

F). However, in the absence of promoter, low temperature and reflux condition did not yield any solid material even after 144 h. The molar gel composition of the different synthesis mixtures are shown in Table 1

**Table 1: Molar gel composition of different synthesis mixture**

Sample	Molar gel composition
A	30 TEOS: 10 TPAOH : TNBT : 28.5 IPA: 2 H <sub>3</sub> PO <sub>4</sub> : 900 H <sub>2</sub> O
B	30 TEOS: 10 TPAOH : 0.54TNBT : 28.5 IPA: 2 H <sub>3</sub> PO <sub>4</sub> : 900 H <sub>2</sub> O
C	30 TEOS: 10 TPAOH : 0.379 TNBT : 28.5 IPA: 2 H <sub>3</sub> PO <sub>4</sub> : 900 H <sub>2</sub> O
D	30 TEOS: 10 TPAOH : TNBT : 28.5 IPA: 2 H <sub>3</sub> PO <sub>4</sub> : 900 H <sub>2</sub> O
E	30 TEOS: 10 TPAOH : TNBT : 28.5 IPA: 2 H <sub>3</sub> PO <sub>4</sub> : 900 H <sub>2</sub> O
F	30 TEOS: 10 TPAOH : TNBT : 28.5 IPA: 900 H <sub>2</sub> O

## II.4. Characterization:

All TS-1 samples synthesized were characterized by well-known characterization techniques such as XRD, UV-VIS, IR, SEM and EDX.

### II.4.1. X-ray diffraction:

XRD measurements of all the samples were done in Rigaku D MAX III VC diffractometer using Ni filtered Cu K<sub>α</sub> radiation ( $\lambda = 1.5404 \text{ \AA}$ ). The samples exhibiting maximum area (in the  $2\theta$  range =  $6^\circ - 48^\circ$ ) were taken as reference samples. XRD were recorded in the range  $6^\circ 2\theta$  to  $48^\circ 2\theta$ .

#### **II.4.2. UV-Vis Spectroscopy:**

UV-Vis spectra were recorded in a Shimadzu UV-VIS spectrometer (UV - 2101 PC). The base line correction was made using barium sulphate as the standard. All the spectra were recorded in the range 200-600 nm.

#### **II.4.3. IR Spectroscopy :**

IR spectra were recorded in a FTIR spectrometer (Perkin Elmer Series 1600) in the range 400 - 1300  $\text{cm}^{-1}$  using nujol mull or KBr pellet technique.

#### **II.4.4. SEM / EDX analysis:**

Scanning electron micrograph was recorded on JEOL JSM 5200, operated at 20 kV. Elemental analysis was performed through electron probe micro analysis on a EDX detector, KEVEX 7000 system. Samples were loaded on a stub and coated with gold film before scanning.

### **II.5. Results and discussions:**

Physico-chemical properties of different TS-1 samples are shown in Table 2. From the table it is seen that, keeping all the parameters constant, TS-1 is obtained after only 6 h when phosphoric acid was used as a promoter. The sodium salts of phosphoric acid was not used in this case because of the known detrimental effect of sodium in the synthesis of TS-1<sup>5</sup>. However, the corresponding time required to synthesize the TS-1 under the same condition in absence of promoter is 36 h. When the synthesis of TS-1 at low temperature in absence of promoter was tried, nothing was obtained even after 168 h. The same situation happened also in the case of refluxing synthesis of TS-1 at atmospheric pressure. Nothing was obtained after 168 h. The % yield of the solid mass of fully crystalline material was always higher for the sample prepared in the presence of promoter (comparison of sample A and F). This indicates that the presence of

promoter enhances the nucleation process, with increased rate of crystal growth leading to increased mass of the crystalline solid<sup>9</sup>.

**Table 2**  
**Physico-chemical properties of different TS-1 samples.**

Sample	Synthesis		PH		Solid yield %	Particle size nm
	Temp., K	Time, h	Initial	Final		
A	433	6	11.4	12.2	82	100-200
B	433	6	11.5	12.1	81	100-200
C	433	6	11.5	12.3	79	100-200
D	378	36	11.4	12.1	75	300
E	383	48	11.5	12.2	70	500
F	433	36	11.4	12.2	71	100-200

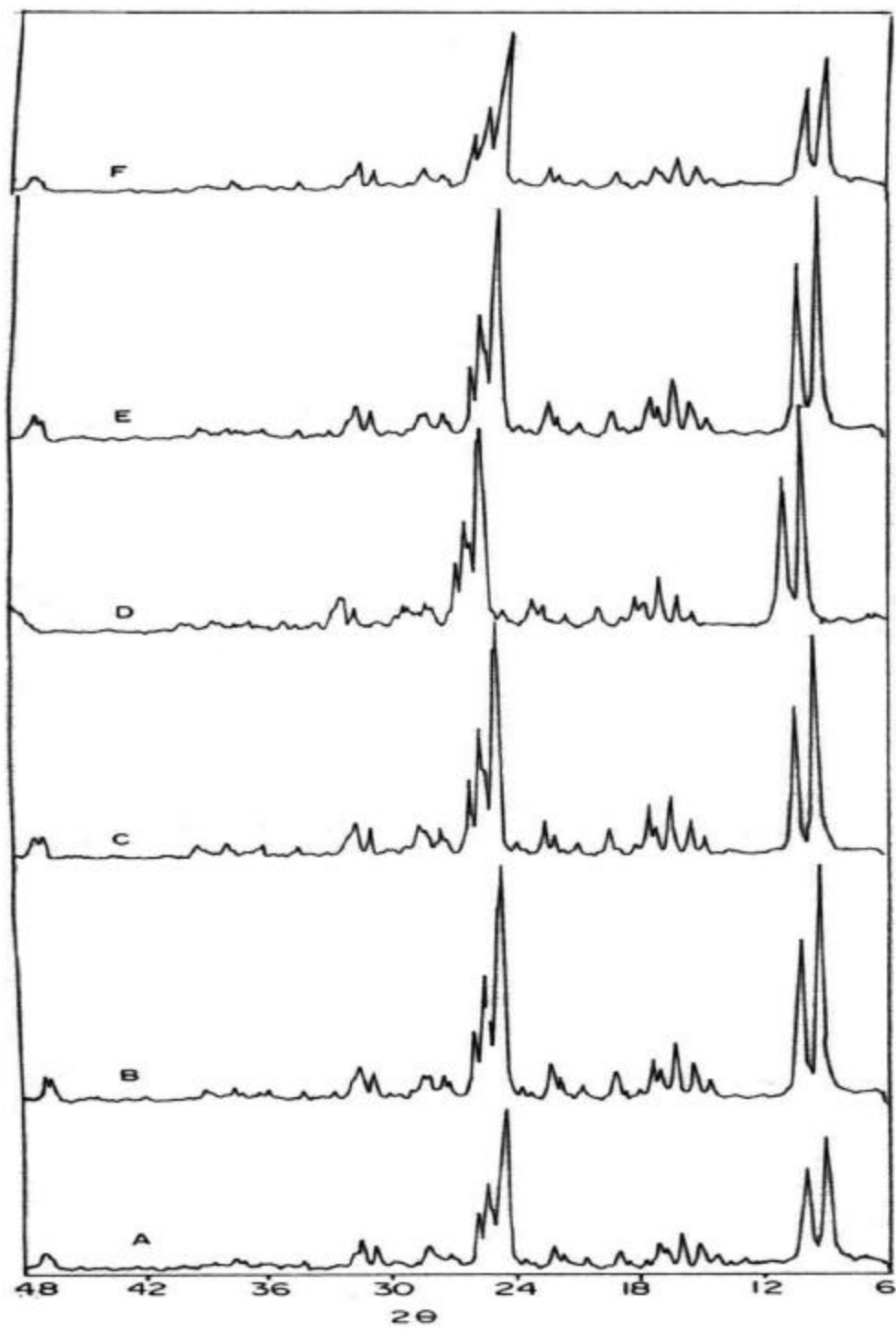
#### **II.5.1. XRD analysis:**

The XRD pattern of all the samples show the typical MFI character without any contaminating phases. All the samples are highly crystalline and preserve the orthorhombic character (Fig. 2). XRD pattern of the sample F, prepared in the absence of promoter is the same as the sample A, prepared in the presence of promoter. They both preserve the orthorhombic<sup>10</sup> character, as there was no splitting in the XRD pattern in the range  $2\theta = 24.4^\circ$  and  $2\theta = 29.3^\circ$ .

#### **II.5.2. IR analysis:**

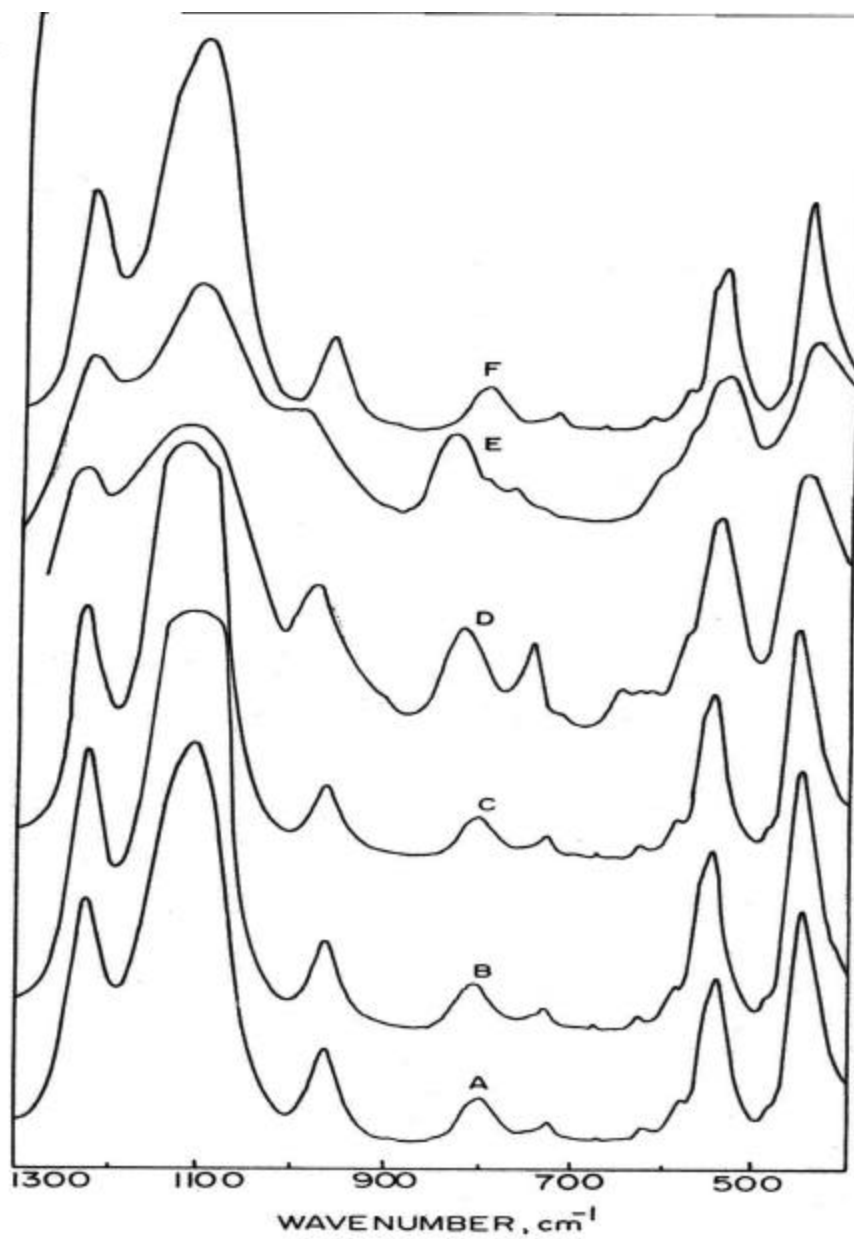
The IR spectra of all the samples in the framework region is shown Fig. 3. The ratio of the band at  $550\text{ cm}^{-1}$  and  $440\text{ cm}^{-1}$  is more than 0.7 in all the cases, indicating the fully crystalline materials. The presence of a band at  $960\text{ cm}^{-1}$  is observed in all the samples which is

Fig.2. XRD pattern of different TS-1 samples





**Fig.3. Framework IR Spectra of different TS-1 samples**



the indication of  $\text{Ti}^{+4}$  incorporation in the silicalite framework<sup>11</sup>. It is also observed that the intensity of the  $960\text{ cm}^{-1}$  band also increases with increase in Ti-content of the materials. The ratio of the band at  $960\text{ cm}^{-1}$  to  $540\text{ cm}^{-1}$  gradually decreases from sample A to C, with decrease in Ti-content of the materials, indicating the incorporation of the  $\text{Ti}^{+4}$  in the framework position in the TS-1 samples. The same trend is observed when the optical density ratio of  $960\text{ cm}^{-1}$  band and  $800\text{ cm}^{-1}$  was observed<sup>11</sup> (Fig. 4). The ratio of the band was found to decrease with decrease in the titanium content of the materials. This confirms the incorporation of  $\text{Ti}^{+4}$  in the framework position in the TS-1 samples.

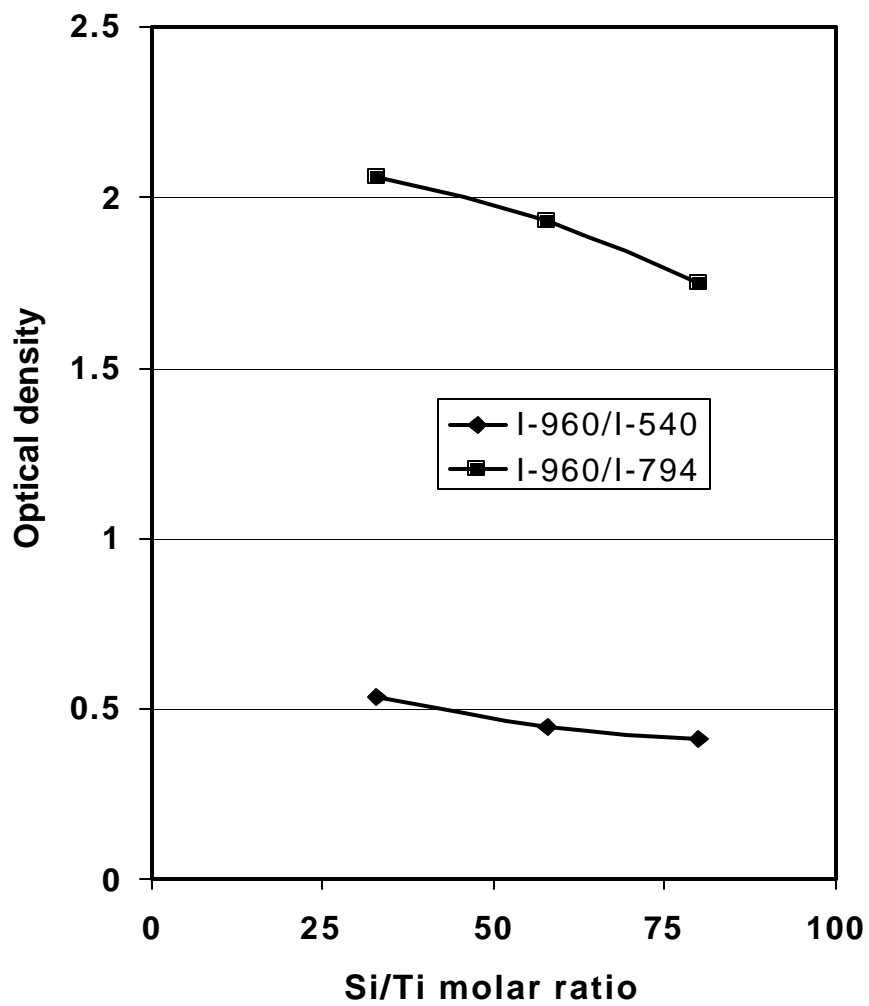
### **II.5.3. UV analysis:**

The UV-Vis spectra of all the samples were shown in Fig. 5. All the samples exhibit a sharp absorption in the range 210-215 nm. This is the characteristic of tetrahedrally isolated  $\text{Ti}^{+4}$  species in the framework position of TS-1 samples. There is no other absorption in the higher wavelength indicating the absence of extra framework Ti- species or higher co-ordinated Ti-species<sup>12</sup>.

