

## CHAPTER V

### RESULTS AND DISCUSSION

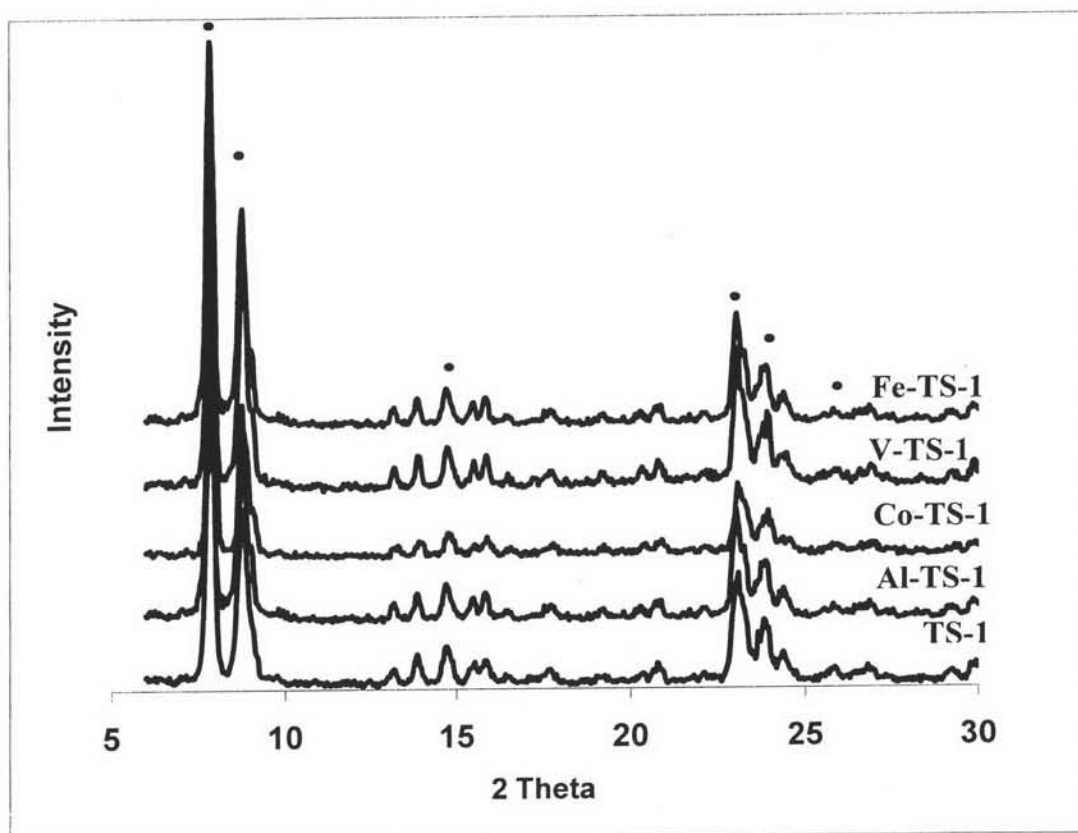
This chapter, result and discussion, is divided into two parts. The first part is the results of characterization of catalysts by using XRD, BET, FT-IR, XRF and NH<sub>3</sub>-TPD. The second part is the results of hydroxylation of toluene and ethyl benzene.

#### 5.1 Characterization of catalysts

The physical and chemical properties of TS-1 and TS-1 modified with second metals were analyzed by several techniques in order to gain some basic information of the catalysts when they are used in the hydroxylations in latter part.

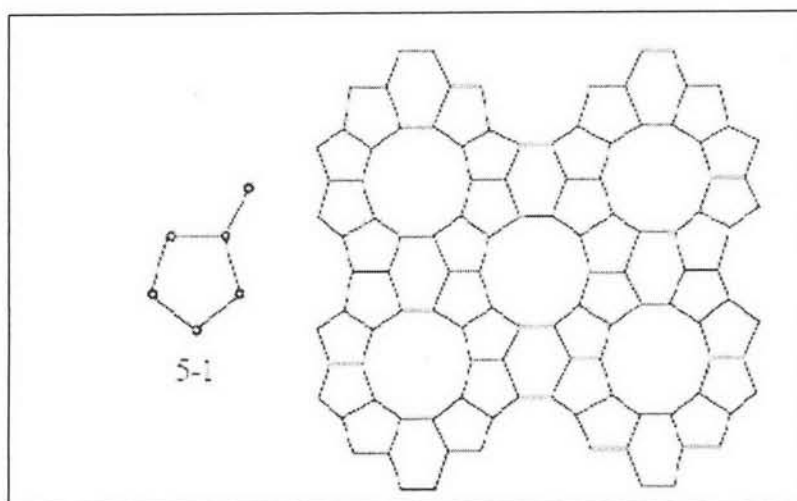
##### 5.1.1 X-ray diffraction (XRD)

Figure 5.1 shows the XRD patterns of TS-1 and TS-1 modified with second metal (M-TS-1). All the XRD graphs present six main characteristic peaks at 2 theta as 8, 8.8, 14.8, 23.1, 24 and 26.7. There is no peak at 2 theta  $\approx$  25.3, represents the characteristic peak of anatase TiO<sub>2</sub> phase. Therefore, all TS-1 synthesized using TPABr as template does not contain anatase.



**Figure 5.1** The XRD patterns of the modified TS-1.

The patterns obtained are the common pattern found for a crystalline zeolite having a MFI structure [15]. This structure is built up by 5-1 secondary building units (SBU; the smallest number of  $\text{TO}_4$  unit where T is Si or Al but TS-1 has Ti component replacing at Al position, so this case T is Si or Ti.) which are linked together to form chain that reveals in Figure 5.2 and the interconnection of these chain leads to the formation of the channel system structure. The MFI structure has a three dimensional pore system consisting of sinusoidal 10-ring channel ( $5.1 \times 5.5 \text{ \AA}$ ) and intersecting straight 10-ring channels ( $5.3 \times 5.6 \text{ \AA}$ ) [16].