### **II.5.4. SEM-EDX analysis:**

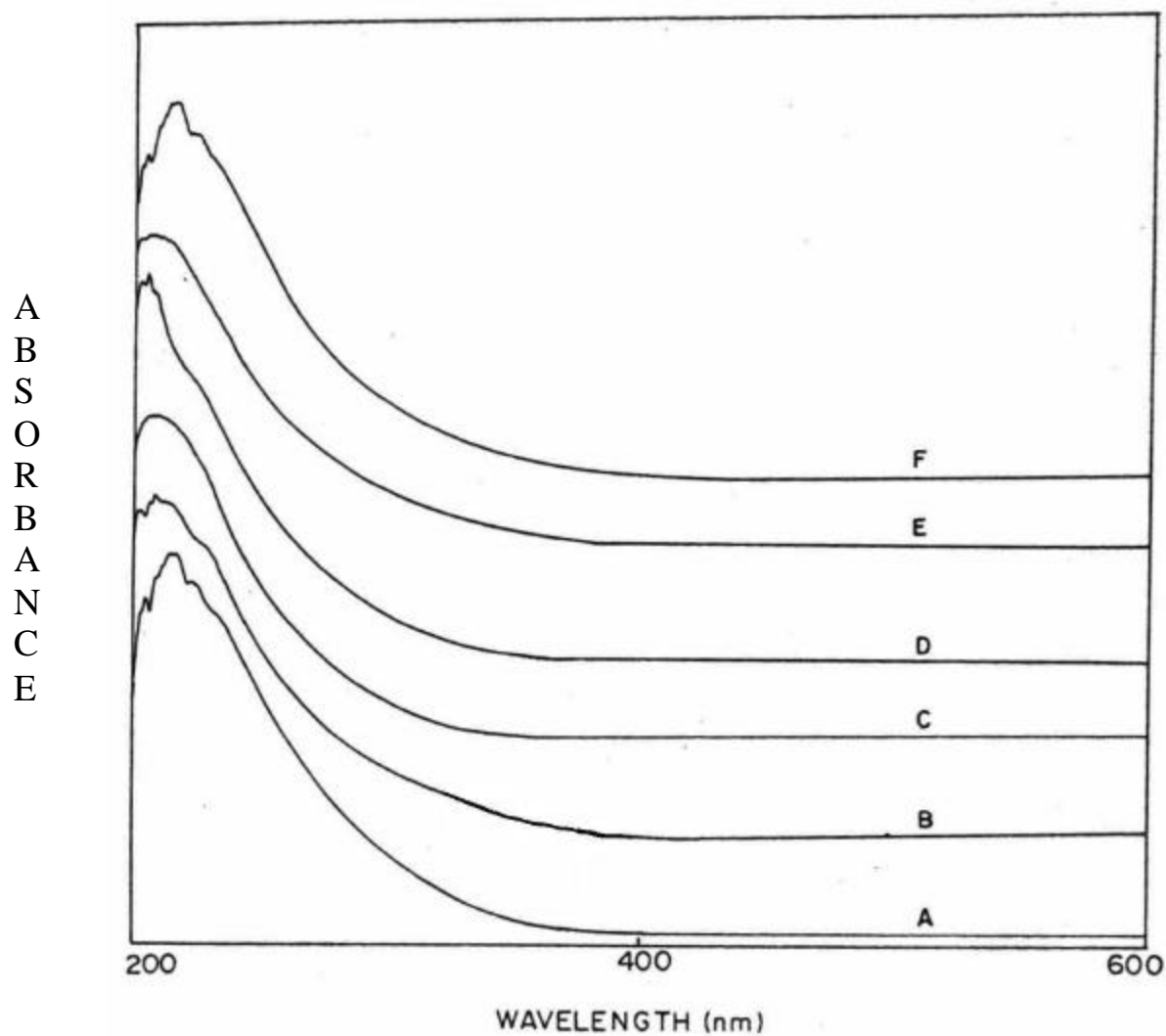
The scanning electron micrographs of some of the samples are shown below (Fig. 6) and the properties are summarized in the table 3. It is observed that the TS-1 samples prepared in the presence of promoter in the autoclave under autogeneous pressure at high temperature gives smaller crystals. However, the samples prepared under (i) relatively low temperature (378K) in an autoclave under autogeneous pressure and (ii) reflux condition in a flask under atmospheric pressure, lead to the formation of slightly bigger crystals (300 - 500 nm). The bigger crystal formation in the case of low temperature synthesis could be due to the decrease in nucleation

**Fig.4: Change of optical density of 960 to 540 and 960 to 794 bands**

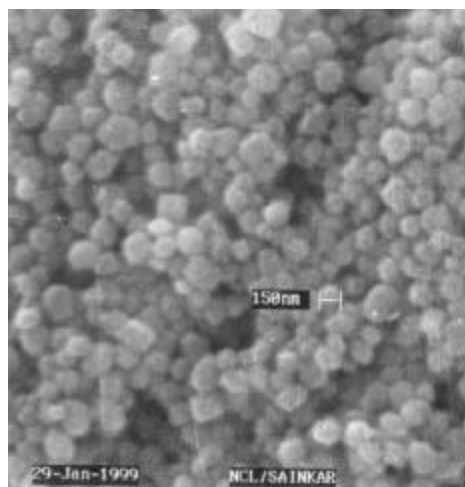


time. The increase in nucleation time leads to the formation of larger crystals. The chemical analysis by EDX

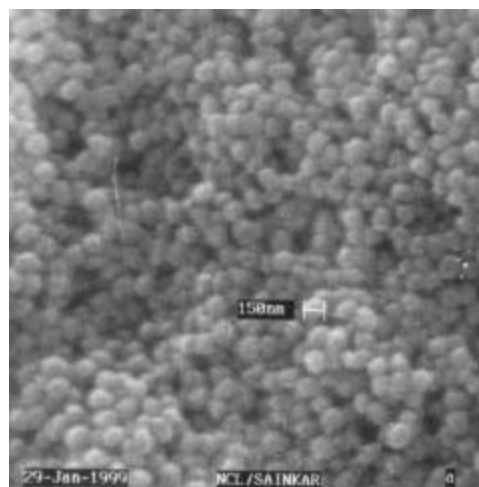
**Fig.5. UV-Vis spectra of different TS-1 samples**



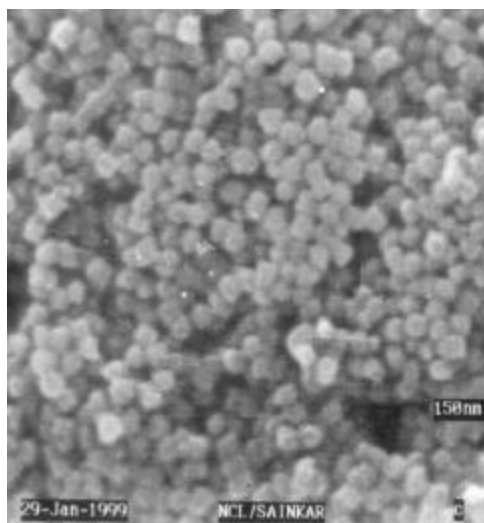
**Fig. 5: SEM pictures of TS-1 samples**



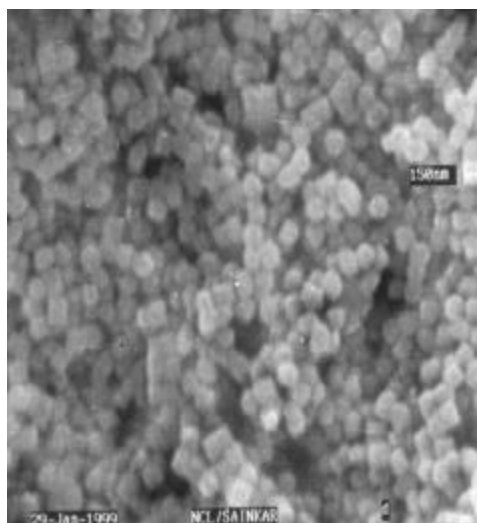
Sample A (Si/Ti = 33)



Sample B (Si/Ti = 58)



Sample C (Si/Ti = 80)



Sample F (Si/Ti = 33)  
Without promoter

measurement shows that the % uptake of  $Ti^{+4}$  in the framework is comparable with the Si/Ti molar ratio in the initial reaction mixture.

**Table 3: Physico - chemical characterizations of TS-1 samples.**

Samples	Si / Ti		Particle Size nm	UV- VIS Abs cm <sup>-1</sup>	I <sub>960</sub> / I <sub>540</sub>
	Gel	Solid			
A	30	33.9	100 - 200	215	0.54
B	55.5	58	100 - 200	207	0.46
C	79	80	100 - 200	215	0.41
D	30	34.4	300 - 400	212	0.52
E	30	35.1	400 - 500	215	0.53
F	30	34.1	200 - 250	215	0.52

## II.6. Conclusion:

1. The hydrothermal synthesis of the samples in the presence of promoter at 433 K leads to the formation of smaller crystals with almost uniform particle size distribution.
2. The samples synthesized at low temperature (378K) under autogeneous pressure slightly bigger crystallites (300 nm) were obtained. Similar results were obtained when the synthesis was carried out at reflux conditions and at atmospheric pressure (500 nm particle size).
3. Incorporation of  $Ti^{+4}$  in the framework remains almost comparable with the Si/Ti molar ratio in the initial reaction mixture. The % uptake was maximum when the Si / Ti molar ratio is 79 and minimum when the ratio is 30.
4. The optical density ratio of 960  $cm^{-1}$  and 540  $cm^{-1}$  band increases with decrease in Si/Ti molar ratio. Similar observations were made in the optical density ratio of 960  $cm^{-1}$  and 795  $cm^{-1}$  band.
5. Quality of the TS-1 samples prepared in the presence of promoter and in the absence of it is almost the same.

## II.7. Experimental for reactions and product analysis:

The liquid phase catalytic reactions were carried out in glass batch reactor. In a typical reaction X mole of the substrate and Y mole of  $\text{H}_2\text{O}_2$  (35 % aqueous) were reacted over the Z g of the catalyst in the presence of water (triphase) and in presence of a co-solvent (biphase) under vigorous stirring. For comparison two sets of experiments, one in biphasic system in the presence of co-solvent like acetonitrile, or acetone or methanol, and the other in solvent free triphasic system, were carried out. The substrate to water and substrate to co-solvent ratio (wt/wt) was kept constant to maintain the same dilution level of the reaction mixture in both the biphasic and triphasic systems. The additional water, apart from coming through aqueous  $\text{H}_2\text{O}_2$ , was used for dispersion of the catalyst in this heterogeneous system and to maintain the dilution level. Generally,  $\text{H}_2\text{O}_2$  (35 %) was slowly injected dropwise using a syringe pump (Sega, USA) during 30 minutes unless stated otherwise. The products were collected at various intervals of reaction time and were analyzed by high resolution capillary gas chromatography (Shimadzu, GC 17 A) using flame ionization detector. The  $\text{H}_2\text{O}_2$  selectivity is defined as the moles of  $\text{H}_2\text{O}_2$  consumed in the formation of oxygenated products and selectivity of a particular product is defined as the moles of that product obtained among the total moles of oxygenated products formed in the reaction.

For competitive adsorption experiment under triphasic condition water was used for the dispersion of the catalyst, whereas acetonitrile was used instead of water in the case of biphasic system. 5 g calcined TS-1 sample was taken in a 100 ml round bottom flask. At first 5 g benzene was fed into it followed by the addition of 25 g water. The mixture was then stirred with help of a magnetic stirrer at 333 K for 2 h. The mixture was then filtered, dried in air and finally dried in a desiccator. The same sequence was followed during the competitive adsorption experiment



under biphasic system except that acetonitrile was used instead of water. The adsorbed TS-1 samples were characterized for the adsorbed materials by IR spectroscopy (Nicolet 60 SXB spectrometer using KBr pellet technique). For desorption experiment 5 g of TS-1 / acetonitrile / benzene sample was loaded in a tubular downflow glass reactor and then flushed with dry nitrogen at 523 K for 1 h. The desorbed material was cooled (in a liquid nitrogen trap), collected and analyzed by G.C.

For silylation 1.0 g of TS-1 is reacted with 2 g TMSCl in 10 ml dry toluene and refluxed for 48 h in a 50 ml double neck round bottom flask under argon atmosphere. After the reflux is over, the sample was collected by centrifugation, washed several times with toluene and finally with acetone. The sample is then calcined at 833 K for 8 h in air.

The inert atmosphere reactions (static nitrogen) were carried out in a glass batch reactor where the reactor was first evacuated by flushing with dry nitrogen. Then nitrogen balloon was fitted on the top of the condenser on a two-way stopcock. For flowing nitrogen, the nitrogen was bubbled continuously through the reaction mixture through a septum.

## II.8. References

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## **CHAPTER III: CATALYSIS**

## III. Catalysis

### III (1): Hydroxylation of benzene

#### III.1.1. Introduction

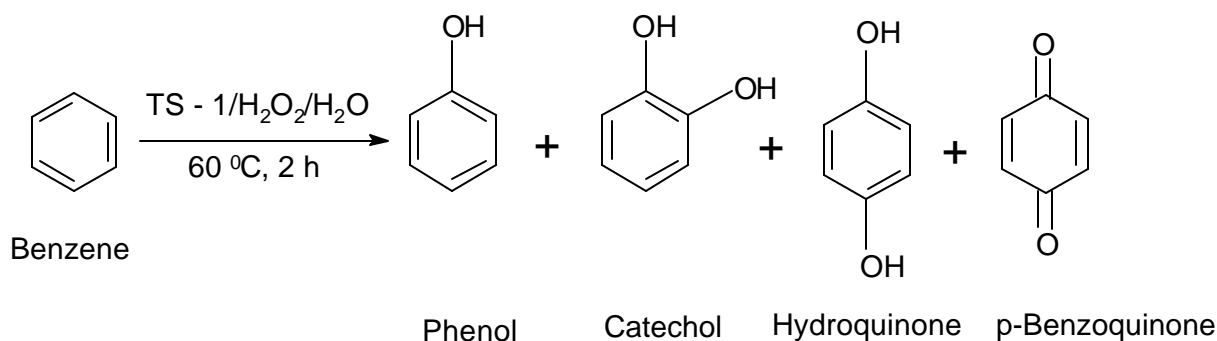
One of the major problems encountered in catalytic, liquid phase organic transformations is the reaction between mutually immiscible reagent(s) and substrate<sup>1</sup>. Under heterogeneous conditions (organic phase - aqueous phase reaction) the observed reaction rates are very slow, owing to the low concentration of at least one of the reactants in each phase. To overcome this problem co-solvents are generally used to bring about a homogeneous state and thereby completely eliminating the phase boundaries. Although, the use of co-solvents often finds its utility, product separation suffers from the drawback of complex work-up procedure. Phase-transfer catalysts<sup>2-4</sup>, used to overcome this problem, also suffer from the drawback that the catalyst used promotes the formation of emulsions, giving rise to severe problems in recycling and work-up. Tetraalkylammonium cation supported resins<sup>5, 6</sup> and aluminas<sup>7</sup> have also been reported to be efficient triphase catalysts (solid catalyst resides at the interface of two liquid layers) in certain organic transformations.

During the last decade crystalline, microporous titanium silicate, TS-1<sup>8, 9</sup>, has been extensively used in oxidation of various organic substrates in the presence of dilute H<sub>2</sub>O<sub>2</sub> using co-solvents<sup>10-14</sup>. However, the use of environmentally detrimental organic solvent creates problems related to product separation and solvent recycle, which are energy intensive steps. Hence, it is desirable to develop suitable methodology where the oxidation reactions catalyzed by the TS-1 / H<sub>2</sub>O<sub>2</sub> system could be carried out without using organic solvents so that the whole process becomes environmentally favorable, even if comparable conversion and selectivity, with respect to conventional processes, are obtained.

Recently, it was reported that TS-1 can efficiently be used under triphase conditions in the

oxidation of water-immiscible organic substrates, such as toluene, anisole, m-cresol, benzylalcohol and cyclohexanol<sup>15</sup>. Quite interestingly, under such triphase conditions where no organic solvent was used (solid TS-1+ water immiscible organic substrate + water + H<sub>2</sub>O<sub>2</sub>), a significant enhancement in activity (4-6 times) and para-selectivity was achieved<sup>15</sup>.

Although, phenol hydroxylation catalyzed by TS-1 / H<sub>2</sub>O<sub>2</sub> system has been extensively studied<sup>8-13</sup>, very little is known about benzene hydroxylation<sup>14</sup>. In this chapter we report detailed studies using TS-1 as a very efficient catalyst for the oxidation of benzene under solvent free, triphase conditions (solid catalyst, organic and aqueous phases) with significant enhancement in the activity over conventional biphasic system.



**Scheme 1: Benzene hydroxylation under triphase over TS - 1/ H<sub>2</sub>O<sub>2</sub> system**

### III.1.2. Experimental:

The liquid phase catalytic reactions were carried out in glass batch reactor. In a typical reaction X mole of benzene and Y mole of  $\text{H}_2\text{O}_2$  (35 % aqueous) were reacted over the Z g of the catalyst in the presence of water (triphasic) and in presence of a co-solvent (biphasic) under vigorous stirring. For comparison two sets of experiments, one in biphasic system in the presence of co-solvent like acetonitrile, or acetone or methanol, and the other in solvent free triphasic system, were carried out. The benzene to water and substrate to co-solvent ratio (wt/wt) was kept constant to maintain the same dilution level of the reaction mixture in both the biphasic and triphasic systems. The additional water, apart from coming through aqueous  $\text{H}_2\text{O}_2$ , was used for dispersion of the catalyst in this heterogeneous system and to maintain the dilution level. Generally,  $\text{H}_2\text{O}_2$  (35 %) was slowly injected dropwise using a syringe pump (Sega, USA) during 30 minutes unless stated otherwise. The products were collected at various interval of reaction time and were analyzed by high resolution capillary gas chromatography (Shimadzu, GC 17 A) using flame ionization detector. The  $\text{H}_2\text{O}_2$  selectivity is defined as the moles of  $\text{H}_2\text{O}_2$  consumed in the formation of oxygenated benzene products and selectivity of phenol is defined as the moles of the phenol obtained among the total moles of oxygenated benzene products formed in the reaction

For competitive adsorption experiment under triphasic condition water was used for the dispersion of the catalyst, whereas acetonitrile was used instead of water in the case of biphasic system. 5 g calcined TS-1 sample was taken in a 100 ml round bottom flask. At first 5 g benzene was fed into it followed by the addition of 25 g water. The mixture was then stirred with help of a magnetic stirrer at 333 K for 2 h. The mixture was then filtered, dried in air and finally dried in a desiccator. The same sequence was followed during the competitive adsorption experiment under biphasic system except that acetonitrile was used instead of water. The adsorbed TS-1 samples were

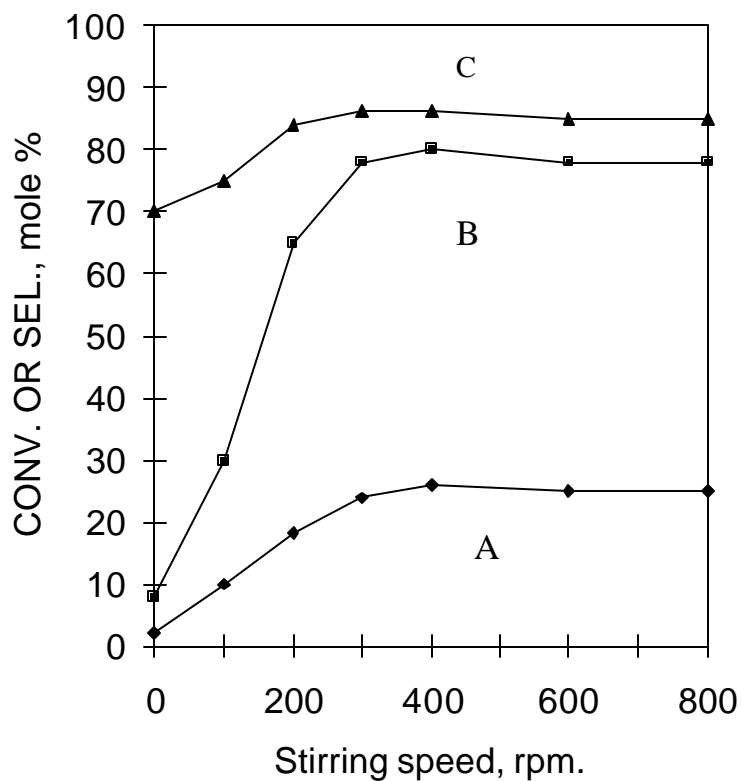
characterized for the adsorbed materials by IR spectroscopy (Nicolet 60 SXB spectrometer using KBr pellet technique). For desorption experiment 5 g of TS-1 / acetonitrile / benzene sample was loaded in a tubular downflow glass reactor and then flushed with dry nitrogen at 523 K for 1 h. The desorbed material was cooled (in a liquid nitrogen trap), collected and analyzed by G.C.