**Figure 5.2** A 5-1 secondary building unit and the MFI structure [16].

### 5.1.2 Determination of surface area by BET

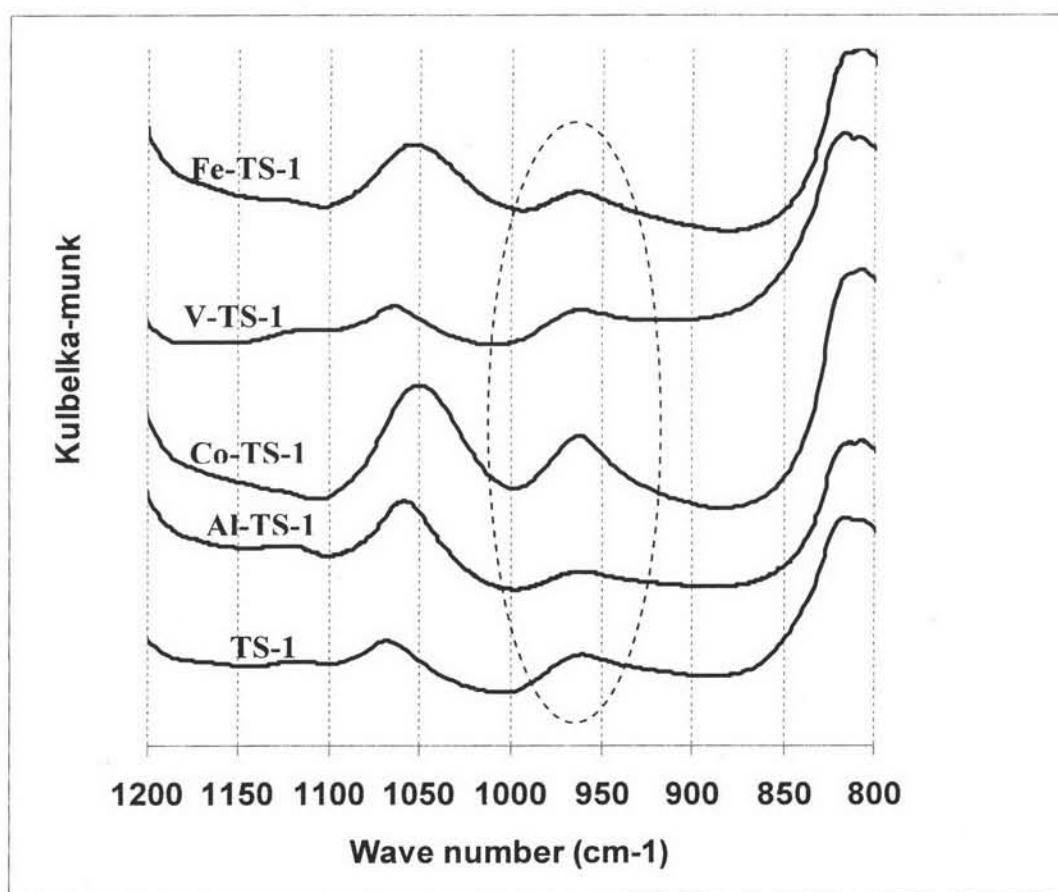
**Table 5.1** Composition and surface area

Catalyst	Surface area (m <sup>2</sup> /g)	Pore size (Å)
TS-1	323	29
Co-TS-1	357	27
Fe-TS-1	358	28
V-TS-1	313	26
Al-TS-1	368	25

The surface areas of all catalysts investigated are reported in Table 5.1. The BET surface areas and average pore size diameters of each sample is in the range 25-30 Å. They present that the mesoporous being a contributor to the area surfaces.

### 5.1.3 Fourier-transform Infrared spectroscopy (FT-IR)

Figure 5.3 presents the characteristic absorption band of tetrahedral  $Ti^{4+}$  in the modified TS-1 and the modified M-TS-1 which have the adsorption band at  $960\text{ cm}^{-1}$ . These results demonstrate that with the amount of the second metal added to TS-1, the tetrahedral  $Ti^{4+}$  in the structure can retain. It has been reported that the stronger the band at  $960\text{ cm}^{-1}$  the more titanium atoms incorporated into the framework [12]. Besides, the band around  $960\text{ cm}^{-1}$  can also be assigned the tetrahedral group  $Ti(OSi)_4$  appears in the silicalite spectrum [12, 18-19].



**Figure 5.3** The wave number of TS-1 and the modified TS-1.

#### 5.1.4 Temperature programmed desorption (NH<sub>3</sub>-TPD)

NH<sub>3</sub>-TPD was used to determine the strength and amount of the acid site of the catalysts. It is found that the NH<sub>3</sub>-TPD profile of each catalyst can be split into two main desorption peaks, but the locations of the first peak and the second peak of each profile are different. The overall results are presented in Appendix B. To determine the strength, amount, and type of acidic sites, each NH<sub>3</sub>-TPD profile is deconvolved using a “fityk” deconvolution programme after base line subtraction. The results obtained from the programme suggest that the acidic site can be categorized into 3 groups, according to their desorption peaks. The first one locates around 130-150 °C which will be named here “the weak acid site”. The second one locates around 150-180 °C which will be named here “the medium strength acid site” and the last group locates higher than 180 °C and will be named here “the strong acid site”. The location of each peak and amount of peak type of the acidic site (determined from the area under each peak are summarized in Table 5.2 )

Using the type of acid site each catalyst possesses, the catalysts can be classified into two groups, i.e. first group is catalysts having weak acid and strength acid site such as TS-1 and TS-1 modified with Co and V and second group is Al-TS-1 and Fe-TS-1 having the medium strength acid and strong acid site. However, when compared with total acid site, the second group has amount of total acid site lower than first group.

**Table 5.2** The strength and amount of the acid site of the catalysts

Catalyst	Total acid site ( $\mu\text{mol/g}$ )	Weak acid		Medium strength acid		Strong acid	
		Temp	Site	Temp	Site	Temp	Site
		( $^{\circ}\text{C}$ )	( $\mu\text{mol/g}$ )	( $^{\circ}\text{C}$ )	( $\mu\text{mol/g}$ )	( $^{\circ}\text{C}$ )	( $\mu\text{mol/g}$ )
TS-1	468	132	280	159	188	-	-
Co-TS-1	539	146	285	175	254	-	-
Al-TS-1	93	-	-	164	52	336	41
V-TS-1	122	144	26	168	96	-	-
Fe-TS-1	100	-	-	154	62	284	38

### 5.1.5 X-ray fluorescence spectroscopy (XRF)

The chemical composition of TS-1 and M-TS-1 were determined by XRF and summarized in Table 5.3. It should be noted here that though the same amount of Ti was used for each catalyst, the amount of Ti atoms can be incorporated in the TS-1 structure are not the same. This suggests that the presence of another metal species affects the ability of  $\text{Ti}^{4+}$  ion in the formation of TS-1 structure. For TS-1 in which the second metals are incorporated during the catalyst synthesis process, the results show that the ability of the second metal which can be incorporated (% mole of metal) with TS-1 follows the following order  $\text{Fe} \geq \text{Co} > \text{V} \approx \text{Al}$ .

**Table 5.3** The chemical composition of TS-1 and M-TS-1

Catalyst	% Mole of metal				
	%Si	%Ti	%M	Si/Ti	Si/M
TS-1	98.45	1.48	none	66.43	None
Al-TS-1	93.90	5.15	0.78	18.24	120.55
Co-TS-1	98.53	1.21	0.20	81.46	489.13
Fe-TS-1	93.16	4.18	2.58	22.31	36.04
V-TS-1	92.23	7.23	0.33	12.76	277.75

The chemical compositions and the atomic ratio of Si, Ti, and M including ratio of Si/Ti and Si/M of the samples values are illustrated in Appendix C.

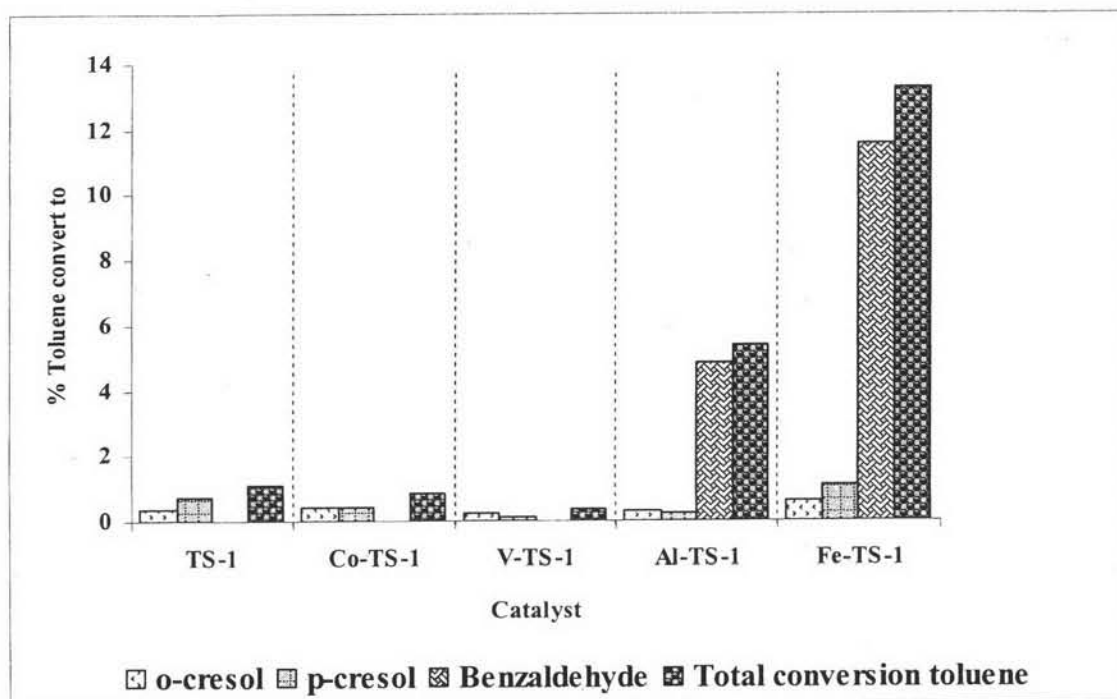
## 5.2 The catalytic reaction

The catalytic performance of the synthesized catalysts was evaluated by using the hydroxylation of toluene and ethyl benzene with hydrogen peroxide as a test reaction. The experimental results imply the total percent of converted toluene and ethyl benzene to product, mole of each product formed. In adding, the mechanism of hydroxyl group substitution is also discussed in the latter.

## 5.2.1 Hydroxylation of toluene

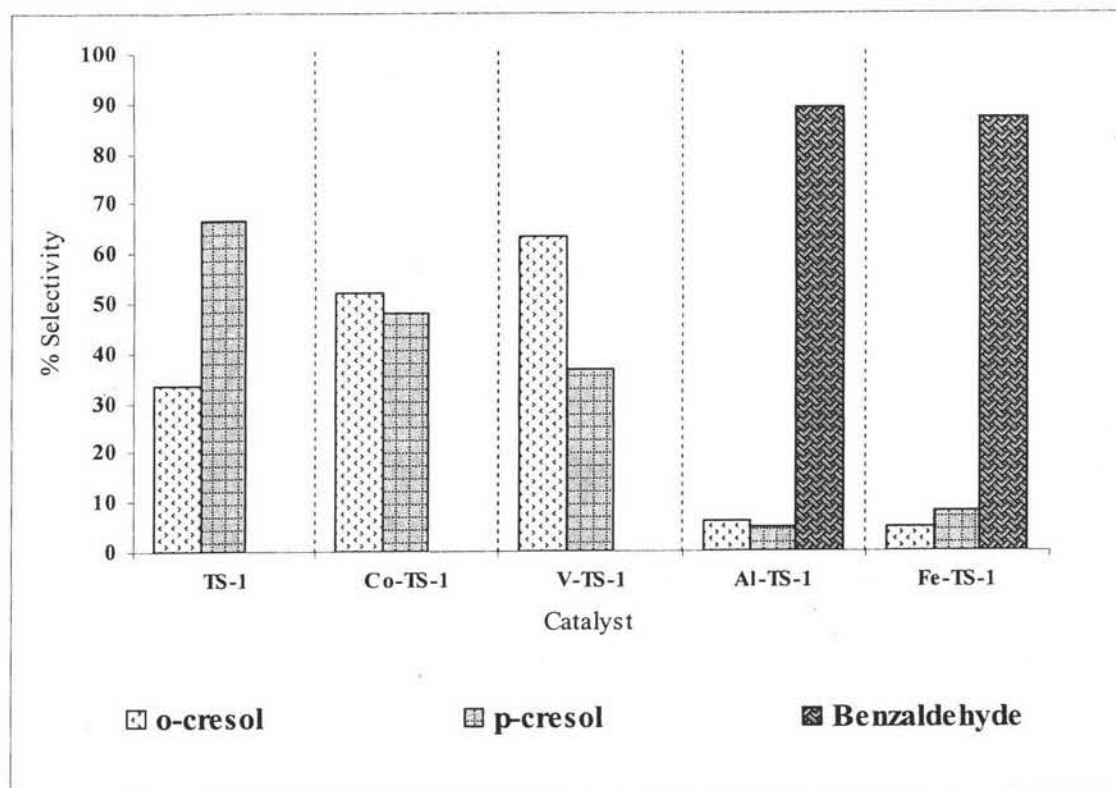
### 5.2.1.1 The of hydroxylation of toluene at 70 °C