**III.1.3. Effect of stirring:** Fig.1 depicts that under triphase the conversion increases with the stirring speed up to ca. 400 rpm before leveling off. The effect of stirring was rather pronounced in triphase system. By contrast in biphasic conditions no significant change in the conversion was observed under mild (200-300 rpm) and vigorous (400-1000 rpm) stirring, in triphase conditions vigorous stirring only was effective. For further experiments simple glass batch reactor with magnetic stirring (ca 800 rpm) was used as the results obtained using Parr autoclave and the glass batch reactor, under otherwise same condition, were comparable.

**III. 1.4. Effect of benzene / H<sub>2</sub>O molar ratio:** In Table 1, the effect of the benzene to H<sub>2</sub>O<sub>2</sub> molar ratio in the hydroxylation of benzene over TS-1 / H<sub>2</sub>O<sub>2</sub> system under tri- and bi-phase conditions is reported. With increasing benzene / H<sub>2</sub>O<sub>2</sub> molar ratio, both the H<sub>2</sub>O<sub>2</sub> selectivity (utilization towards the formation of phenol, and its further oxidation products like parabenzoquinone, catechol and hydroquinone), and phenol selectivity among products were also increased, as expected. However, the benzene conversion and H<sub>2</sub>O<sub>2</sub> selectivity towards oxygenated benzenes are considerably higher (4-6 times) in triphase than that could be achieved in the presence of organic co-solvent (biphase). The corresponding increase in reaction rate (T.O.F.) is about 15-25 times (Table 1). The benzene conversion, H<sub>2</sub>O<sub>2</sub> selectivity, rate of reaction (TOF) and phenol selectivity increase with the benzene to H<sub>2</sub>O<sub>2</sub> molar ratio. A small amount of secondary oxidation products (10-20 %) like parabenzoquinone, catechol and hydroquinone formed due to further hydroxylation of primarily

formed phenol, were also obtained. In all other experiments, mentioned below, only triphase conditions were used.

**Fig. 1. Effect of stirring**



Reaction condition: Benzene = 0.1 mole, H<sub>2</sub>O<sub>2</sub> = 0.033 mole, Catalyst = 1.17 g, H<sub>2</sub>O = 39 g, reaction was carried out in a stainless steel Parr (USA) autoclave, temperature = 333K, A = Conversion, B = H<sub>2</sub>O<sub>2</sub> selectivity, C = Phenol selectivity.



**Table 1: Effect of benzene to H<sub>2</sub>O<sub>2</sub> molar ratio**

Benzene / H <sub>2</sub> O <sub>2</sub>  molar ratio	Phase <sup>b</sup>	Conv. (%)		H <sub>2</sub> O <sub>2</sub> Sel (mole %) <sup>c</sup>	TOF <sup>d</sup> (h <sup>-1c</sup> )	Phenol Sel. <sup>e</sup> (mole%)
		Exp.	Theo.	(mole %)		
1.0	Tri	74.4	100	84.8	72.5	85.6
	Bi	11.6	100	13.7	2.9	82.0
1.5	Tri	52.3	66.7	86.2	49.1	89.5
	Bi	9.8	66.7	16.6	2.4	86.9
2.0	Tri	41.1	50.0	87.2	37.2	90.4
	Bi	8.7	50.0	19.2	2.1	90.1
3.0	Tri	28.8	33.3	90.5	25.5	95.0
	Bi	6.4	33.3	20.6	1.5	92.8

- a: Catalyst TS-1 (15 wt % with respect to substrate, H<sub>2</sub>O<sub>2</sub> was slowly fed into the reaction mixture for a period of 30 min. Temperature 333 K, benzene : H<sub>2</sub>O = 1 : 5 (wt/wt), Reaction time = 2 h (triphasic) and 8 h (biphase).
- b: In biphasic acetonitrile was used as solvent, benzene : solvent = 1 : 5 (wt/wt). Almost similar results were obtained when acetone or methanol was used as solvent in place of acetonitrile.
- c: Calculated considering the utilization of one mole H<sub>2</sub>O<sub>2</sub> in the formation of phenol + two moles for the formation of catechol, hydroquinone and parabenzoquinone, and mole % H<sub>2</sub>O<sub>2</sub> selectivity is based on the mole of H<sub>2</sub>O<sub>2</sub> used.
- d: Turn over frequency = moles of H<sub>2</sub>O<sub>2</sub> converted for producing phenol + secondary products (catechol, hydroquinone and p-benzoquinone) per mole of Ti per h.
- e: The rest of the products include parabenzoquinone, catechol and hydroquinone, orthobenzoquinone was not detected.

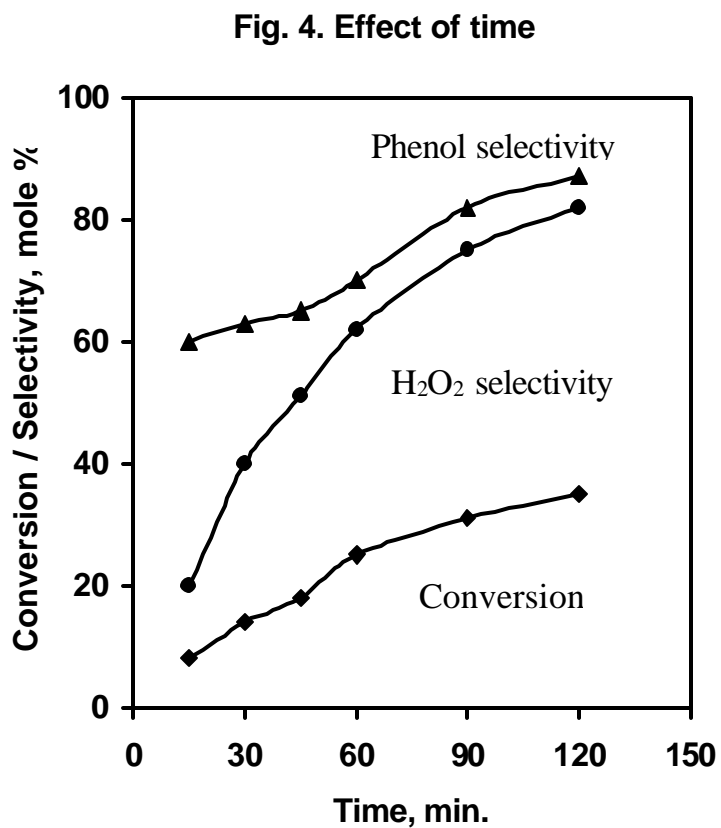
**III. 1. 5. Effect of reaction time:** In Fig. 2, the rates of reaction of benzene hydroxylation, i.e. a plot of the conversion (%) of benzene and  $\text{H}_2\text{O}_2$  as a function of reaction time under triphase conditions is shown. In the presence of co-solvent the reaction was very slow and only ca. 20 %  $\text{H}_2\text{O}_2$  efficiency could be obtained after 8 h (not plotted in Fig 3). However, under the presently used triphase conditions, the reaction was very fast from the beginning reaching maximum conversion level (ca. 85 mole %  $\text{H}_2\text{O}_2$  efficiency) in 2 h. The selectivity for phenol also increases (curve B), at the expense of secondary products (curve C, p-benzoquinone, catechol and hydroquinone), with time (Fig. 1). Since in this case the total amount of  $\text{H}_2\text{O}_2$  was added in one lot at the beginning of the reaction, it is quite likely that secondary oxidation products are also formed at increased rate in the beginning. However, as the reaction proceeds, with the progressive utilization of oxidant, the relative formation of secondary products also decreases with time.

**III.1.6. Effect of reaction temperature:** In Table 2, the effect of temperature on the conversion and product selectivity of the hydroxylation of benzene under solvent-free triphase is shown. Upon increasing the temperature from 323 K to 353 K, the rate of reaction (T.O.F.) increases along with the formation of secondary products, as expected. However, the optimum reaction temperature, under the present conditions, was found to be 333 K. Hence, all other experiments were carried out at 333 K.

**III.1.7. Effect of mode of addition of  $\text{H}_2\text{O}_2$ :** Table 3 illustrates the effect of continuous addition of  $\text{H}_2\text{O}_2$  on the conversion and selectivity in the oxidation of benzene under triphase conditions. High  $\text{H}_2\text{O}_2$  efficiency could be achieved from the beginning if the oxidant is added slowly. Table 3 also shows the amount of  $\text{H}_2\text{O}_2$  added after different interval of times. Here also, phenol selectivity increases slightly with time at the initial stages of the reaction at the cost of secondary oxidation

products.

**III.1.8. Effect of catalyst concentration:** In Table 4, the effect of catalyst concentration on benzene hydroxylation is reported. Increasing the catalyst concentration (with respect to benzene) resulted in an increase



Reaction Conditions: temp. = 333K, Catalyst A = 15 wt % with  
r.p.to benzene, H<sub>2</sub>O: Benzene = 5, benzene : H<sub>2</sub>O<sub>2</sub> = 2

**Table 2: Effect of temperature**

Temperature (K)	Benzene conv. (mole %)	H <sub>2</sub> O <sub>2</sub> Eff. (%)	Time h <sup>a</sup>	TOF h <sup>-1</sup>	Phenol Sel. (mole%)
323	67.8	70.5	3.0	40.2	96.0
333	74.4	84.8	2.0	72.5	85.6
343	78.6	85.7	1.5	90.7	86.5
353	72.3	88.2	1.0	150.8	78.4

a: Time at which maximum benzene conversion was achieved.

b: Benzene : H<sub>2</sub>O<sub>2</sub> molar ratio = 1 : 1, other conditions are same as that given in Table 1.

**Table 3: Effect of continuous addition of H<sub>2</sub>O<sub>2</sub>**

Reaction time (min)	15	30	45	60	90	120
H <sub>2</sub> O <sub>2</sub> added (mole % of benzene)	12.5	25.0	37.5	50.0	75.0	100.0
Benzene conv. (mole%)	9.1	19.0	30.3	41.0	63.0	80.8
H <sub>2</sub> O <sub>2</sub> eff. (mole%) <sup>c</sup>	91.0	92.7	92.5	92.3	91.1	91.3
Phenol selectivity (%)	75.0	79.8	84.6	87.4	91.6	88.6

a: Reaction conditions: Temperature 333 K, Catalyst TS-1 (15 wt % with respect to benzene), H<sub>2</sub>O : benzene = 5 : 1 (mass / mass), benzene : H<sub>2</sub>O<sub>2</sub> = 1 : 1 (mole / mole).

b: The remaining products were the mixture of secondary products, p-benzoquinone, catechol and hydroquinone.

c: Conversion of H<sub>2</sub>O<sub>2</sub> with respect to the moles of H<sub>2</sub>O<sub>2</sub> added at that reaction time.

in H<sub>2</sub>O<sub>2</sub> efficiency initially before leveling off at ca. 85 ± 5 %. Based on these results, ca. 12.5 - 15 wt% catalyst with respect to benzene was found to be an optimum for achieving a high H<sub>2</sub>O<sub>2</sub> efficiency and phenol selectivity. At 20 wt % catalyst concentration not only benzene conversion decreases but also phenol selectivity decreases drastically due to enhanced secondary reactions. It is quite understandable that due to increased utilization of H<sub>2</sub>O<sub>2</sub> for secondary products, the benzene conversion has decreased.

**Table 4: Effect of catalyst concentration**

Catalyst conc. in wt % <sup>a</sup>	Conv. (mole %) <sup>b</sup>	H <sub>2</sub> O <sub>2</sub> Sel. (mole %)	TOF (h <sup>-1</sup> )	Time (min.)	Phenol Sel. (mole%)
5.0	26.8	58.6	37.6	4.0	90.8
10.0	37.3	84.7	36.2	3.0	86.4
12.5	38.1	87.6	36.0	2.5	85.0
15.0	41.1	87.2	37.2	2.0	90.4
20.0	33.6	90.3	38.6	1.5	65.7

a: Catalyst TS-1 in wt % with respect to the substrate.

b: Benzene : H<sub>2</sub>O<sub>2</sub> molar ratio = 2:1 (maximum theoretical benzene conversion = 50 mole), other conditions are same as Table 1.

**III.1.9. Effect of dilution:** Table 5 illustrates the effect of water concentration on benzene conversion and product selectivities. At a water to benzene ratio = 5: 1(wt/wt), maintaining 15 wt %catalyst w.r.t. benzene (entries 1-6), maximum benzene conversion as well as optimum H<sub>2</sub>O<sub>2</sub>

selectivity were observed. Although increasing this ratio beyond 5 with increased dilution resulted in higher phenol selectivity, the benzene conversion and H<sub>2</sub>O<sub>2</sub> selectivity decrease considerably. However, decrease of the H<sub>2</sub>O-benzene ratio resulted in progressive decrease of benzene conversion, H<sub>2</sub>O<sub>2</sub> and phenol selectivities, indicating that at lower dilution the secondary reactions (i.e. oxidation of phenol to catechol, hydroquinone and parabenzoquinone) are facilitated. Although, the substrate to catalyst ratio was the same in these experiments, the catalyst concentration with respect to total reaction volume was also changed considerably. Hence in the next set of experiments, the effect of water to benzene wt. ratio was also studied keeping the catalyst concentration in the total reaction volume constant (at different benzene / catalyst ratio). These results, also given in Table 5 (entries 5, 7-9), suggest that optimum catalyst concentration with respect to both the substrate and the total reaction mixture is needed for achieving high phenol yields (i.e. high H<sub>2</sub>O<sub>2</sub> utilization and phenol selectivity).

Under triphase conditions during the hydroxylation of substituted benzenes like anisole, toluene and *m*-cresol, a significant enhancement in conversions as well as in regio-selectivity towards para-hydroxy products was observed<sup>15</sup>. In fact, a reversal of regio-selectivity was observed in the case of toluene and anisole. Since, the microporous zeolites and related molecular sieves possess restricted pore dimensions and channel structure, bulkiness of the products plays an important role of monitoring the shape selective product-distribution. It is known<sup>15</sup> that significantly higher activity as well as high *para* selectivity (in the case of substituted benzenes like toluene, anisole, etc) obtained in the triphase system indicate that the reaction may be occurring predominantly inside the zeolite channels. However, in the biphasic system, low conversion as well as very high ortho selectivity in the case of substituted benzenes like toluene, anisole<sup>15</sup> probably indicate that the reaction takes place on the external surface of the catalyst as well to a significant extent.

**Table 5: Effect of dilution**Temp. 333 K, H<sub>2</sub>O<sub>2</sub> was added in one lot; Reaction time = 2 h.

Entry	H <sub>2</sub> O:Benzene (wt / wt)	Catalyst wt% w.r.t.		Conv. <sup>a</sup> (%)	H <sub>2</sub> O <sub>2</sub> Eff. (%)	T.O.F. (h <sup>-1</sup> )	Pheno <sup>b</sup> (mole%)
		Benzene	Total				
1	1.0	15	6.0	14.3	39.9	17.1	60.3
2	2.0	15	4.3	30.1	81.3	34.7	64.9
3	3.0	15	3.3	33.4	85.7	36.6	71.7
4	4.0	15	2.8	36.2	88.3	37.8	79.8
5	5.0	15	2.4	41.1	87.2	37.2	90.4
6	7.5	15	1.7	34.6	75.9	32.4	90.3
7	1.0	5.2	2.4	13.0	14.5	17.8	88.9
8	3.0	9.8	2.4	40.0	86.1	36.7	92.9
9	5.0	15	2.4	41.0	87.8	37.5	89.9

a: Benzene : H<sub>2</sub>O<sub>2</sub> = 2 : 1 (mole / mole)

b: the rest were secondary products like PBQ, catechol, hydroquinone.

In relatively hydrophobic high silica titanium silicate molecular sieves, organic substrates are expected to be competing more favorably with water (vis-à-vis with organic solvent in biphasic) for diffusion and adsorption in triphasic condition, which is free from organic solvent. When an organic solvent is present along with the reactant, the diffusion and adsorption of the reactant will be hindered by the solvent. If this is true, then it may explain the higher activity in triphasic compared to that in biphasic.

**III.1.10. Competitive adsorption:** To confirm this hypothesis some competitive adsorption experiments under bi- and tri-phase conditions (in the absence of  $\text{H}_2\text{O}_2$ ) were carried out. The experimental details are given before in the section experimental for catalysis and adsorption. Fig. 3 illustrates the FTIR spectra of various TS-1 samples used in the competitive experiments. The TS-1 / acetonitrile / benzene sample, (sample c, curve C) shows a doublet at ca. 2350-2360  $\text{cm}^{-1}$  (characteristic peaks of acetonitrile<sup>17</sup> in non-overlapping range with TS-1 vibrations), whereas the TS-1 /  $\text{H}_2\text{O}$  / benzene sample (sample b, curve B) shows major peaks at 3060-3120  $\text{cm}^{-1}$  and 1480  $\text{cm}^{-1}$ , corresponding to benzene<sup>18</sup>. Curve C also indicates the presence of small amount of benzene (peaks represented by asterisk, Fig. 3). It is quite clear from these results that benzene is the main adsorbate in sample B while in sample C acetonitrile is mainly adsorbed. Curve A represents the FT-i.r. spectrum of the parent TS-1 sample.