The hydroxylation of toluene results from using TS-1, Co-TS-1, V-TS-1, Al-TS-1 and Fe-TS-1 at 70 °C for 2 hr are showed in Figures 5.4 and 5.5.



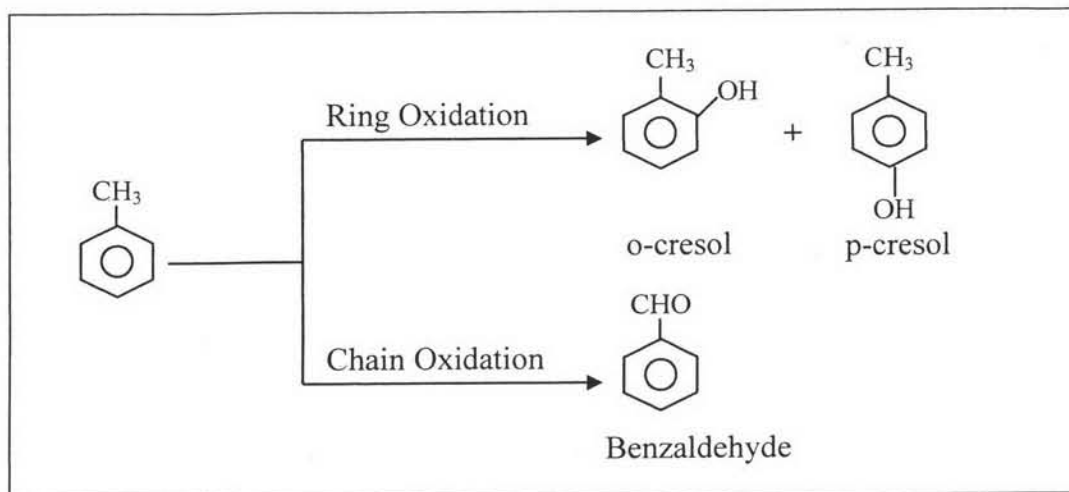
**Figure 5.4.** The conversion of hydroxylation of toluene at 70 °C.





**Figure 5.5** The percentage of selectivity of hydroxylation of toluene at 70 °C.

The results indicate that TS-1, Co-TS-1 and V-TS-1 give two reaction products i.e. o-cresol and p-cresol. When Al-TS-1 and Fe-TS-1 were used, three major products were observed i.e. o-cresol, p-cresol and the last one benzaldehyde which is the predominant product. The catalytic activity of TS-1 and M-TS-1 follows the follow sequence: Fe-TS-1 (10.01%) > Al-TS-1 (5.39%) > TS-1 (1.09%) > Co-TS-1 (0.85%) > V-TS-1 (0.34%) and the selectivity of product observed follows the following order: TS-1 > Co-TS-1 > V-TS-1 > Al-TS-1 > Fe-TS-1. The appearance of benzaldehyde in the hydroxylation with Al-TS-1 and Fe-TS-1, indicates that the hydrogen peroxide substitution takes place at both of benzene ring and methyl group which are showed schematically in Figure 5.6. It should be notes here that through Al and Fe significantly improve the catalytic activity; i.e. higher loss of toluene to benzaldehyde which is the undesired product in this study.