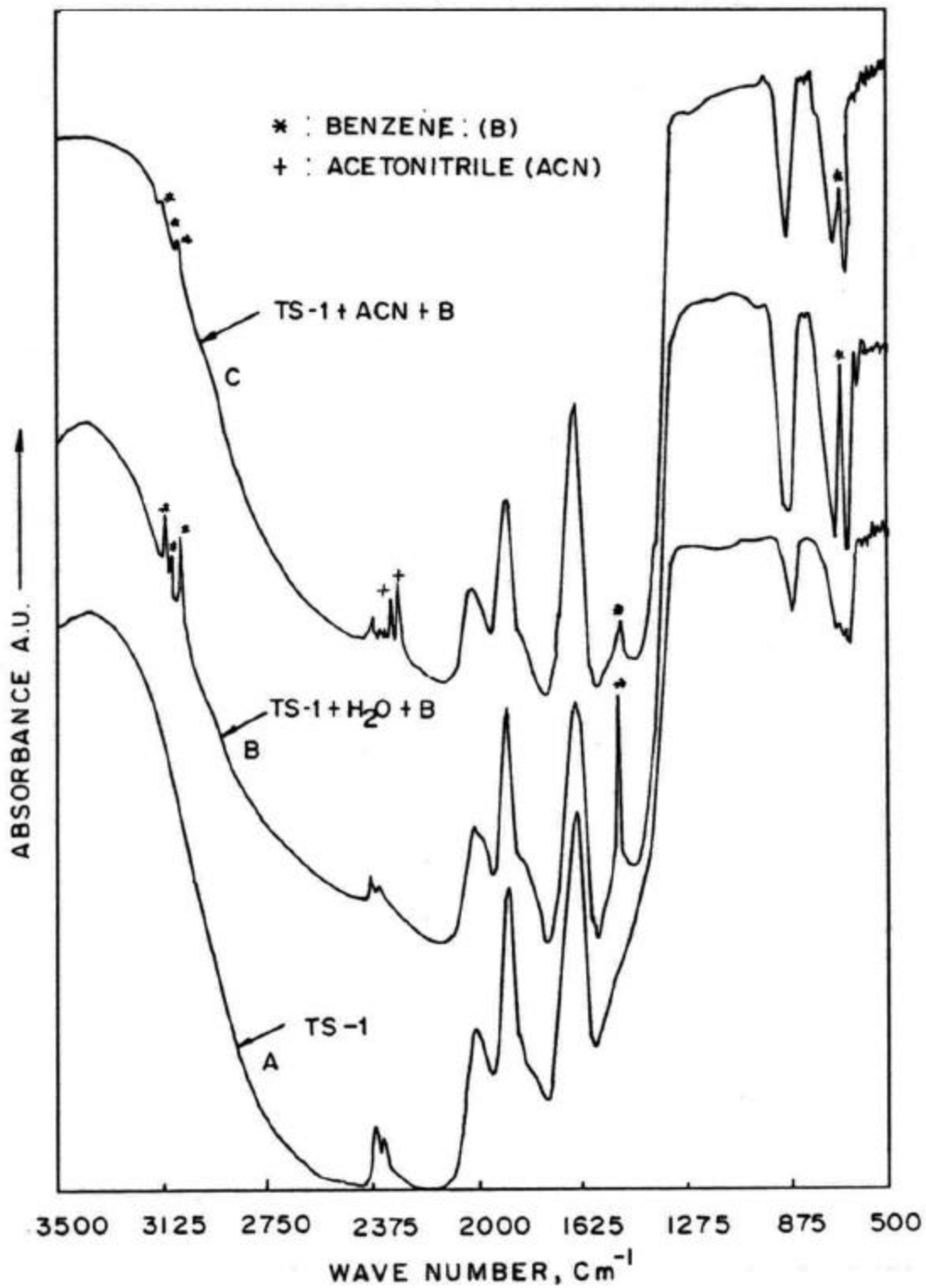
Since the aim of qualitative IR measurements was to confirm the relative presence of adsorbate in the TS-1 catalyst, desorption experiments were carried out for quantitative measurement. The desorbed material was mainly acetonitrile (92 wt%), benzene being only 8 wt%. In a similar desorption experiment of sample b (spectrum B, Fig. 5) it was found that ca. 90 wt % benzene was desorbed, the remaining being water (analyzed by G.C. using TCD). The total weight loss was ca. 10 wt% on dry TS-1 in both the cases. These results clearly demonstrate that the presence of acetonitrile provides strong resistance to benzene for diffusion inside the TS-1 channels, while such diffusional hindrance is not encountered by benzene in triphase conditions in the absence of organic solvent, resulting in high conversions in triphase.

Although the above mentioned explanation in triphase conditions may be accepted as far as



the adsorption and diffusion of reactants inside the TS-1 channels (intraparticle diffusion) is concerned, the transport of reactant (benzene) to the solid surface through the aqueous phase (external mass transfer) poses an additional problem. Recently, Desikan and

**Fig 3: FTIR spectra of adsorbed samples on TS-1**



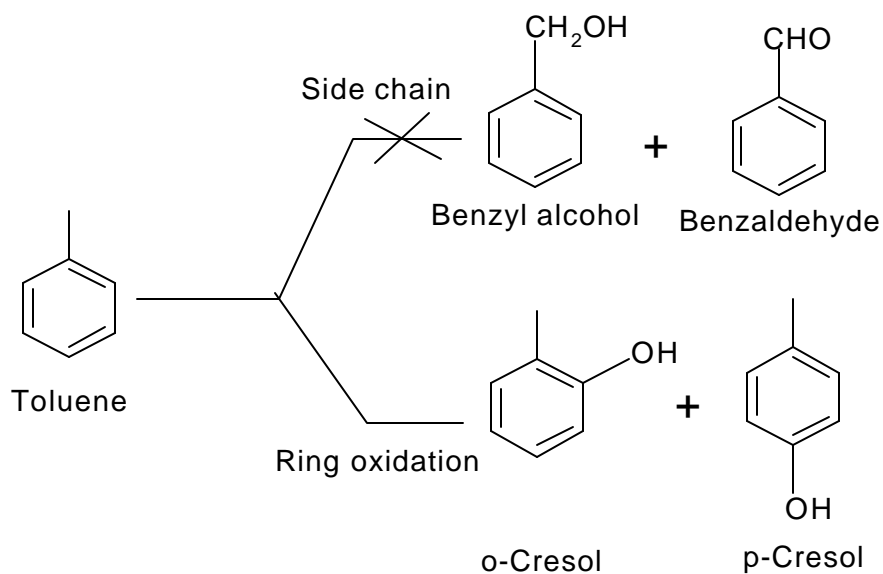
Doraiswamy<sup>19</sup> have reviewed this diffusion-reaction problem in triphase catalysis dealing with polymer-supported phase transfer catalysts in various types of triphase catalytic systems, including the solid-liquid-liquid (S-L-L) type. In any such S-L-L systems the overall activity depends on (i) external mass transfer, (ii) intraparticle diffusion, and (iii) intrinsic reactivity of the catalytic sites. Although the last two phenomena are unique to TS-1 (molecular sieves) and are already discussed above in the present case of triphase catalysis over TS-1 / H<sub>2</sub>O<sub>2</sub> system, the external mass transfer is a common and most complicated problem in triphase catalysis in general<sup>19</sup>.

In triphase conditions vigorous stirring, needed for the reaction to occur (external mass transfer, Fig. 1), may help the dispersion of the organic phase in aqueous one through micro droplet formation and thereby facilitating the transport of the reactant to the catalyst surface. Although a detailed treatment of chemical engineering and theoretical aspects of this interesting phenomenon is obviously beyond the scope of the present thesis, however, the interesting results are interpreted on the basis of present experimental data.

**III.1.11. Summary and conclusions:** In summary, it has been demonstrated that using triphase system (solid-liquid-liquid), in the absence of an organic co-solvent, a considerable increase (ca. 20 times) in conversion of benzene during oxidation by the TS-1 / H<sub>2</sub>O<sub>2</sub> system can be achieved. The effect of various reaction parameters such as time, temperature, benzene to oxidant molar ratio, catalyst concentration, mode of addition of H<sub>2</sub>O<sub>2</sub> and dilution level on conversion and selectivity was studied. Vigorous stirring was needed for the reaction to occur in triphase. Since titanium silicate molecular sieves are relatively hydrophobic in nature, the benzene (reactant) competes more favorably with water for diffusion and adsorption under triphase conditions resulting in higher conversion and shape selectivity. Apart from enhancement in activity (and para selectivity in the case of toluene / anisole), the present triphase method offers distinct advantages in easier product separation and thus contributing to the development of eco-friendly process.

## III.2. Toluene hydroxylation

**III.2.1. Introduction:** Direct hydroxylation of toluene is an attractive route for the preparation of cresols. Although TS-1 has been used as catalyst for toluene hydroxylation in the presence of dilute  $\text{H}_2\text{O}_2$  and an organic solvent<sup>9</sup>, the  $\text{H}_2\text{O}_2$  efficiency and reactions were too low to be of any practical interest in the formation of cresols. In the case of toluene there are two oxidation sites. One is primary carbon atom of the side chain methyl group and the other one is the ring. The scheme for toluene hydroxylation is shown below (Scheme 2). Further, in the case of substituted benzenes such as toluene, anisole etc., triphasic reactions favor the *p*-selective product whereas biphasic reaction conditions prefer *o*-isomer as the major product. Additionally, under triphase conditions the reaction takes place almost without an induction period where the reaction is reasonably fast from the very beginning, while under biphasic conditions it requires relatively long induction period.



**Scheme 2: Toulene oxidation scheme**

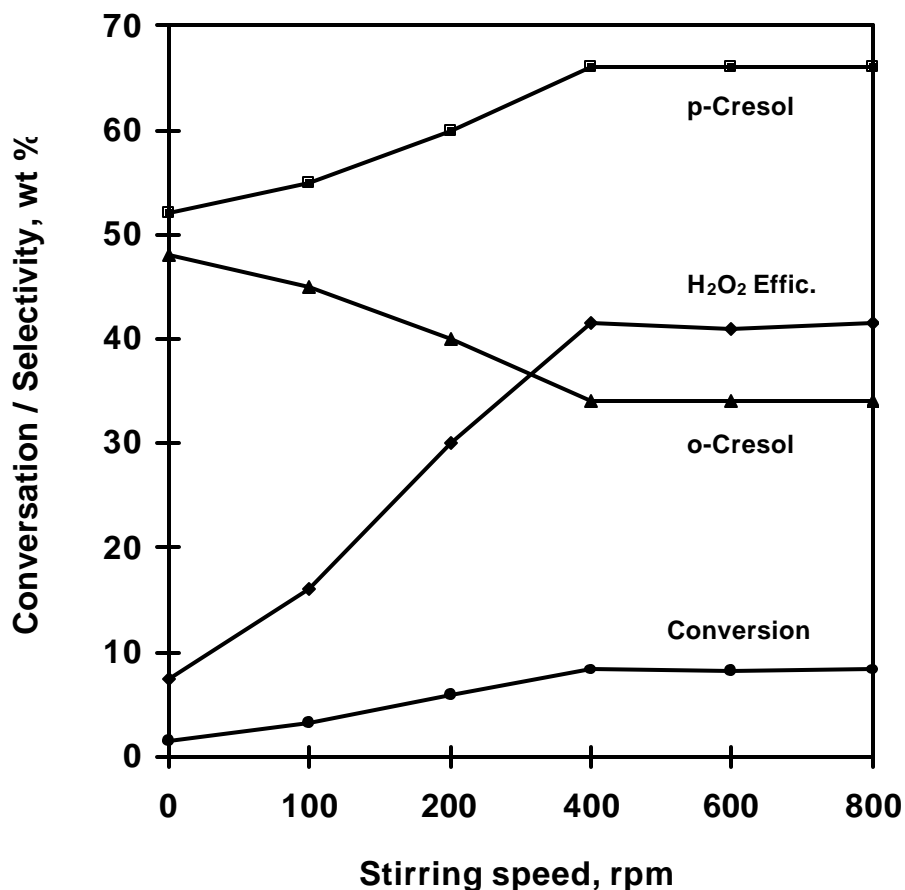
In part-1 we have reported detailed studies on the direct hydroxylation of benzene using TS-1 as catalyst and dilute  $\text{H}_2\text{O}_2$  under solid triphase conditions. Now, this part of this chapter III reports detailed study on the hydroxylation of toluene using TS-1 as a catalyst and dilute  $\text{H}_2\text{O}_2$  as an oxidant under triphase conditions in the absence of any organic solvent. The effect of various reaction parameters such as stirring, temperature, catalyst concentration, dilution, toluene to  $\text{H}_2\text{O}_2$  molar ratio and reaction time was studied. For comparative purpose, relevant data collected in the presence of different organic solvents under biphasic conditions are also presented. The experimental sections are already presented in chapter II.

**III.2.2 Effect of stirring:** Figure 1 deals with the effect of stirring on catalytic hydroxylation of toluene in triphase. The conversion as well as *p*-selectivity increased with an increase in stirring speed before it leveled off at ca. 400 rpm. This is in line with our earlier report<sup>6</sup>. All other experiments were carried out under vigorous stirring. As expected, with increasing stirring the diffusion of the reactant from the bulk to the catalyst surface will also increase, resulting in increased conversion. Interestingly, the selectivity for *p*-cresol also increased with stirring speed along with conversion. The increase in *p*-cresol formation was at the cost of *o*-cresol formation indicating that the enhanced stirring speed and increased conversion favor *p*- isomer formation. This may be due to the reason that with an increase in stirring rate (and therefore increased transport of the reactant to the catalyst and its diffusion inside the pore) probably the reaction mainly occurs inside the relatively hydrophobic TS-1 channels resulting in increased conversion and *p*-selectivity.

**III.2.3. Effect of time:** In Fig. 2, the progress of the reaction was monitored with time. This figure showed that the reaction was reasonably fast from the beginning and both the *o*- and *p*- cresol formations took place simultaneously. The increase in conversion and H<sub>2</sub>O<sub>2</sub> efficiency with time was associated with progressive increase in *p*-selectivity. Maximum H<sub>2</sub>O<sub>2</sub> efficiency and *p*-selectivity was observed at 6 h before leveling off.

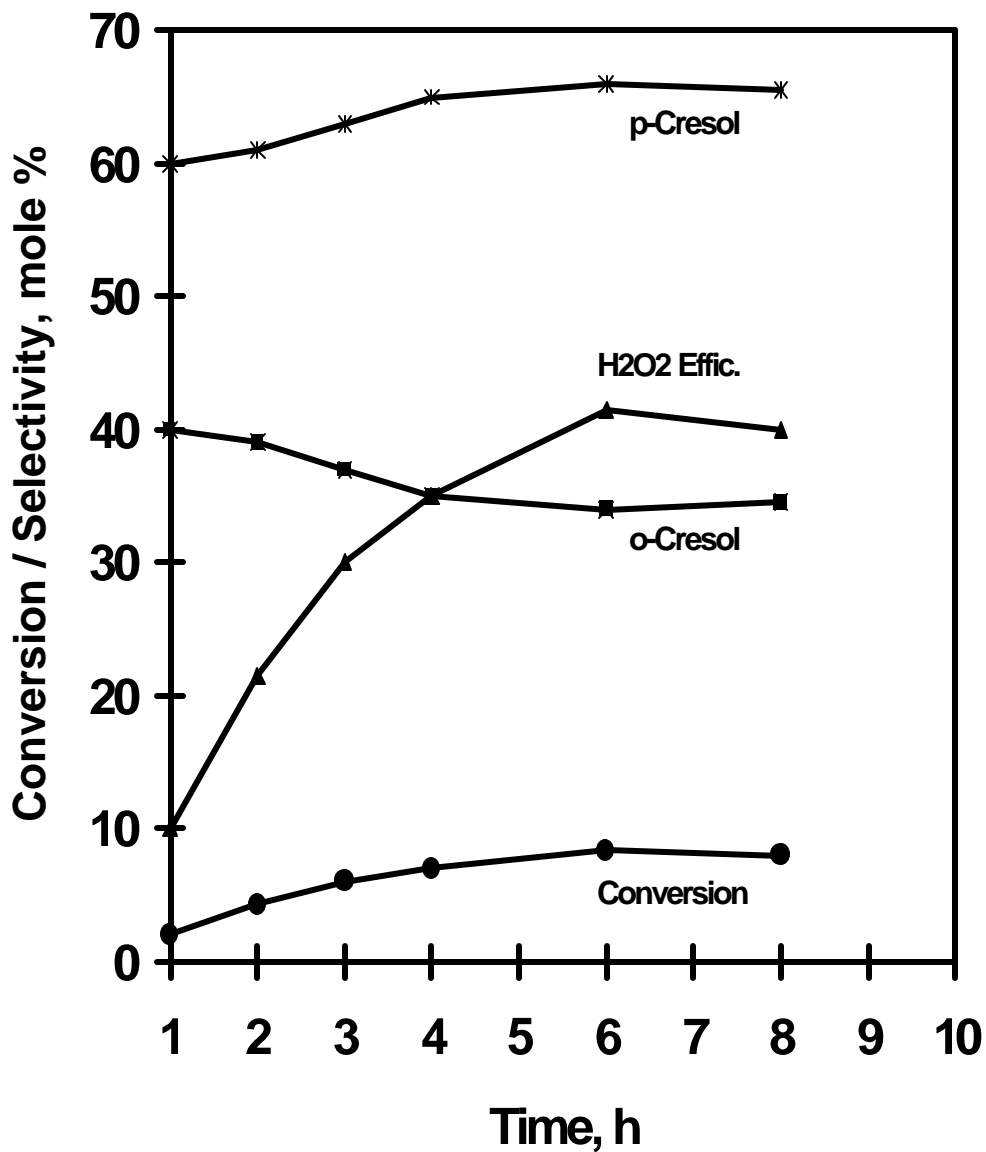
**III.2.4. Effect of temperature:** Table 1 deals with the effect of temperature on conversion and selectivity in the formation of cresols from toluene using TS-1/H<sub>2</sub>O<sub>2</sub>

**Fig. 1. Effect of stirring**



system under triphase condition. At room temperature, both the  $\text{H}_2\text{O}_2$  efficiency and p-cresol selectivity were low. The selectivity for p-cresol and  $\text{H}_2\text{O}_2$  efficiency increased with increase in temperature. At  $80^\circ\text{C}$ , maximum  $\text{H}_2\text{O}_2$

**Fig. 2. Effect of time**



efficiency and p-cresol selectivity were obtained. As the activation energy for a reaction was increasingly available at higher temperature, so the reaction became faster at 80°C compared to room temperature.

**Table 2:Effect of temperature <sup>a</sup>**

Temp. (K)	Conv. Wt %	<sup>b</sup> H <sub>2</sub> O <sub>2</sub> Effic.	TOF h <sup>-1</sup>	o- Cresol	p- Cresol
303	2	10	1.84	45	55
323	3	15	2.70	38	62
333	5	25	4.62	34	66
353	8.3	41.5	7.67	34	66

<sup>a</sup> Reaction conditions: Toluene: H<sub>2</sub>O<sub>2</sub> = 5: 1 (mole / mole), H<sub>2</sub>O<sub>2</sub> was added in a lot. Toluene: H<sub>2</sub>O = 5 (wt / wt), Catalyst TS-1/33 = 20 wt % with r. p. to. Toluene, Temperature = RT, 323, 333 and 353 K, Time = 8 h

<sup>b</sup> Conversion of H<sub>2</sub>O<sub>2</sub> with respect to the moles of H<sub>2</sub>O<sub>2</sub> added for the formation of oxygenated products of toluene.

**III.2.5. Effect of catalyst concentration:** Table 3 depicts the effect of catalyst concentration on hydroxylation of toluene. An increase in catalyst concentration resulted in an increase in H<sub>2</sub>O<sub>2</sub> efficiency and p-cresol selectivity up to 20-wt % catalyst concentration with respect to toluene. This is expected because increase in catalyst concentration was associated with increase in utilization of H<sub>2</sub>O<sub>2</sub>. However, at 30-wt % of the catalyst with respect to toluene, though the H<sub>2</sub>O<sub>2</sub> efficiency increased, p-cresol selectivity decreased. The active species present on the surface might play an increased contributory role with increase in optimum catalyst concentration.



**Table 3: Effect of catalyst concentration**

Conc. Wt %	Conv. wt %	<sup>b</sup> H <sub>2</sub> O <sub>2</sub> Effic.	TOF h <sup>-1</sup>	o- Cresol	p- Cresol
5	5	25	4.62	34	66
10	6	30	5.94	35	65
20	8.3	41.5	7.67	34	66
30	10	50	9.24	42	58

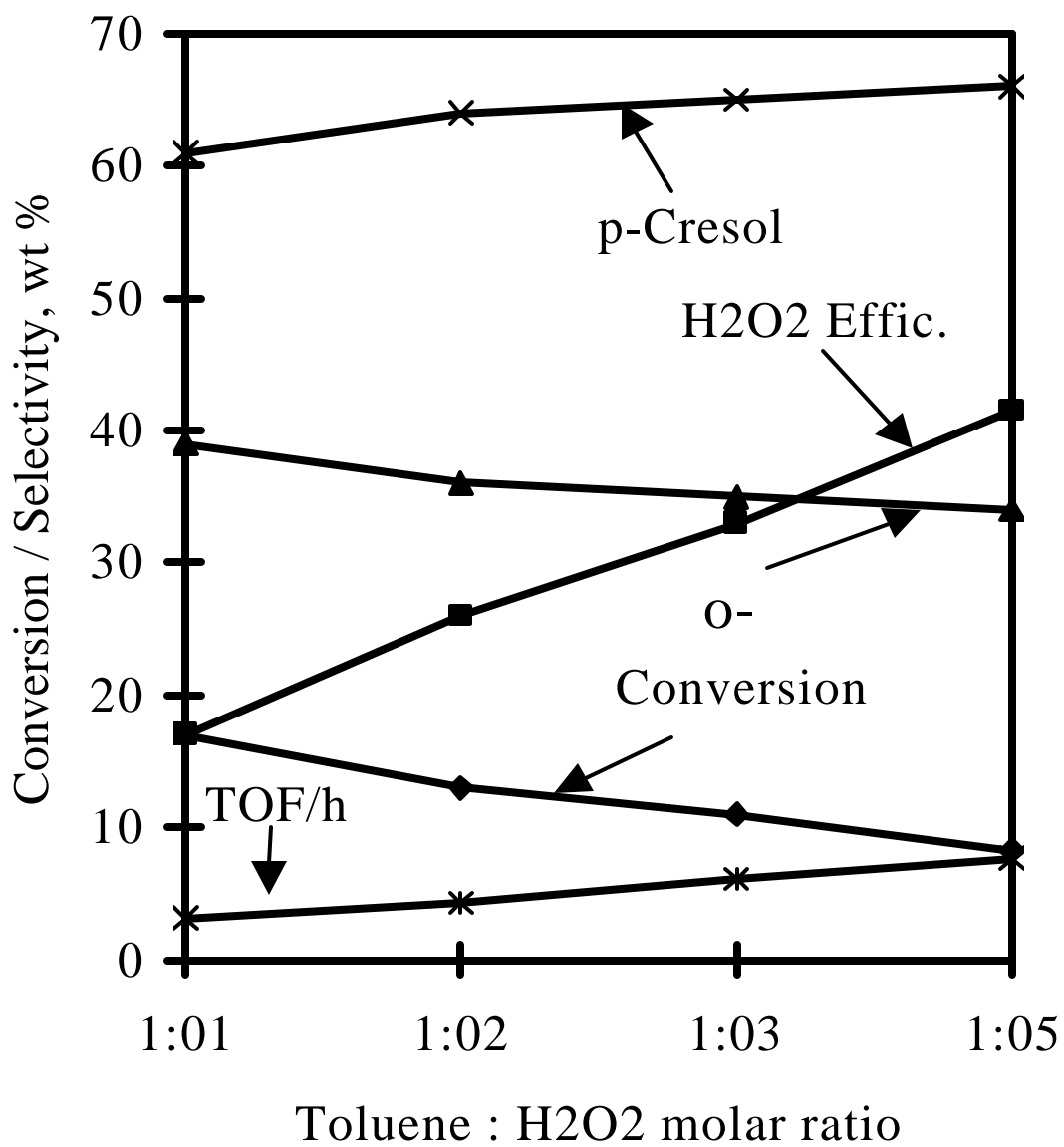
Reaction conditions are same as Table 1 except the change in catalyst concentrations.

**III.2.6. Effect of H<sub>2</sub>O<sub>2</sub> molar ratio:** Figure 3 describes the effect of toluene to H<sub>2</sub>O<sub>2</sub> molar ratio on triphase catalytic hydroxylation of toluene. With an increase in toluene to H<sub>2</sub>O<sub>2</sub> molar ratio, there was a progressive increase in H<sub>2</sub>O<sub>2</sub> efficiency as well as p-selectivity. At lower toluene to H<sub>2</sub>O<sub>2</sub> molar ratio, e.g. 1:1, surface active species might play a considerable role. While at high ratio of toluene to H<sub>2</sub>O<sub>2</sub>, active species inside the pores may be mainly contributing catalytic sites. Thus at low toluene to H<sub>2</sub>O<sub>2</sub> molar ratio, the selectivity for p-cresol was less compared to that at higher molar ratio.

**III.2.7. Effect of dilution:** Table 4 describes the effect of dilution on triphasic hydroxylation of toluene over TS-1/H<sub>2</sub>O<sub>2</sub> system. With increase in dilution, there was an increase in H<sub>2</sub>O<sub>2</sub> efficiency and p-cresol selectivity. The optimum dilution level was found to be at toluene: H<sub>2</sub>O (wt / wt) = 1:5. Beyond this value, there is no improvement either in H<sub>2</sub>O<sub>2</sub> efficiency or in p-cresol selectivity. Table 5 discusses the effect of different TS-1 catalysts (with different Ti- content) on the triphase catalytic hydroxylation of toluene under triphase. The table showed that with increasing Si / Ti ratio, there was a progressive increase in p-cresol selectivity, although, there was a

decrease in  $\text{H}_2\text{O}_2$  efficiency. This could be explained with the relatively hydrophobic hydrophobic behavior of TS-1.

Fig. 3. Effect of  $\text{H}_2\text{O}_2$  molar ratio



**Table 4: Effect of dilution**

H <sub>2</sub> O : Tol	Conv. Wt %	<sup>b</sup> H <sub>2</sub> O <sub>2</sub> Effic.	TOF h <sup>-1</sup>	o- Cresol	p- Cresol
1	3	15	2.77	44	56
3	8.5	42.5	7.85	40	60
5	8.3	41.5	7.67	34	66
10	10	50	9.24	39	61

Reaction conditions same as Table 1 except the change in the amount of water.

**Table 5: Effect of different TS-1**

Catalyst <sup>a</sup>	Conv. wt %	<sup>b</sup> H <sub>2</sub> O <sub>2</sub> Effic.	TOF h <sup>-1</sup>	o-Cresol	p- Cresol
A (33)	8.3	41.5	7.76	34	66
B (58)	3.5	17.5	5.6	27.4	72.6
C (80)	2	10	2.19	29.9	74.1

Reaction conditions are same as in Table 1, and number in the parenthesis denotes Si/Ti molar ratio.

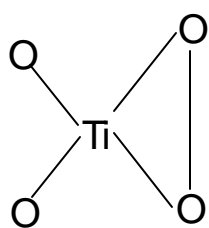
It was obvious that the relative hydrophobicity of different TS-1 species would increase with decrease in Ti- content in the catalyst. The less the amount of Ti-, the less would be the local polarization of Si-O-Ti bond and more would be the hydrophobicity. Greater the hydrophobicity, more would be the adsorption of the hydrophobic molecules inside the TS-1 channels leading to the increase in the shape selective para product. Therefore, among the three TS-1 samples, the sample C with Si / Ti = 80 was most hydrophobic, whereas sample A with Si / Ti = 33, was the least hydrophobic. As a result of this, catalyst C (80) resulted in higher p- selective product compared to both sample B

(55) and sample A (33). However, decrease in  $\text{H}_2\text{O}_2$  efficiency with increase in Si / Ti ratio was due to decrease in the number of active sites with decrease in Ti- content.

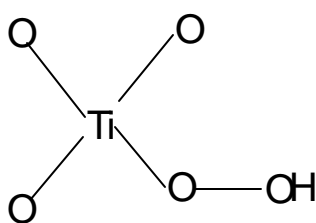
**III.2.8. Competitive reaction:** The result of competitive reactions between toluene and cyclohexane in presence of TS-1/  $\text{H}_2\text{O}_2$  system under triphase was presented in Table 6. The result showed that there was no reaction of cyclohexane in the presence of toluene under triphase. Only toluene was preferentially converted to o- and p- cresols. But the  $\text{H}_2\text{O}_2$  efficiency and p- selectivity was considerably lower in the presence of cyclohexane. The blank reaction of cyclohexane over TS-1 /  $\text{H}_2\text{O}_2$  system under triphase was not found to take place. These results might be explained by the way that both the cyclohexane and as well as toluene gets adsorbed inside the TS-1 channels. Cyclohexane did not respond to any reaction and at the same time it prevented, to some extent, the adsorption of toluene. Therefore, in the presence of cyclohexane surface reactions contributed considerably to the product distribution. This phenomenon explained the lower reactivity and lower p- selectivity in presence of cyclohexane. From this competitive experiment the possibility of radical intermediate under the triphase conditions was ruled out. Because had the radical intermediate been involved in the reaction, then it is more likely that cyclohexane should undergo oxidation and not the aromatic compound, as in the later case radical will be formed on the aromatic ring, which is energetically highly unfavorable. Therefore, the possibility of the involvement of radical intermediate may be ruled out. This was further supported when the reaction was carried out under nitrogen and under flowing nitrogen.

**III.2.9. Effect of inert atmosphere:** The purpose of carrying out the reaction under inert atmosphere is two fold, (i) to find out whether oxygen in air is taking part in the reaction

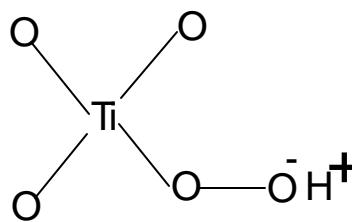
(ii) to understand the possible reactive intermediate responsible for hydroxylation under present triphase conditions. If molecular oxygen is responsible for the reaction, the nitrogen flow as well as reaction under nitrogen blanket will suppress the reaction. Further, if the titanium-peroxo species (I) is responsible for hydroxylation, then the flow of nitrogen will break the species and so will suppress the reaction. And if there is no such effect the reaction may well go through the titanium hydroperoxo species (II) rather than peroxo species. The results of the effect of inert atmosphere are tabulated in Table 7. From the table it was observed that there was no significant change (within the experimental limit) either in conversion or in selectivity. Therefore, considering the



(I)



(II)



(III)

competitive reaction between toluene and cyclohexane and the observation obtained under inert atmosphere, the titanium-peroxo species as the reaction intermediate can be ruled out. Therefore, the possible reactive species responsible for the hydroxylation of toluene under triphase could be either II or III.

**Table 6<sup>a</sup>: Competitive reaction between toluene and cyclohexane**

Substrate 1	Substrate 2	Conv. Wt %	<sup>b</sup> H <sub>2</sub> O <sub>2</sub> Effic.	o- Cresol	p- Cresol	Cy-ol	Cy-one
Toluene	Cyclohexane	3.0	15.0	45.0	55.0	nil	nil
	Cyclohexane	nil	nil	nil	nil	nil	nil
Acetone	Cyclohexane	8.5	42.5	-	-	18.0	66.0*
H <sub>2</sub> O	Cyclohexane	8.6	43.0	-	-	17.7	65.6*

<sup>a</sup> Reaction conditions: Toluene: H<sub>2</sub>O<sub>2</sub> = 5: 1, Cyclohexane: H<sub>2</sub>O<sub>2</sub> = 5: 1, Toluene: H<sub>2</sub>O = 1: 5, Cyclohexane: H<sub>2</sub>O = 1: 5, Catalyst TS-1/33 = 20 wt % with respect to toluene and cyclohexane, Temperature = 80<sup>0</sup> C, Time = 6 h

Cy-ol = cyclohexanol, Cy-one = cyclohexanone

<sup>b</sup> Conversion of H<sub>2</sub>O<sub>2</sub> with respect to the moles of H<sub>2</sub>O<sub>2</sub> added for the formation of oxygenated products of toluene.

\* Indicates 16 % & 16.3 % other product respectively.

**Table 7: Effect of inert atmosphere**

Conditions	Conv. wt %	H <sub>2</sub> O <sub>2</sub> Effic.	o- Cresol	p- Cresol	TOF h <sup>-1</sup>
Under nitrogen blanket	8.3	41.5	34.0	66.0	7.7
Under flowing nitrogen	9.0	45.0	34.0	66.0	7.8

<sup>a</sup>Reaction conditions are same as in Table 1.

Under triphase condition it was the organic substrate which was competitively adsorbed inside the TS-1 channels. But in biphasic it was the solvent, which was competitively adsorbed in preference to organic substrate. The competitive adsorption

experiments were carried out under same experimental conditions as the reactions except  $\text{H}_2\text{O}_2$  was not added. The competitively adsorbed samples were filtered, dried in air and finally dried in dessicator.

The above fact was supported by desorption experiments. In the desorption experiments of the competitively adsorbed samples 5.0 g of each of the catalyst was loaded in a tabular down flow reactor and heated at 573 K for 1 h under flushing nitrogen. The material desorbed was collected under liquid nitrogen trap and analyzed by high-resolution gas chromatography. The analysis of the desorbed materials, obtained from sample prepared in presence of solvents, gives 90 % methanol and whereas the samples prepared in presence of water gives 95 % toluene. This conclusively proved that in presence of water, i.e. in triphase, the diffusion and adsorption of toluene inside the TS-1 channels were facilitated whereas in presence of solvents, i.e., in biphasic, the diffusion and adsorption of toluene was competitively hindered by the small solvent molecules. This phenomenon had been attributed to the relatively hydrophobic character of TS-1.

**III.2.10. Effect of solvent:** Further, the effect of different solvents (Table 8) indicates the solvent behavior in the hydroxylation of toluene over TS-1 /  $\text{H}_2\text{O}_2$  system. When acetone and methanol were used as the solvent the selectivity for *o*-cresol was higher compared to that for *p*-cresol. The conversion and  $\text{H}_2\text{O}_2$  efficiency were also very low. But when *t*-BuOH was used as the solvent, though the system is biphasic in nature, *p*-cresol was the major product. This interesting result obtained with different solvents with different molecular dimension supports our view that, under biphasic condition, it is the solvent, which is the main adsorbate. When the dimension of the solvent is large (as in *t*-

butanol) compared to the channel dimension of TS-1, it is again the substrate, which is the main adsorbate. The lower H<sub>2</sub>O<sub>2</sub> efficiency observed in the case of t-BuOH may be due to the hydrophobic association between toluene and the alcohol, which might hinder the diffusion of toluene into the TS-1 channels.

**Table 8: Effect of solvent/dispersion<sup>a</sup>**

Solvent / Dispersion Medium	Conv. Wt %	H <sub>2</sub> O <sub>2</sub> Effic <sup>b</sup>	TOF h <sup>-1</sup>	o- Cresol	p- Cresol
Acetone	1.0	5.0	0.9	75.0	25.0
Methanol	2.0	10.0	1.8	61.5	28.5
t- BuOH	2.5	12.5	2.3	12.4	87.6
Water	8.3	41.5	7.6	34.0	66.0

<sup>a</sup> Reaction conditions: Toluene: H<sub>2</sub>O / solvent = 5 (wt / wt), Catalyst A = 20 wt % with r. p. to. Toluene, Temperature = RT, 323, 333 and 353 K Time = 8 h, Toluene: H<sub>2</sub>O<sub>2</sub> = 5: 1 (mole / mole), H<sub>2</sub>O<sub>2</sub> was added in one lot.

<sup>b</sup> Conversion of H<sub>2</sub>O<sub>2</sub> with respect to the moles of H<sub>2</sub>O<sub>2</sub> added for the formation of oxygenated products of toluene.

### III.2.11. Summary and conclusions:

The unique pore architecture of TS-1 along with its relatively hydrophobic nature enables organic substrates to diffuse and adsorb more easily, in presence of water, inside the three dimensional channels of TS-1, whereas, organic solvent is preferentially adsorbed inside the TS-1 channels under biphasic. Thus triphasic catalytic hydroxylation of toluene is associated with more shape selective product i.e. p- cresol is formed as major isomer, whereas, biphasic catalytic hydroxylation of toluene gives o- cresol as the

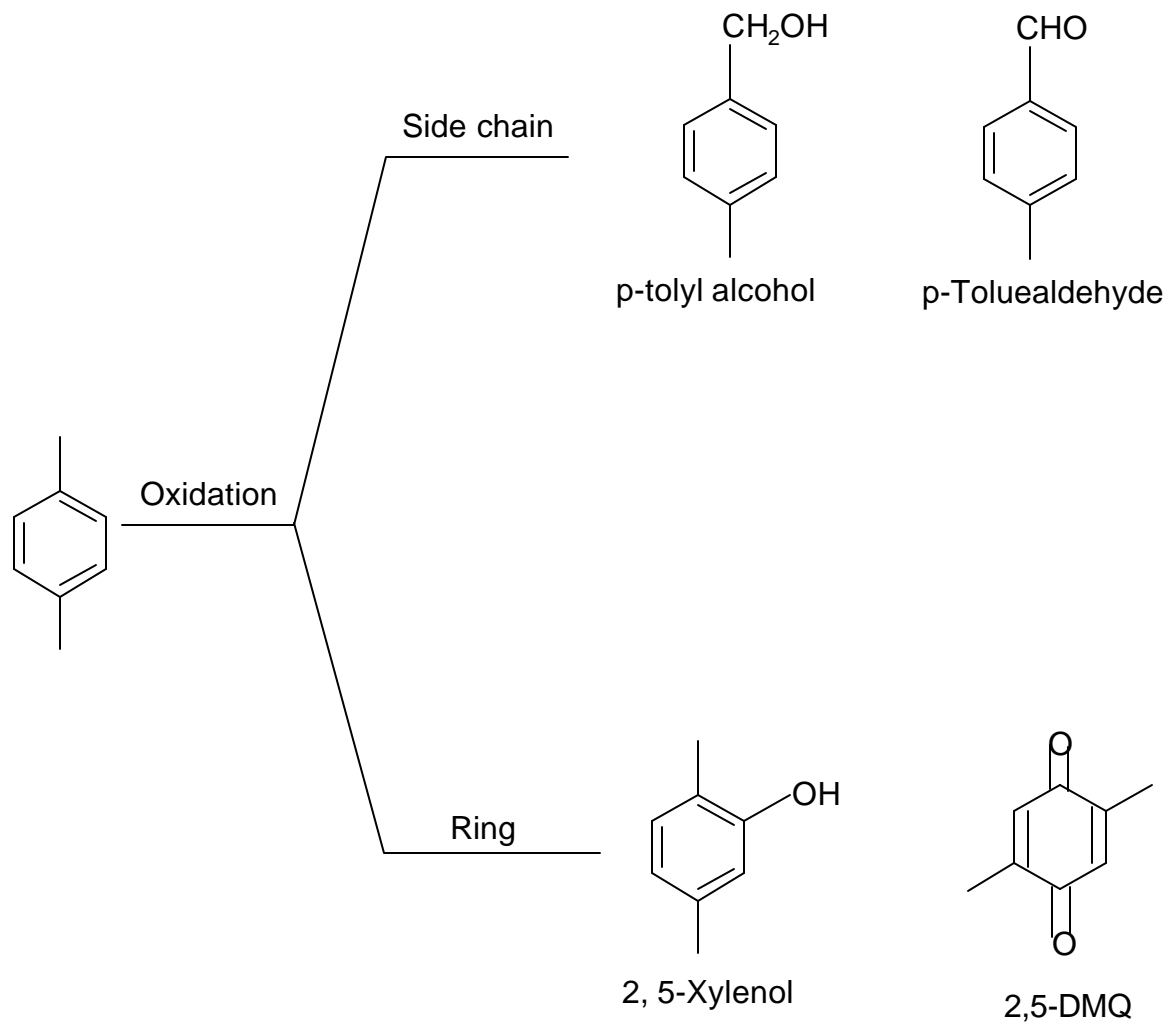


major isomer. Under triphase the reaction mainly occurs inside the TS-1 channels, whereas under biphasic the surface reaction may play a predominant role. The competitive reaction between toluene and cyclohexane rules out the possibility of radical intermediate as the hydroxylating species. The reactions under inert atmosphere support the above facts.