**Figure 5.6.** The hydroxylation of toluene at side chain and ring.

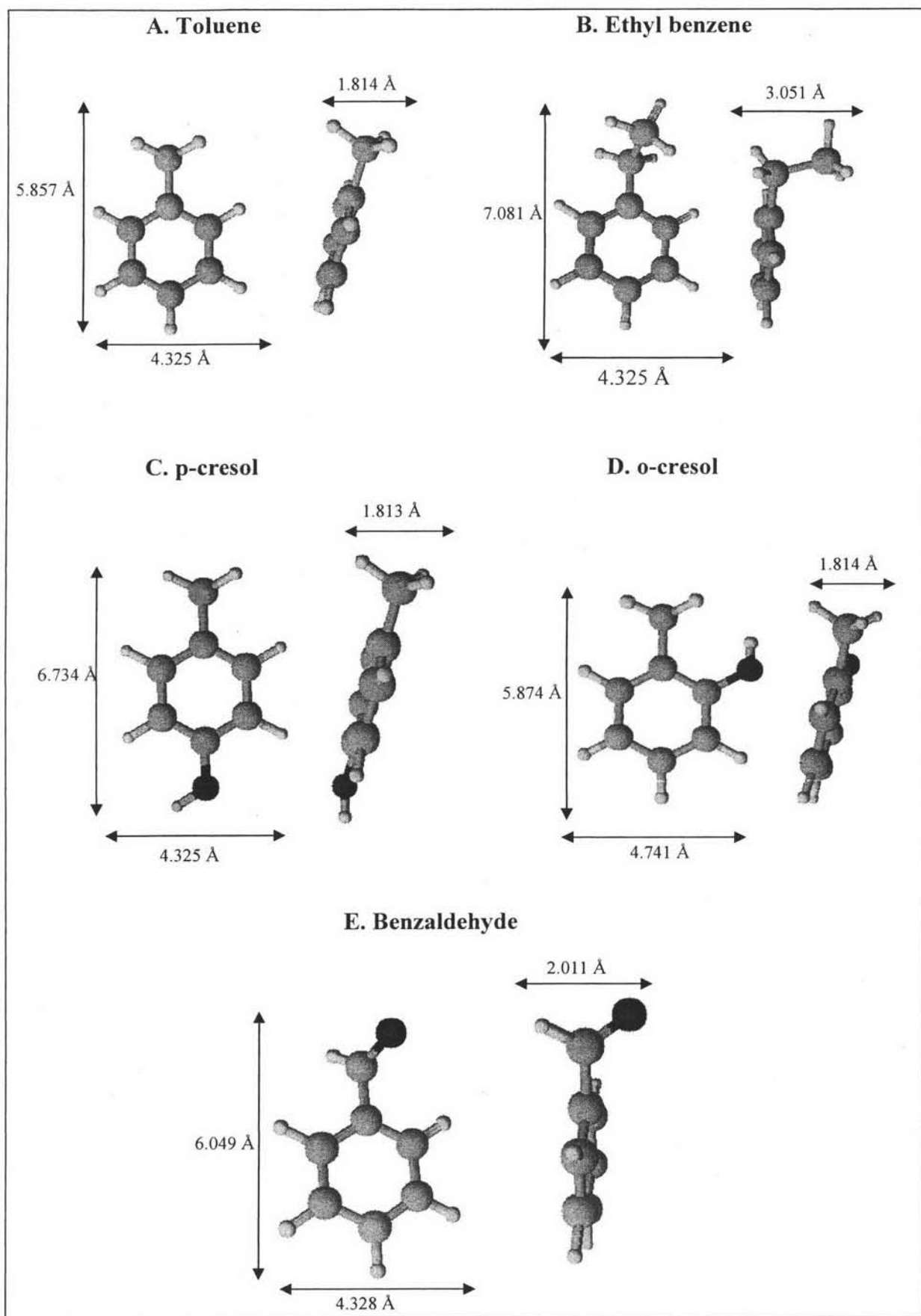
Figures 5.4 and 5.5 show that the distribution of the hydroxylation products, i.e. o-cresol and p-cresol, varied with the catalysts used. In the case of using TS-1 and Fe-TS-1, p-cresol is more predominant than o-cresol. On the contrary o-cresol is slightly higher than p-cresol when Co-TS-1, V-TS-1 and Al-TS-1 were used in reaction. These phenomena should be effected from

**I.** Theoretically, the presence of an alkyl group promotes the electrophilic substitution at ortho- and para- positions. For a small alkyl group in a homogenous reaction the substitution of a small electrophile at the ortho-position is more preferred than the substitution at the para-position due to the faster ability of the alkyl group in stabilizing the intermediate formed. In addition, there are two ortho-positions and only one para-position. Therefore, the ratio of ortho-substitution product to para-substitution product should be at least two. However, the results from the hydroxylation of toluene present that hydrogen peroxide, when used with TS-1 and Fe-TS-1, is more favorable substitute at the para-position than the ortho-position. In case of Co-TS-1, V-TS-1, and Fe-TS-1, the reaction prefers the ortho-substitution, the ortho-substitution product found is only marginally higher than the para-substitution product found. Therefore, there is a need for other explanations which can explain the observed product distribution.

**II.** In fact, the shape selective effect of the medium pore of zeolite affects the formed product molecules which can pass through the opening pore of zeolite. The formed product molecule must have its kinetic diameter smaller than the diameter of the opening pore in order to be able to move out of the pore. Therefore, dynamics and structure of the formed product molecule must be taken into account when considering which product(s) should appear in the bulk fluid. In addition, it should be kept in mind that the diffusion in the opening pore is the counter-diffusion between the reactants that diffuse from the outside to the inside and the products that diffuse from the inside to the outside. In this situation, for a pair of molecules having similar structure and/or volume, the linear shape molecule (such as p-cresol) can diffuse through the opening pore much easier than the branch shape molecule (such as o-cresol).

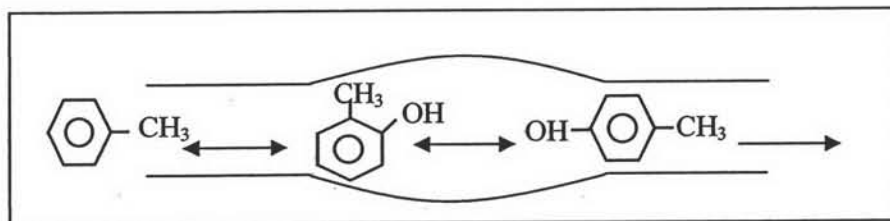
In the present work, the Chem Sketch version 11.0 freeware program is used to create the planar structure molecule (2-dimension) transformed into a realistic 3-dimension by 3D optimization algorithm. The characteristic 3-dimensionnal molecule is based on modified molecular mechanism which take into account bond stretching, angle bending, internal rotation and Van der Waals non-bonded interactions. Modifications include minor simplification of potential functions and enforcement of the minimization scheme by additional heuristic algorithms for dealing with “bad” starting conformations.

The kinetic diameters of the organic reactants (toluene and ethyl benzene) and the organic products formed (o-cresol, p-cresol and benzaldehyde) are calculated using the above mentioned freeware “Chem Sketch” program. The calculation results are showed schematically in Figure 5.7. The dimension of molecule is measured from one atom to another atom, the maximum distances (the distance between two atoms located at the opposite furthest end measured in different directions) are used as the dimensions of the molecule.