### III.3. Hydroxylation of p-xylene

**III.3.1. Introduction:** The selection of p-xylene as the subject of investigation has two fold importance. The one is that it is more hydrophobic than benzene and toluene and the another one is that it is bulkier than both the toluene and the benzene. The oxidation of p-xylene is found to occur at side chain in most of the cases studied earlier<sup>20-25</sup>. There is hardly any report on the oxidation of p-xylene using TS-1 as catalyst and aq. H<sub>2</sub>O<sub>2</sub> as oxidant. The scheme for p-xylene hydroxylation is shown in scheme 1. There are mainly two sites of oxidation. One is the side chain and the other is the aromatic ring. All the reactions were performed under vigorous stirring as it was observed that stirring has a marked influence on conversion as well as p-selectivity. The effect of various reaction parameters such as H<sub>2</sub>O<sub>2</sub> molar ratio, temperature, dilution effect, catalyst concentration, inert atmosphere, effect of silylation on TS-1, effect of TS-1 with different Ti content, etc. has been studied in detail.

**III.3.2 Effect of time :** When progress of the reaction is studied with time it as observed that the reaction is reasonably fast from the beginning (Table 1). This indicates that the reaction almost lacks an induction period. Thus even only at 0.5 h, H<sub>2</sub>O<sub>2</sub> efficiency of 30 % and 2,5 - xylenol selectivity of 70 % was achieved. The distribution of other products is also considerable even at the initial stage of the reaction. The conversion and selectivity almost levels off around 6 h. With increase in selectivity of 2,5 - xylenol with time, the selectivity for 2,5-DMQ also increases. The selectivity for p-tolylalcohol decreases with time and that of p-tolualdehyde increases.



**Scheme 3: p-Xylene oxidation over TS-1/ $\text{H}_2\text{O}_2$  under triphase**

**Table 1: Effect of time**

Time, h	Conv. Mole %	H <sub>2</sub> O <sub>2</sub> Effic., mole %	2,5-xylenol mole %	p-tolalc. mole %	p-tolald mole %	2,5-DMQ mole %
0.5	3	30	70	22	5	3
1	4	40	71	20	5.5	3.5
2	4.5	45	72	17.5	7	4.5
4	5.5	55	74	13	8.5	4.5
6	6	60	73.5	10	10	6.5
8	6	60	74	8	12	6

Reaction conditions: p-xylene: H<sub>2</sub>O<sub>2</sub> = 10: 1, Temperature = 90 °C, Time = 8 h, H<sub>2</sub>O: p-xylene = 3, Catalyst = 20 % with respect to p-xylene, p-tolalc = p-tolylalcohol, p-tolald = p-tolylaldehyde, 2,5 DMQ = 2,5 dimethyl quinone

**III.3.3. Effect of temperature:** Table 2 deals with the effect of temperature on the p-xylene hydroxylation. It is observed that both, the p-xylene conversion and selectivity for 2,5-xylenol increases with increase in temperature. At room temperature, the ring hydroxylation is low compared to higher temperature. The maximum conversion and 2,5 - xylenol selectivity was observed at 100 °C. No reaction was performed above 100 °C, as in that case decomposition of H<sub>2</sub>O<sub>2</sub> may be the predominant phenomenon.

**Table2: Effect of temperatrure**

Temp., °C	Conv. mole %	H <sub>2</sub> O <sub>2</sub> Effic, mole %	2,5-xylenol mole %	p-tolalc. mole %	p-tolald mole %	2,5-DMQ mole %
30	2.0	20.0	50.0	25.0	17.0	8.0
60	4.0	40.0	65.0	18.0	10.0	7.0
80	5.5	55.0	74.0	12.0	9.0	7.0
100	6.0	60.0	75.0	10.0	9.0	6.0

**III.3.4. Effect of dilution:** Table 3 deals with the effect of dilution in p-xylene hydroxylation. At lower dilution level (H<sub>2</sub>O / p-xylene = 1), both the conversion and 2,5 - xylenol selectivity were less. Probably at low dilution the contribution of non-selective surface reaction may be significant. Therefore, under low dilution level the selectivity of p-tolyl alcohol and aldehyde is more than what was obtained at higher dilution level. At H<sub>2</sub>O / p-xylene ratio 3, the conversion as well as selectivity for 2,5 xylenol were as good as in the case of ratio 5. At higher dilution level such as 10, there is no appreciable change in conversion as well as in 2, 5 - xylenol selectivity.

**Table 3: Effect of dilution**

H <sub>2</sub> O : p- Xylene	Conv. mole %	H <sub>2</sub> O <sub>2</sub> Effic, mole %	2,5-xylenol mole %	p-tolalc. mole %	p-tolald mole %	2,5-DMQ mole %
1	2.5	25	68	20	2	10
3	6.0	60	74	10	9.5	6.5
5	6.5	65	74	10.5	9	7
10	6.0	60	72	12	8	8

Reaction conditions are same as in Table 1.

**III.3.5. Effect of catalyst concentration:** Table 4 describes the effect of catalyst concentration on conversion and selectivity. Although, the selectivity for 2,5-xyleneol passes through a maximum at ca. 20 wt % catalyst concentration, the difference in the 2,5-xyleneol was not very high. The increase in conversion with increase in catalyst concentration is expected due to the increased number of active sites at higher concentration of the catalyst. However, at very high catalyst concentration, the non-selective external surface of the catalyst may be contributing significantly lowering the selectivity for 2,5-xyleneol. At low concentration of the catalyst, the amount of  $H_2O_2$  used may not be enough for optimum  $H_2O_2$  utilization.

**III.3.6. Effect of  $H_2O_2$  molar ratio:** Table 5 deals with the effect of p-xylene to  $H_2O_2$  molar ratio. The  $H_2O_2$  efficiency and 2,5-xyleneol selectivity increase with increase in p-xylene to  $H_2O_2$  molar ratio, as expected. Best utilization of  $H_2O_2$  to the oxygenated product is obtained at high value of substrate to  $H_2O_2$  molar ratio. As in this case self non-selective decomposition of  $H_2O_2$  to  $H_2O$  to  $O_2$  as well as the side reaction is minimized. Thus highest  $H_2O_2$  efficiency and 2,5-xyleneol selectivity was obtained at the ratio 10. Thus the selectivity to 2,5-xyleneol increases from 69 % at ratio 5 to 74 % at ratio 10. The formation of other reaction products such as p-tolylalcohol, aldehyde and DMQ also decreases with increase in p-xylene to  $H_2O_2$  molar ratio.

**Table 4: Effect of catalyst concentration**

Catalyst, wt %	Conv. Mole %	H <sub>2</sub> O <sub>2</sub> Effic, mole %	2,5-xylenol mole%	p-tolalc. mole%	p-tolald mole%	2,5-DMQ mole%
5.0	2.0	20.0	68.0	20.0	8.0	4.0
10.0	4.0	40.0	70.0	15.0	10.0	5.0
20.0	6.0	60.0	74.0	10.0	9.5	6.5
30.0	5.5	60.0	70.0	18.0	6.0	6.0

Reaction conditions: Same as above in Table 1

**Table 5: Effect of H<sub>2</sub>O<sub>2</sub> molar ratio**

p-Xylene: H <sub>2</sub> O <sub>2</sub>	Conv. mole %	H <sub>2</sub> O <sub>2</sub> Effic, mole %	2,5-xylenol	p-tolalc.	p-tolald	2,5-DMQ
1.0	10.0	10.0	60.0	18.0	12.0	10.0
5.0	8.0	40.0	68.0	15.0	10.0	7.0
7.5	7.0	52.5	71.0	12.5	9.5	7.0
10.0	6.0	60.0	74.0	10.5	9.0	6.5

**III.3.7. Effect of different TS-1:** The effect of different TS-1 samples was described in Table 6. As the relative hydrophobic character of TS-1 increases with increase in Si/Ti ratio of the catalyst, there is a progressive increase in 2,5 - xylenol selectivity. Thus in the sample A where Si/Ti ratio is 33 the selectivity of 2,5 xylenol is less (74 %) compared to the sample with Si/Ti ratio is 80 (79 %). The characterizations of all the samples are already described in the chapter II. However, the conversion gradually decreases with increase in Si/Ti ratio because of the presence of less number of active sites in catalyst with high Si/Ti ratio. However, in the case of samples D & E, the conversion as well as

selectivity was low. It may be due to the particle size effect. The particle size of the sample D and E is 300 -500 nm, whereas, for sample A to C they are 100 - 200 nm. So may be here the intraparticle diffusion is playing the main role in dictating the conversion and selectivity during p-xylene hydroxylation.

**Table 6: Effect of different TS-1**

Catalysts	Conv. mole %	H <sub>2</sub> O <sub>2</sub> Effic, mole %	2,5-xylenol mole %	p-tolalc. mole %	p-tolald mole %	2,5-DMQ mole %
A	6.0	60.0	74.0	10.5	9.0	6.5
B	5.0	50.0	76.0	10.0	8.5	5.5
C	4.7	47.0	79.0	8.5	7.5	5.0
D	4.0	40.0	68.0	20.0	6.0	6.0
E	4.0	40.0	69.0	21.0	6.0	5.0

Reaction condition is same as in Table 1.

**III.3.8. Effect of silylation:** The effect of silylation of TS-1 along with its physico-chemical characterization on p-xylene hydroxylation was discussed in Table 7a and Table 7b. The ratio of intensity of the band at 960 to 540 cm<sup>-1</sup> changes from 0.52 of parent sample [TS-1(p)] to 0.44 to silylated sample [TS-1(s)]. This indicates that the surface silanol as well as surface titanol group are successfully silylated. The selectivity of 2,5 -xylenol increases from 74 % in the case of parent sample to 80 % in the case of silylated sample, though conversion decreases slightly in the case of silylated sample. The increase in 2,5-xylenol selectivity after silylation may be due to the reduction of the surface active sites because of silylation, as the side chain oxidation product decreases after silylation.



**Table 7a: Effect of silylation of TS-1 (Physical Characterization)**

Sample	Si/Ti		Particle size, nm	UV-Vis Abs. Cm <sup>-1</sup>	I <sub>960</sub> / I <sub>540</sub>
	Parent	Silylated			
TS - 1(p)	33	-	100 - 200	215	0.52
TS - 1(s)		37	100 - 200	212	0.44

**Table 7b: Effect of silylation of TS-1 on conversion and selectivity**

Catalyst	Conv. mole %	H <sub>2</sub> O <sub>2</sub> Effic, mole %	2,5-xylenol mole %	p-tolalc. mole %	p-tolald mole %	2,5-DMQ mole %
TS - 1(s)	4.7	47	80	7.5	7	5

**III.3.9. Effect of inert atmosphere:** The effect of inert atmosphere discussed in Table 8. The purpose of carrying out the reaction under inert atmosphere is already discussed in previous section of this chapter (III.2). No change either in the reaction rate or in 2, 5- xylenol selectivity was observed. These results indicate that molecular oxygen formed from the decomposition of H<sub>2</sub>O<sub>2</sub> is not involved in the oxidation. Since no significant change is observed even after flowing nitrogen condition, the involvement of Ti-peroxo species as the reaction intermediate may be overruled. This indicates that p-xylene hydroxylation under present triphase conditions may not be going by radical intermediate.

**Table 8: Effect of inert atmosphere**

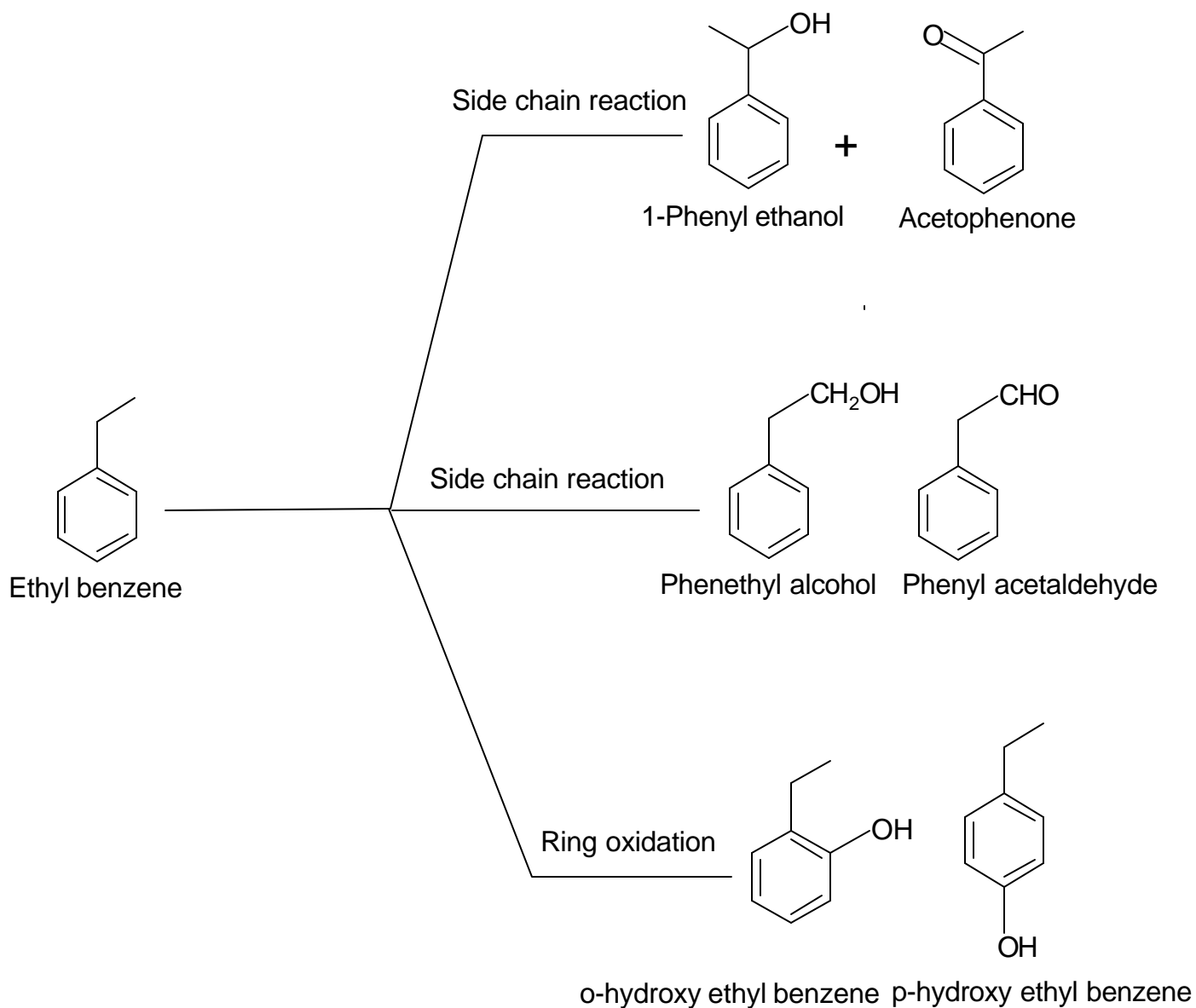
Condition	Conv. mole %	H <sub>2</sub> O <sub>2</sub> Effic, mole %	2,5-xyleneol mole %	p-tolalc. mole %	p-tolald mole %	2,5-DMQ mole %
Nitrogen blanket	6	60	74	10.5	9	6.5
Flowing nitrogen	6.5	65	74	10.5	9	6.5

**III.3.10. Conclusion:** Considerable amount of ring hydroxylation is possible under triphasic catalytic oxidation of p-xylene over TS-1/H<sub>2</sub>O<sub>2</sub> system. The oxidation takes place both on the side chain and on the ring, the ring oxidation being the major reaction. This study indicates that the activation of primary C-H bond is possible under triphase conditions. This activation of primary C-H bond may well be related to the presence of another -CH<sub>3</sub> group in the ring. Because of the +I effect of the -CH<sub>3</sub>, the ring becomes more electron rich and consequently the carbon atoms attached to the ring. The presence of excess electron density makes the primary C-H bond active for oxidation. The reactions with silylated sample clearly indicate that the surface-active species are responsible for the side chain oxidation. The reactions under inert atmosphere indicate the hydroxylation of p-xylene under triphase over TS-1/H<sub>2</sub>O<sub>2</sub> is not going through radical intermediate.

### III. 4. Hydroxylation of ethylbenzene

**III.4.1 Introduction:** Partial oxidation of alkyl aromatic compounds is an important area of research, both industrially and as well as scientifically. These aromatic compounds are obtained in abundance from petrochemical industry. The industrial point of view is to convert them to value added product. The scientific importance is to find out a process suitable for partial oxidation of these aromatic compounds to industrially more important compounds and to know the role played by the active sites. The oxidation of the alkyl aromatics in gas phase usually leads to the complete oxidation products such as acids. Sometimes even cleavage of the ring also takes place. The study of ethyl benzene is important in the sense that it has various types of oxidation sites. It has primary carbon, a secondary carbon as well as it has ring position for hydroxylation. Therefore, there will be competition for the oxidation in all of these sites. This will be an important study to follow as it may help in better understanding the catalytic sites in TS-1 and its interaction with the different reactant molecules.

So far only few reports have come on the study of ethyl benzene hydroxylation and it was found that in all the cases it is the side chain oxidation, which is the main reaction<sup>26-29</sup>. There are reports of ethyl benzene hydroxylation by cytochrome p450 cam, which exclusively hydroxylates at the secondary carbon with a 2:1 ratio of R:S alcoholic product<sup>30</sup>. Recently, transition metal species supported on chemically modified silica gel species are used for the liquid phase oxidation of alkyl aromatics under heterogeneous conditions. Thus the Cr-version of the catalyst yields acetophenone from the ethyl benzene<sup>31</sup>. The ethyl benzene hydroxylation scheme over TS – 1/H<sub>2</sub>O<sub>2</sub> system under triphasic condition is shown below.



**Scheme 4. Ethyl benzene hydroxylation under triphase over TS-1/H<sub>2</sub>O<sub>2</sub> system**

**III.4.2. Effect of solvent:** We have shown earlier that the stirring speed has a marked influence on the reaction under triphase and so all the reactions are carried out under vigorous stirring. Table 1a and 1b indicate the effect of solvent on the hydroxylation of ethyl benzene. The maximum conversion and H<sub>2</sub>O<sub>2</sub> efficiency was observed under triphase and the minimum was observed in the case of acetonitrile. However, in all the cases and even under triphase the ratio of acetophenone to 1-phenyl ethanol is almost 1:1. The side chain oxidation is maximum in the case of acetonitrile and minimum in the case of water. Table 1b compares the side chain versus ring oxidation. The side chain oxidation gradually decreases as we go down the series from acetonitrile to water where the ratio of side chain to ring oxidation product varies from 5.3 in acetonitrile to 1.06 in water (in triphase). Therefore, biphasic reaction is more susceptible to side chain oxidation than the triphasic one. It was further observed that the ratio of secondary carbon oxidation (C<sub>2</sub>) to primary carbon oxidation (C<sub>1</sub>) is almost same in the case of acetonitrile and water (triphase). However, the ratio is much more in the case of acetone. Though in all the cases the secondary carbon is preferentially oxidized compared to the primary one, acetone renders secondary carbon oxidation more facile than the primary one. No primary carbon oxidation was detected in the case of methanol. Under triphase conditions around 45 % ethyl phenol selectivity can be achieved, which is higher than the earlier report<sup>2,3</sup>. However, here considerable amount of 1-phenyl ethanol was obtained, unlike the other report where acetophenone is the main product<sup>7</sup>. We also observe that the primary carbon activation in our triphase conditions, which is in contrast with earlier report (2, 3). It may be that there is an optimum basicity of the primary carbon atom

above which primary C-H bond activation takes place. The electron push by Ph-CH<sub>2</sub>-group makes the primary carbon more electronically rich and hence it becomes vulnerable to oxidation under suitable conditions, though the selectivity is very less.

**Table 1a**  
Effect of solvent on ethyl benzene hydroxylation over TS-1/H<sub>2</sub>O<sub>2</sub> system

Solvent	Conv. mole %	H <sub>2</sub> O <sub>2</sub> Effi. mole %	A mole %	B mole %	C mole %	D mole %	o- mole %	p- mole %	Others
Acetonitrile	1.1	5.5	-	8.5	37.8	37.6	10.2	6.0	n.d
Methanol	1.7	7.5	n.d.	n.d.	30.8	30.8	7.1	12.8	18.4
Acetone	4.6	23	1.1	2.9	30.5	30.5	7.0	12.0	10.0
Water	7	35	3.9	1.0	20.5	20.5	15.9	27.5	11.7

A = Phenyl acetaldehyde, B = Phenethyl alcohol, C = Acetophenone, D = 1-Phenyl ethanol, n.d. = not detected. Reaction condition: Solvent: Ethyl benzene = 3, Ethylbenzene: H<sub>2</sub>O<sub>2</sub> = 5, Catalyst TS - 1 (Si/Ti = 33) = 20 wt % with respect to ethyl benzene, Temperature = 80<sup>0</sup>C, Time = 6 h

**Table 1b**  
Effect of solvent on ring by side chain hydroxylation

Solvents	p / o	Ring oxidation	Side chain oxidation	Side chain / Ring	C2/C1
Acetonitrile	0.55	18.3	75.3	5.3	8.8
Methanol	1.8	20.0	62.0	3.1	-
Acetone	1.7	18.9	61.0	1.8	15.2
Water	1.7	43.4	46.0	1.1	8.3

When the progress of the reaction was monitored with time it is observed that the reaction is reasonably fast from the beginning (Table 2a). The formation of side chain oxidation product is also very at the initial stage of the reaction (ca. 57 %). However, with progress of time the ring oxidation product increases and the side chain oxidation product decreases. At 6 h of the reaction the ratio of side chain oxidation product to ring oxidation product is almost 1:1 though side chain oxidation product dominates preferentially. Another interesting feature is that the ratio of acetophenone to 1-phenyl ethanol is 1:1 even at the start of the reaction and the ratio remains the same through out the whole time interval although the amount of both the products gradually decreases with time.

**Table. 2a**  
**Progress of ethyl benzene hydroxylation with time under triphase over TS-1/ H<sub>2</sub>O<sub>2</sub> system**

Time, h	Conv., mole %	H <sub>2</sub> O <sub>2</sub> Effi. mole %	A mole %	B mole %	C mole %	D mole %	o- mole%	p- mole%	Others
0.5	2.0	10	2.9	n.d.	22.2	22.2	9.5	34.6	8.6
1	2.2	11	3.17	n.d.	22.0	22.0	10.1	33.7	8.9
1.5	2.7	13.5	3.49	n.d.	21.7	21.7	11.2	32.6	9.2
2	3.1	15.5	3.65	n.d.	21.5	21.5	12.0	31.9	9.4
3	3.7	18.5	3.8	n.d.	21.9	21.2	13.0	30.9	9.8
4	4.7	23.5	4.1	0.5	20.8	20.8	13.8	30.0	9.9
5	5.4	27	4.2	0.5	20.7	20.7	14.4	29.4	10.1
6	7	35	3.9	1.0	20.5	20.5	15.9	27.5	11.7
7	7.1	35.5	3.8	1.1	20.4	20.4	16.0	28.6	11.7

A, B, C & D are same as in Table 1. Reaction conditions are same as in table 1.

**III.4.3. Effect of time:** From the table 2b it is seen that the ratio of side chain to ring oxidation gradually decreases with time. At the same time the p- / o- isomeric ratio also decreases with time. However, the over all oxidation to ring gradually increases with time. It is also observed that the formation of primary carbon oxidation product is present from the very beginning of the reaction though the phenethylalchol is detected only after 4 h of reaction. It is likely that as soon as it is formed it is immediately converted to phenyl acetaldehyde because of the presence of relatively larger amount of oxidant (aq. H<sub>2</sub>O<sub>2</sub>) in the initial stage of reaction. In this case there is a mutual competition whether the oxidation will take place in the ring or in the side chain. It may be that because of the relatively larger size of the ethyl benzene, it faces diffusional hindrance to enter the pores of TS-1. Therefore, the reaction is predominantly dominated by surface reactive species. However, between the ring oxidation product, the p- isomer always predominates although the p- / o- ratio decreases with time.

**Table 2b**  
**The effect of time on side chain oxidation to ring oxidation during ethyl benzene hydroxylation over TS - 1 / H<sub>2</sub>O<sub>2</sub> under triphase**

Time, h	p/o	side chain / ring	C2 / C1
0.5	3.7	1.07	15.3
1	3.3	1.07	13.9
1.5	2.9	1.07	12.4
2	2.7	1.06	11.8
3	2.4	1.06	11.2
4	2.2	1.05	9.1
5	2.0	1.05	8.8
6	1.7	1.05	8.2



**III.4.4. Effect of temperature:** The effect of temperature was shown in Table 3. It is seen that from room temperature to up to 80 °C, there is gradual decrease in side chain oxidation and an increase in ring oxidation product. Beyond 80 °C, the side chain oxidation again increases. The primary carbon activation was not observed at room temperature. It may be that such low temperature may not favor the energetics for the primary carbon activation. The formation of ring oxidation product increases with increase in temperature from RT to 80 °C. High temperature (110 °C) favors the side chain oxidation product.

**Table 3: Effect of temperature**

Temp . °C	Conv. mole %	H <sub>2</sub> O <sub>2</sub> Effi. mole %	A mole %	B mole %	C mole %	D mole %	o- mole %	p- mole %	Others
30	1.7	8.5	n.d	n.d	29.5	29.4	5.9	29.7	4.6
50	5.0	25.0	3.0	2.0	26.5	26.5	10.0	24.0	8.0
80	7.0	35.0	3.9	1.0	20.5	20.5	15.7	27.5	10.7
110	4.5	22.5	-	11.2	27.5	27.4	5.4	23.3	4.9

**III.4.5. Effect of H<sub>2</sub>O<sub>2</sub> molar ratio:** Figure 3a & 3b deal with the effect of H<sub>2</sub>O<sub>2</sub> molar ratio on the triphasic hydroxylation of ethyl benzene on TS - 1 catalyst. The conversion gradually decreases but H<sub>2</sub>O<sub>2</sub> efficiency gradually increases with increase in ethyl benzene to H<sub>2</sub>O<sub>2</sub> molar ratio. Thus minimum efficiency was observed at minimum ratio, i.e, 1 and maximum was observed at maximum ratio, i.e. 10. The side chain oxidation is maximum at higher concentration of H<sub>2</sub>O<sub>2</sub> where it gradually decreases with decrease in

the amount of H<sub>2</sub>O<sub>2</sub>. The formation of others also decreases with decrease in the amount of H<sub>2</sub>O<sub>2</sub>. The Table 3b shows that the ratio of p-/o- gradually increases with increase in the ratio. Again at the ratio 10, the ring oxidation exceeds the side chain oxidation.

**Table 3a: Effect of H<sub>2</sub>O<sub>2</sub> molar ratio**

Etb:H <sub>2</sub> O <sub>2</sub>	Conv. mole %	H <sub>2</sub> O <sub>2</sub> Effi. mole %	A mole %	B mole %	C mole %	D mole %	o- mole %	p- mole %	Others
1	10.0	10.0	3.6	4.6	26.6	26.0	9.0	15.2	15.3
5	7.0	35.0	3.9	1.0	20.5	20.5	15.8	27.5	10.7
10	4.0	40.0	1.9	7.0	18.7	18.7	13.7	34.0	6.0

**Table 3b**

**Effect of H<sub>2</sub>O<sub>2</sub> molar ratio on ring Vs side chain hydroxylation**

Etb:H <sub>2</sub> O <sub>2</sub>	p-/o-	Ring oxidation	Side chain oxidation	Side chain / Ring	C <sub>2</sub> / C <sub>1</sub>
1.0	1.7	24.2	56.2	2.3	6.4
5.0	1.7	43.3	45.9	1.7	8.2
10.0	2.5	47.7	46.3	1.0	4.2

**III.4.6. Effect of catalyst concentration:** The effect of catalyst concentration was discussed in Table 4a and Table 4b. The conversion as well as H<sub>2</sub>O<sub>2</sub> efficiency gradually

increases with increase in catalyst concentration up to 20 %, but there is a drop by further increasing the catalyst concentration. Similar observations were also observed in the side chain oxidation. It gradually decreases up to 20 % and then there is again an increase. There is also increase in the formation of o- and p- hydroxy ethyl benzene as well as increase in the formation of side products (Table 4a).

Table 4b shows that with increase in the concentration of the catalyst there is a net increase in the formation of ring oxidation product, but however, above 30 % the side chain oxidation products again increases. Though with increase in catalyst concentration the formation of ring oxidation products increases, however, the p- to o- isomeric ratio decreases. This indicates that at higher catalyst concentration the rate of formation of the o- isomer is more than that of p- isomer in the case of ethyl benzene hydroxylation. The oxidation of primary carbon is also maximum when the catalyst amount is more.

**Table 4a**  
**Effect of catalyst concentration on ethyl benzene hydroxylation**

Catalyst Conc. %	Conv., mole %	H <sub>2</sub> O <sub>2</sub> Effi. mole %	A mole %	B mole %	C mole %	D mole %	o-	p-	Others
5.0	1.0	5.1	nd	5.0	27.7	27.6	7.8	25.7	6.5
10.0	4.7	23.5	1.2	2.5	24.6	24.4	11.0	26.4	9.8
20.0	7.0	35	3.9	1.0	20.5	20.5	15.9	27.5	11.7
30.0	5.6	28	2.9	10.6	26.2	26.2	8.1	19.7	6.2

**Table 4b**  
**Effect of catalyst concentration on side chain vs. ring oxidation**

Catalyst conc. Wt %	Total ring oxidation	Total side chain oxidation	p-/o-	Side chain / Ring	C <sub>2</sub> / C <sub>1</sub>
5	33.5	60.3	3.3	1.8	-
10	37.4	52.8	2.4	1.4	13.0
20	43.4	45.9	1.73	1.0	8.3
30	27.8	65.9	2.42	2.4	3.9

**III.4.7. Effect of dilution:** The effect of dilution on ethyl benzene hydroxylation is depicted in Table 5a and 5b. The maximum conversion as well as H<sub>2</sub>O<sub>2</sub> efficiency was obtained at dilution level 3, i.e. when the dispersion medium is 3 times more than the ethyl benzene. The maximum ring oxidation product is also obtained at this optimum dilution level. However, there is a change in the o- and p- selectivity with dilution. Although the amount of o- and p- product is less in lowest and highest dilution but the relative abundance of the p- isomer is more at minimum and maximum dilution level which is observed from the p- / o- ratio in different dilution level. The side chain oxidation is maximum at minimum dilution level (water: Etb = 1) and intermediate value was obtained at higher dilution level and it is minimum when the dilution level is 3 (water: Etb = 3). It is further observed that the formation of secondary carbon oxidation products gradually decreases with increase in dilution (Table 5b). The ratio of C<sub>2</sub> to C<sub>1</sub>

gradually decreases with increase in dilution level. Thus  $C_2 / C_1$  is maximum at  $H_2O / Etb = 1$  and minimum at  $H_2O / Etb = 10$ .

**Table 5a: Effect of dilution**

$H_2O :$ Etb	Conv. mole %	$H_2O_2$ Effi. mole %	A mole %	B mole %	C mole %	D mole %	o- mole%	p- mole%	Others
1.0	3.5	17.5	1.3	6.2	30.6	30.7	3.9	22.2	4.5
3.0	7.0	35.0	3.9	1.0	20.5	20.5	15.9	27.5	11.7
7.0	6.0	30.0	3.0	4.0	22.0	22.0	12.0	26.0	11.0
10.0	5.5	27.5	2.5	6.4	24.3	24.3	8.8	25.3	8.3

**Table 5b: Effect of dilution on side chain Vs ring oxidation**

$H_2O : Etb$	Total ring oxidation	Total side chain oxidation	p-/o-	Side chain / Ring	$C_2 / C_1$
1.0	26.1	68.8	5.7	2.6	17.5
3.0	43.4	45.9	1.7	1.0	8.3
7.0	28.0	51.0	1.3	1.8	6.3
10	34.1	57.5	3.3	1.8	5.4

**III.4.8. The effect of different TS-1:** The effect of catalysts containing different Ti- content is discussed in Table 6a and Table 6b. Three different catalysts, A (Si/Ti = 33), B (Si / Ti = 58) and C (Si / Ti = 80) was selected for catalysis. It was observed that conversion as well as  $H_2O_2$  efficiency decreases with decrease with Ti- content of the catalyst. But however, the ring oxidation increases with decrease in Ti - content. The ratio of acetophenone to 1-phenyl ethanol ratio remains the same in all the cases (nearly equals to 1). The side chain oxidation gradually decreases with decrease in Ti-content of the catalyst. The side reactions are also minimized with decrease in Ti-content of the catalyst. The p-selectivity of the product gradually increases with increase in Si/Ti ratio.

Therefore, with more hydrophobic catalyst higher p-selectivity was observed. This is clearly shown in Table 6b. The p/o ratio increases from 1.73 to 2.33 with increase in Si/Ti ratio from 33 to 80 respectively. The secondary carbon oxidation increases with increase in Ti-content of the catalyst. Thus the C<sub>2</sub> / C<sub>1</sub> ratio increases from 8.29 to 9.6 with increase in Si/Ti ratio from 33 to 80 respectively. The relative hydrophobicity increases with increase in Si/Ti ratio. Therefore, at high Si/Ti ratio, higher p-selective product was obtained.

**Table 6a: Effect of different TS-1**

Different TS - 1	Conv. mole %	H <sub>2</sub> O <sub>2</sub> Effi. mole %	A mole %	B mole %	C mole %	D mole %	o- mole %	p- mole %	Others
A (33)	7.0	35.0	3.9	1.0	20.5	20.5	16.0	27.5	10.7
B (58)	5.0	25.0	3.1	1.3	20.3	20.3	15.0	30.0	10.0
C (80)	3.0	15.0	2.5	1.7	20.2	20.2	14.2	33.2	8.0

A = Phenyl acetaldehyde, B = Phenethyl alcohol, C = Acetophenone, D = 1-Phenyl ethanol. Reaction conditions: water: Ethylbenzene = 3, Ethylbenzene: H<sub>2</sub>O<sub>2</sub> = 5, Catalyst TS - 1 = 20 wt % (A = Si/Ti = 33, B = Si/Ti = 58, C = Si/Ti = 80) with respect to ethylbenzene, Temperature = 80<sup>0</sup>C, Time = 6 h.

**Table 6b**  
**Effect of titanium content on side chain vs. ring oxidation of the ethyl benzene**

Different TS - 1	Ring oxidation	Side chain oxidation	p- / o-	Side chain / Ring	C2/C1
A (33)	43.4	48.94	1.73	1.05	8.29
B (58)	45	47.0	2	1	9.2
C (80)	47.5	44.7	2.33	0.92	9.6

The effect of inert atmosphere is described in Table 7. It is observed that there is no significant change either in product distribution or in H<sub>2</sub>O<sub>2</sub> efficiency when the reaction was performed either in nitrogen blanket or under flowing nitrogen. No change either in conversion or selectivity under nitrogen blanket rules out the possibility molecular oxygen as the reactive species in the reaction. Since no change is observed even in under nitrogen flow, it indicates that the reaction is not going through Ti-peroxo intermediate, as the flow of nitrogen will break the intermediate, if formed, and a decrease in conversion should be observed. Since no such change was observed it can be said the triphasic hydroxylation of ethyl benzene over TS-1/H<sub>2</sub>O<sub>2</sub> system is not going through Ti-peroxo intermediate and hence not through radical mechanism.