**Figure 5.7** The kinetic diameter of reactant and product molecules

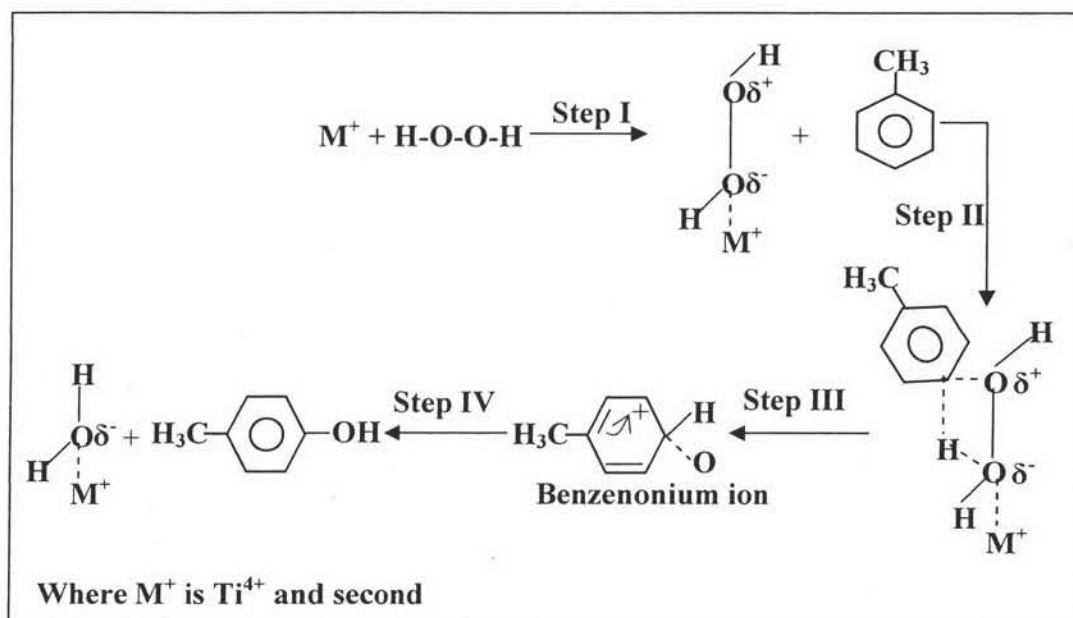
The calculated molecule dimensions exhibited in Figure 5.7 show that p-cresol molecule has more linearity than o-cresol molecule. The linearity here is the ratio between the length and the width of the molecule. For p-cresol this ratio equals to 1.557 (6.734/4.325) while for o-cresol this ratio equals to 1.239 (5.874/4.741). Due to this fact, p-cresol can diffuse out of the catalyst pore faster than o-cresol. The o-cresol, having longer resident time inside the catalyst pore, therefore, has more chance for the reverse reaction. This phenomenon is illustrated schematically in Figure 5.8.



**Figure 5.8.** The hydroxylation in the medium pore zeolite.

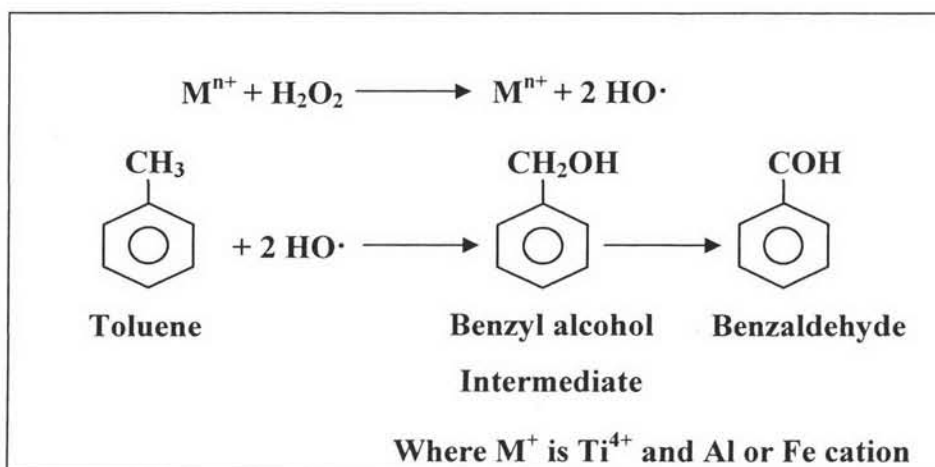
**III.** For a solid catalyst system, the surface profile of the catalyst can affect the position where the reaction can occur of the reactant molecule. At atomic level, the surface of the catalyst is not a smooth surface but consists of atoms or ions locate at different depth. For example in the structure showed in Figure 5.9.,  $O^{2-}$  and  $-OH$  are at the outermost of the surface while  $Si^{4+}$  and  $Ti^{4+}$  locate deeper into the surface. With such surface structure, the para position of toluene molecule can reach the active sites on the catalyst surface much easier than the ortho position because the ortho position may be obstructed by the methyl group if toluene molecule does not approach the catalyst surface in the appropriate angle. Therefore, occurrences of products are depend on the substitution of hydroxyl group on toluene and the characteristic toluene molecule attach on active site that present in Figure 5.9.





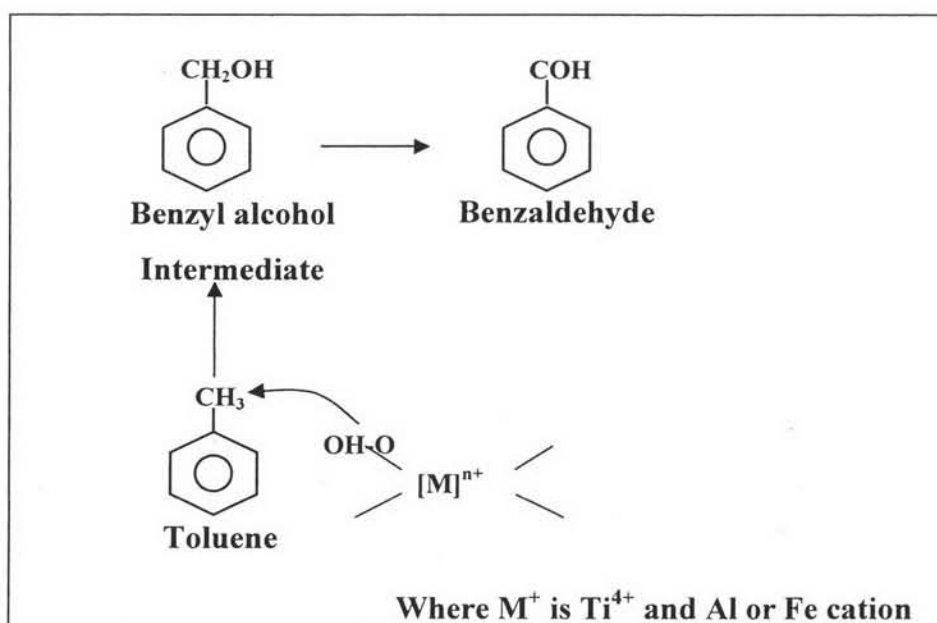
**Figure 5.10** The mechanism of hydroxylation toluene.

The formation of benzaldehyde may take a different route from the formation of cresols. It is well known that for any alkyl aromatic compounds, hydrogen atoms of the alkyl group attached to the ring can be replaced by a free radical more easily than hydrogen atoms of the ring. The free radicals such as  $H-O\cdot$  and  $H-O-O\cdot$  formed during the decomposition of  $H-O-O-H$  can replace hydrogen atoms on the methyl group of toluene leading to the formation of an intermediate (possibly benzyl alcohol). Because there is no intermediate found in the product mixture, the intermediate formed must be further oxidized immediately to benzaldehyde. The mechanism of the formation of benzaldehyde is showed in Figure 5.11. The active site in Figure 5.11 is possibly the cations of Al, Fe and Ti which act as acidic site having strength higher than any other catalysts.



**Figure 5.11.** The hydroxylation at the side chain using strong acid site.

Another, mechanism for benzaldehyde production is the strong electrophile ( $OH\cdot$ ) directly attaches at methyl group of toluene. Then toluene is converted to intermediate and benzaldehyde respectively, likely Figure 5.10. This mechanism is exhibited in Figure 5.12.



**Figure 5.12** The formation benzaldehyde from strong directly electrophile attachment.



The mechanism showed in Figure 5.11 is likely to be the principal mechanism of benzaldehyde production when Al-TS-1 and Fe-TS-1 are used in reaction at 70 °C. Due to the mechanism in Figure 5.12, it can occur only case using Al-TS-1 and Fe-TS-1 but other catalysts can not produce benzaldehyde at this condition.

### 5.2.1.2 Effect of hydroxylation of toluene at 95 °C

The results obtained from the hydroxylation of toluene at 95 °C with TS-1 and M-TS-1 are reported in Figures 5.13 and 5.14. Fe-TS-1 is not used in the experiment because it makes the solution in reactor boils the severely due to the extreme deposition of hydrogen peroxide. This effect leads to a dangerous condition and a unmeasured result of reaction. At this reaction temperature, o-cresol and benzaldehyde are observed from all the catalysts and benzaldehyde is mainly produced whereas p-cresol is only observed in case of using TS-1 modified with V and Co. The results of catalytic activity in the hydroxylation present following order: Al-TS-1 > TS-1 > V-TS-1 ≈ Co-TS-1.

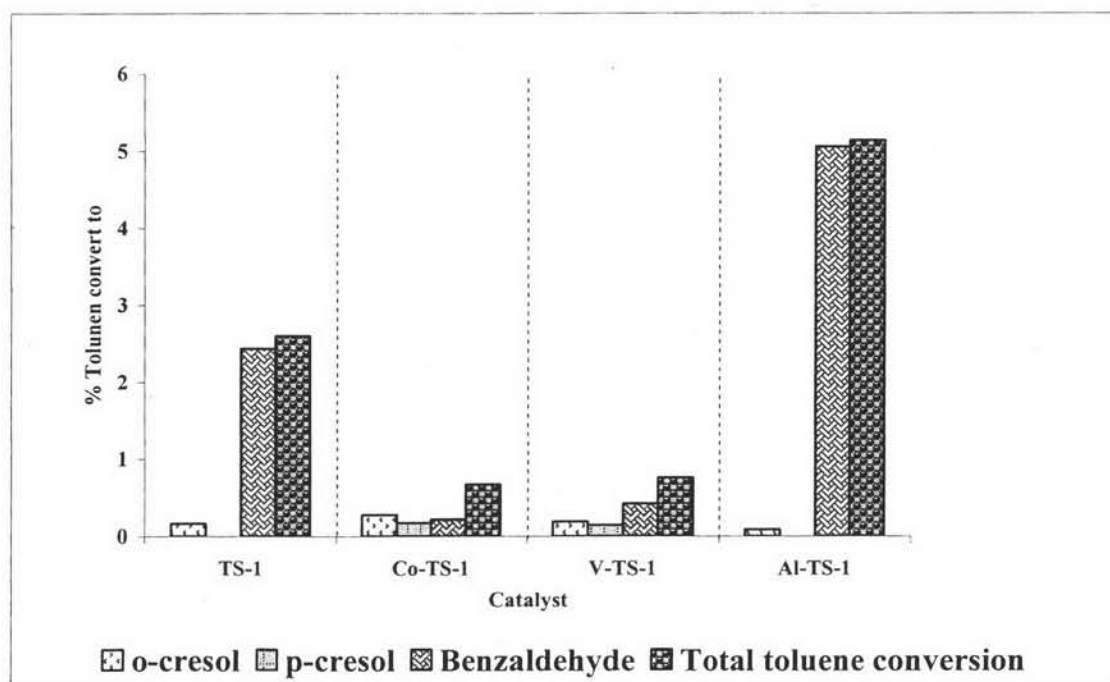
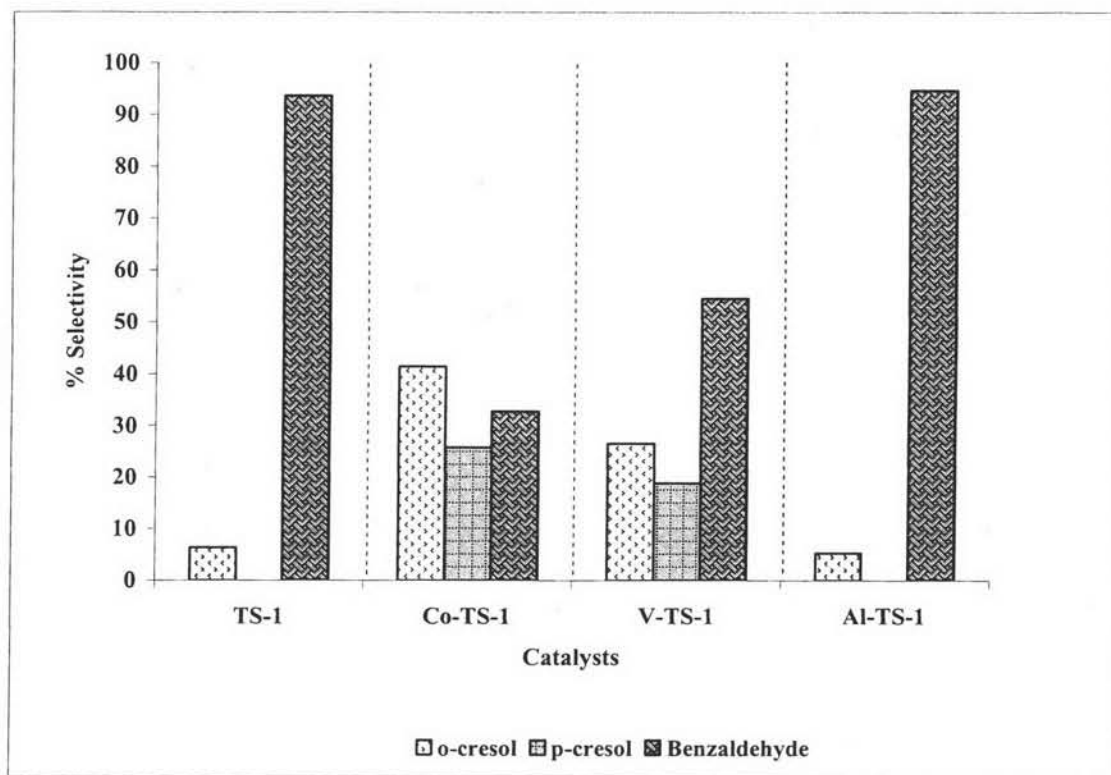
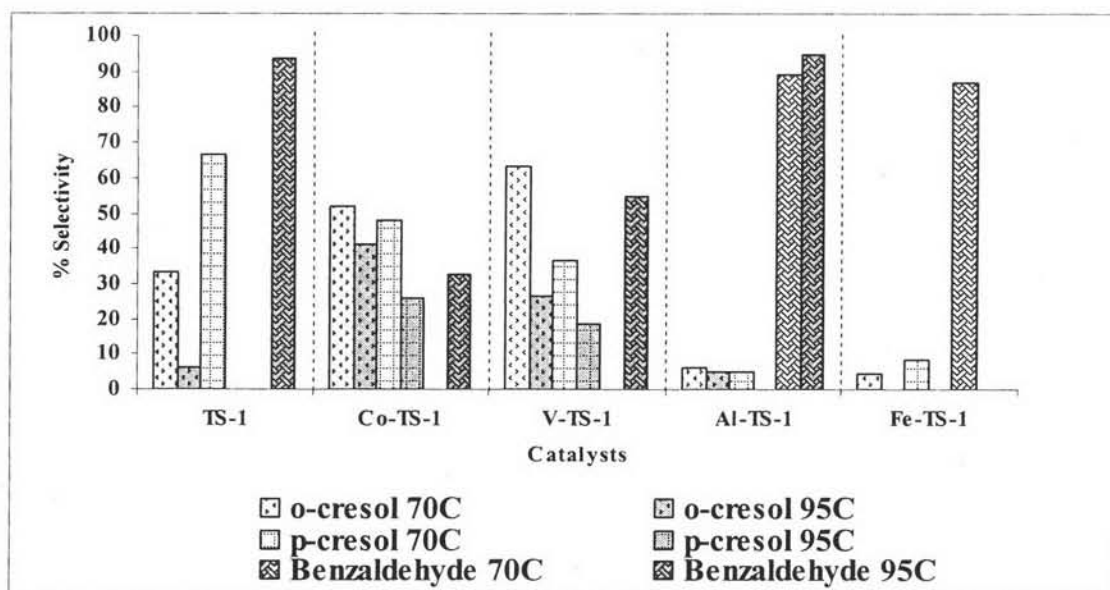