**Table 7: Effect of inert atmosphere**

Inert atmosphere	Conv., mole %	H <sub>2</sub> O <sub>2</sub> Effi. mole %	A mole %	B mole %	C mole %	D mole %	o-	p-	Others
Static nitrogen	7	35	3.9	1.04	20.5	20.5	15.8	27.5	10.7
Flowing nitrogen	7.5	37.5	3.8	1.1	20.0	20.0	16	28.5	10.5

A, B, C & D are same as in Table 1. The reaction conditions are also same as in table 1.

### III.4.9. Conclusion:

The triphasic catalytic hydroxylation of ethyl benzene over TS-1/H<sub>2</sub>O<sub>2</sub> system was carried out in triphase and compared with bipasic system under the similar condition. The reaction is mainly governed by the surface reaction. Maximum ring oxidation, selectivity up to 50 %, can also be achieved by selecting the reaction conditions. The

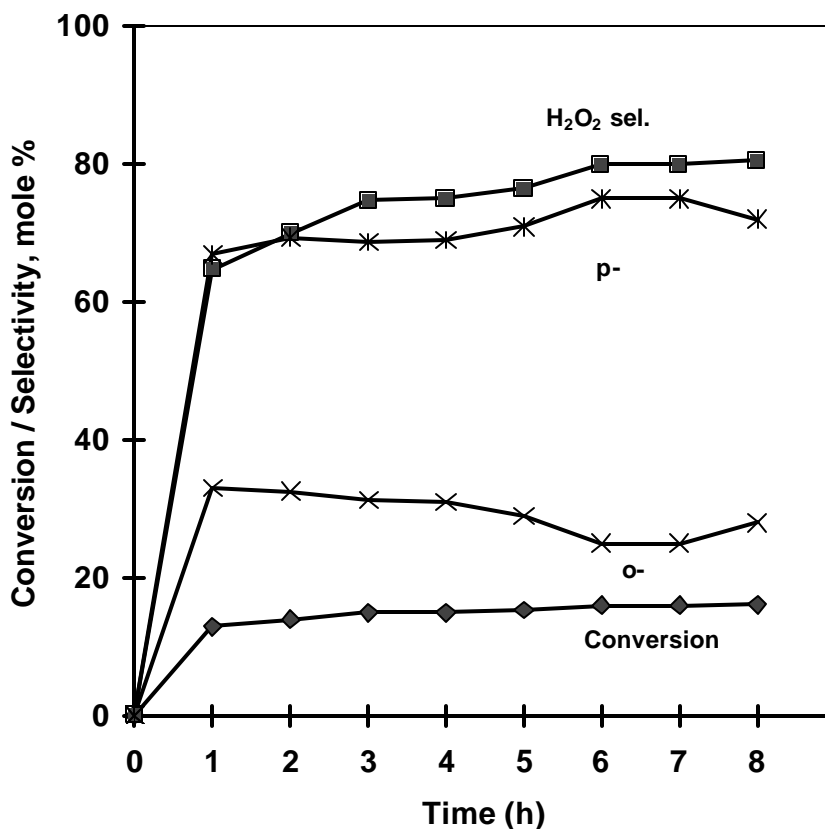
reactions under inert atmosphere indicate that the reaction is not going through radical intermediate. However, unlike the other report, oxidation of primary carbon atom takes place in the triphase conditions. This indicates that the presence of water in the system as dispersion medium provides a path for the reaction to occur which is energetically favorable in presence of suitable group attached to primary carbon atom.





Hydroxy anisoles, both ortho and para- isomers, are quite useful and value added product. Only few reports are there on direct hydroxylation of anisole to its o- and p-hydroxy isomer<sup>32</sup>. The competitive adsorption experiment experiments were carried out to find out the adsorptive behavior of substrate with respect to organic solvent (biphase) or water (in triphase). Competitive reactions and reactions under inert atmosphere were carried out to find out the most probable reactive species responsible in the triphasic hydroxylation of anisole. It may be recalled that (section III.1) that during benzene hydroxylation it is already shown that the stirring rate has

FIG. 1. Effect of time



significant influence on the reactions. It was found that the conversion increases with stirring speed up to 400 rpm, beyond that and up to 1000 rpm there was no further increase in the conversion. Similar observation was found in the case of anisole hydroxylation. Hence, the reaction was carried out under vigorous stirring at ca. 1000 rpm.

**III.5.2. Effect of time:** When the progress of the reaction was followed with time during the hydroxylation of anisole under triphase over TS-1 / H<sub>2</sub>O<sub>2</sub> system (Fig. 1) it was observed that the reaction is reasonably fast from the very beginning which is reflected on the H<sub>2</sub>O<sub>2</sub> efficiency. Both, the H<sub>2</sub>O<sub>2</sub> efficiency and the p- selectivity of products gradually increase with time and almost level off after 7 h. Further, with the progress of the time the selectivity for the p-isomer increases slightly with the corresponding decrease in the selectivity for the o-isomer. It may be due to the reason that the number of surface active species is much less compared to the active sites inside the pores, so with reaction time the rate of reactions inside the pores increases whereas the surface reaction remains the same.

**III.5.3. Effect of solvent:** The effect of different solvents (Table 1) indicates the solvent behavior in the hydroxylation of toluene over TS-1 / H<sub>2</sub>O<sub>2</sub> system. When acetone and methanol were used as the solvent the selectivity for o-hydroxy anisole was higher compared to that for p-isomer. The conversion and H<sub>2</sub>O<sub>2</sub> efficiency were also very low. But when t-BuOH was used as the solvent, though the system is biphasic in nature, p-hydroxy anisole was the major product. This interesting result obtained with different solvents with different molecular dimension supports our view that, under biphasic condition, it is the solvent, which is the main adsorbate. When the size of the solvent molecule increases, its diffusion inside the catalyst channel is limited and as a result the adsorption of the reactant becomes the predominant diffusion phenomenon inside the TS-1

catalyst. The lower H<sub>2</sub>O<sub>2</sub> efficiency observed in the case of t-BuOH may be due to the like-like interaction between anisole and the alcohol, which might hinder the diffusion of anisole into the TS-1 channels. All further experiments were carried out in solvent free triphase conditions using TS-1 as catalyst and dilute H<sub>2</sub>O<sub>2</sub> as oxidant.

**III.5.4. Effect of temperature:** Table 2 deals with the effect of temperature on conversion and selectivity in the formation of hydroxy anisols. At room temperature, both the H<sub>2</sub>O<sub>2</sub> efficiency and p-hydroxy anisole selectivity were low. The selectivity for p isomer and H<sub>2</sub>O<sub>2</sub> efficiency increased with increase in temperature. At 80°C, maximum H<sub>2</sub>O<sub>2</sub> efficiency and p-hydroxy anisole selectivity were obtained, as expected. As the activation energy for a reaction was increasingly available at higher temperature, so the reaction became faster at 80°C compared to room temperature.

**TABLE 1: Effect of solvents / dispersion medium**

Solvent/Dispersion medium	Conversion, mole %	H <sub>2</sub> O <sub>2</sub> Effic. mole %	o- Hydroxy-anisole	p- Hydroxy-anisole
Water	16.0	80.0	25.0	75.0
Methanol	9.1	45.7	60.0	40.0
Acetonitrile	7.6	37.8	53.0	47.0
t- Butanol	3.0	15.0	24.0	76.0

a Reaction conditions: Anisole : Solvent/dispersion medium = 5:1, Catalyst (TS-1/33) = 20 wt % with respect to Anisole, Temperature = 80°C, Time = 6 hr. H<sub>2</sub>O<sub>2</sub> was added in a lot under vigorous stirring.

b Conversion is based on the number of moles of H<sub>2</sub>O<sub>2</sub> taken with respect to toluene

c H<sub>2</sub>O<sub>2</sub> efficiency is defined as the number of moles of H<sub>2</sub>O<sub>2</sub> utilized for the formation of oxygenated anisole products.

**TABLE 2: Effect of reaction temperature**

Temperature, °C	Conversion, mole %	H <sub>2</sub> O <sub>2</sub> Effic. mole %	o- Hydroxy-anisole	p- Hydroxy-anisole
30.0	8.0	40.0	45.0	55.0
40.0	11.3	56.5	34.8	65.2
60.0	13.3	66.5	32.0	68.0
80.0	16.0	80.0	25.0	75.0

Reaction conditions are same as Table 1.

**III.5.5. Effect of catalyst concentration:** Table 3 deals with the effect of catalyst concentration. It is observed that maximum H<sub>2</sub>O<sub>2</sub> efficiency is obtained when the catalyst concentration is 20 wt. % with respect to the substrate. This may be due to the fact that with increase in the concentration of the catalyst, the number of active titanium species involved in the reaction increases and hence the reaction rate. The p- selectivity of the product also increases on increasing the catalyst concentration from 5 wt. % to 20 wt. %. It may well be that, the amount of H<sub>2</sub>O<sub>2</sub> remaining the same, the probability of utilization of H<sub>2</sub>O<sub>2</sub> for the formation of product is also quite high at 20 % and low at 5 %. It may also be that at 5 % catalyst concentration, as the number of active titanium species is less, the self decomposition of H<sub>2</sub>O<sub>2</sub> is much more pronounced than when the concentration is 20 %. Above 20 wt % of the catalyst concentration, the surface reaction may play a contributory role resulting in little decrease in p- selectivity.

**III.5.6. Effect of H<sub>2</sub>O<sub>2</sub> molar ratio:** Table 4 depicts the effect of anisole : H<sub>2</sub>O<sub>2</sub> molar ratio. With an increase in the anisole : H<sub>2</sub>O<sub>2</sub> ratio from 1 to 5, there is a gradual decrease in H<sub>2</sub>O<sub>2</sub> efficiency. This is in line with the earlier reports. The H<sub>2</sub>O<sub>2</sub> efficiency is high at ratio 5 and minimum at ratio 1. This is because the side reactions as well as self decomposition of H<sub>2</sub>O<sub>2</sub> are minimized at

higher anisole : H<sub>2</sub>O<sub>2</sub> molar ratio. Another prominent feature is that the selectivity for the p - isomer also increases with increase in the anisole : H<sub>2</sub>O<sub>2</sub> molar ratio. It could well be that at low anisole : H<sub>2</sub>O<sub>2</sub> molar ratio (presence of relatively larger amount of H<sub>2</sub>O<sub>2</sub>), the discrimination between the surface active species and the active species inside the pore is relatively blurred. As under triphasic conditions, the reaction inside the pores is supposed to be the predominant reactions, therefore, with increase in the anisole : H<sub>2</sub>O<sub>2</sub> molar ratio p- selectivity increases.

**TABLE 3: Effect of catalyst concentration**

Catalyst Conc. Wt %	<sup>b</sup> Conversion, mole %	<sup>c</sup> H <sub>2</sub> O <sub>2</sub> Effic. mole %	o- Hydroxy- anisole	p- Hydroxy- anisole
0.0	0.0	0.0	0.0	0.0
5.0	9.0	45.0	40.0	60.0
10.0	11.0	55.0	34.0	66.0
15.0	14.0	70.0	30.0	70.0
20.0	16.0	80.0	25.0	75.0
30.0	13.0	65.0	28.0	72.0

<sup>a</sup> Reaction conditions same as Table 1 except the change in catalyst concentration and using only water as the dispersion medium.

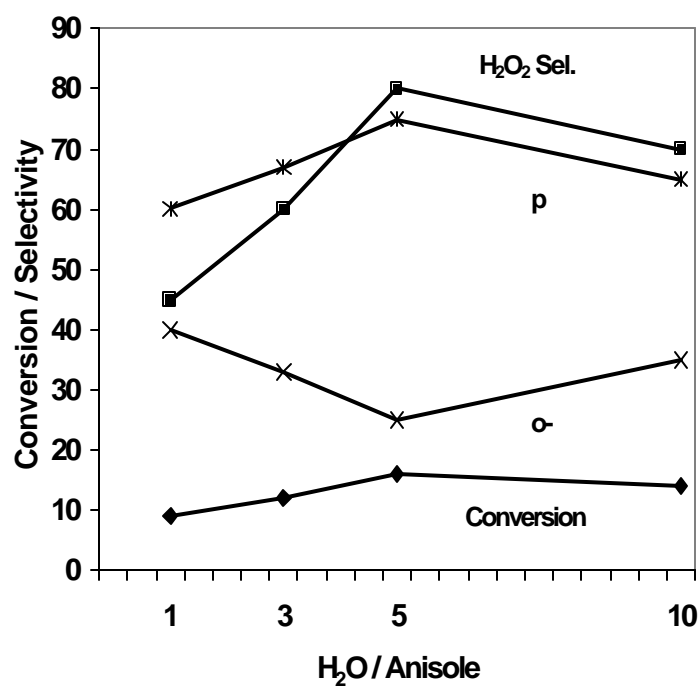
**TABLE 4: Effect of anisole to H<sub>2</sub>O<sub>2</sub> molar ratio**

Anisole/H <sub>2</sub> O <sub>2</sub> m olar ratio	Conversion <sup>b</sup> , mole %	H <sub>2</sub> O <sub>2</sub> Effic <sup>c</sup> . mole %	o- hydroxy- anisole	p- hydroxy- anisole
1.0	60.0	60.0	35.0	65.0
3.0	23.0	69.0	32.0	68.0
5.0	16.0	80.0	25.0	75.0

Reaction conditions are same as in Table 1 except the change in H<sub>2</sub>O<sub>2</sub> molar ratio

**III.5.7. Effect of dilution:** Fig. 2 depicts the effect of the dilution on the hydroxylation of anisole under solvent-free triphase conditions over TS-1/  $\text{H}_2\text{O}_2$  system. The optimum condition is reached when the  $\text{H}_2\text{O}$  : anisole (wt / wt) ratio is 5. This is reflected on both the  $\text{H}_2\text{O}_2$  efficiency and TOF  $\text{h}^{-1}$ . Since TS - 1 is relatively hydrophobic in nature, it may be that at this particular ratio of  $\text{H}_2\text{O}$  : anisole (wt / wt), the transport of the organic mass to the catalyst surface is facilitated through micro-droplet formation. Beyond this value there is no further improvement of the reaction.

**FIG 2. Effect of dilution**



**III.5.8. Effect of different TS-1 samples with different Ti-content:** Table 5 exhibits the effect of different TS-1 catalysts with different Ti- content. It is obvious that an increase in Ti - content will decrease the hydrophobicity as in those case the local polarization of the bonds is much more than those catalysts where the Ti- content is less. Thus the hydrophobicity order of different TS-1 samples is expected to be A (33) < B (58) < C (80). The table shows that with decrease in Ti -content there is a progressive decrease in conversion but there is gradual increase in p-selectivity. The more the hydrophobic a catalyst is, higher is the probability of reaction taking place inside the pores, in the presence of water. So, with decrease in Ti - content, although, there is progressive decrease in conversion but there is gradual increase in p-selectivity. This is further supported by competitive adsorption experiment followed by desorption. In the desorption experiments, 5 gm of catalyst was loaded in a tabular down flow reactor and flashed with dry nitrogen (by gradually increasing the temperature from 40<sup>o</sup> C to 350<sup>o</sup> C at heating rate of 10<sup>o</sup> min<sup>-1</sup>). The desorbed material was collected in a liquid nitrogen trap and analyzed by G.C. The TS-1/acetonitrile/anisole (sample C) and TS-1/H<sub>2</sub>O/anisole (sample A) systems used for the experiments confirmed that acetonitrile was mostly ( 90%) desorbed from the former, while anisole was desorbed from the latter. Since TS-1 is relatively hydrophobic in nature, thus in presence of water, anisole competes favorably with water for diffusion into the TS-1 channels, while in the presence of acetonitrile, acetonitrile competes favorably than anisole for diffusion into the TS-1 channels. Thus it can be said that under triphase conditions the reactions inside the pores are predominant reaction, whereas in biphasic surface reaction plays the significant role.



**III.5.9. Competitive reaction:** An important observation was made when the competitive reaction was carried out between cyclohexane and anisole both in biphase and triphase. Table 6 depicts the competitive reaction between anisole and cyclohexane. The result shows that under triphase it is the anisole which is preferentially oxidized in presence of cyclohexane. The reaction of cyclohexane under triphase is very poor (5 % efficiency). But when acetone is used as the solvent, considerable reaction was observed. When the competitive reaction was carried out in biphase, both the anisole and cyclohexane was oxidized, although the reaction is poor (35 % H<sub>2</sub>O<sub>2</sub> efficiency).

**TABLE 5: Effect of Different catalyst**

Catalyst	<sup>b</sup> Conversion, mole %	<sup>c</sup> H <sub>2</sub> O <sub>2</sub> Effic. mole %	o- Hydroxy-anisole	p- Hydroxy-anisole
A	16	80	25	75
B	12	60	23	77
C	10	50	20	80

Reaction condition is same as in Table 1

**III.5.10. Effect of inert atmosphere:** The triphasic hydroxylation of anisole with TS-1/H<sub>2</sub>O<sub>2</sub> was also carried under inert atmosphere (both in static nitrogen and under nitrogen blanket). The effect of inert atmosphere is depicted in table 8 . The table shows that the inert atmosphere leads to no significant change either in conversion or in selectivity. The preferential reaction of anisole in presence of cyclohexane and the reactions under inert atmosphere indicates that hydroxylation of anisole under present triphase condition is, at least, not going through the radical intermediate and the reactive species could be either (II) or (III) (shown in section III.2).

**TABLE 6: Competitive reaction between anisole and cyclohexane**

Subs. 1	Subs. 2	Conv. mole %	H <sub>2</sub> O <sub>2</sub> Effic. mole %	2-OH-anisole	4-OH-anisole	Cy-ol	Cy-one	Others
Anisole	Cyclo-hexane	12	60	30	70	-	-	-
	Cyclo-hexane	-	-	-	-	-	-	-
	Cyclo-hexane <sup>d</sup>	8.6	43	-	-	17.75	65.6	16.63

<sup>a</sup> Reaction conditions: Anisole : H<sub>2</sub>O =1:5, Cyclohexane : H<sub>2</sub>O =1:5 Catalyst A = 20 wt % with respect to both anisole and cyclohexane, Temperature = 80<sup>o</sup>C, Time = 6 h. H<sub>2</sub>O<sub>2</sub> was added in a lot under vigorous stirring.

b, c, d are same as in Table 1

**III.5.11. Summary and conclusions:** In summary it can be stated that solvent-free triphase catalytic oxidation of substituted benzenes like anisole over TS-1/H<sub>2</sub>O<sub>2</sub> systems leads to an enhancement in the reaction rate as well as p- selectivity. Since titanium- silicate molecular sieve is relatively hydrophobic in nature, reactants competes favorably than water for diffusion inside the zeolite channels under triphase and thereby resulting in greater conversion and better shape selectivity. Apart from these, the present triphase method offers distinct advantage in easier product separation and development of an eco-friendly process. The competitive reactions between cyclohexane and anisole, both under biphasic and triphase, and also the reactions under inert atmosphere suggests the ionic mechanism of the reaction rather than radical one.

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