Figure 5.13 The conversion of hydroxylation of toluene at 95 °C.



**Figure 5.14** The percentage of selectivity hydroxylation of toluene at 95 °C.

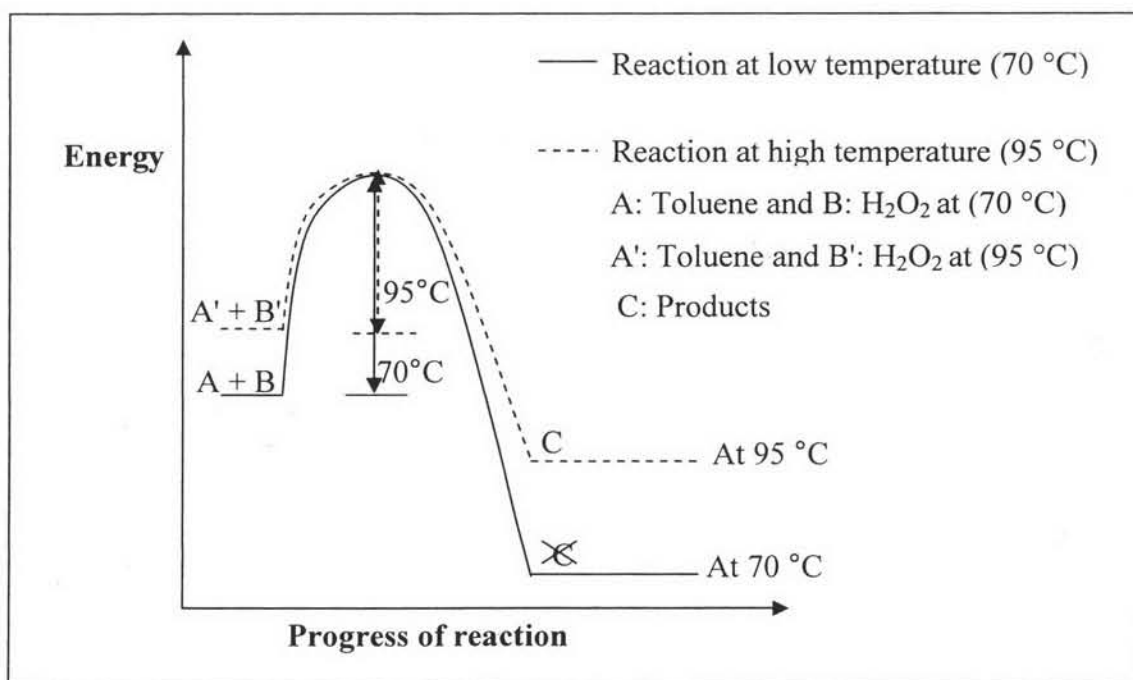


**Figure 5.15** The percentage of product selectivity from hydroxylation toluene at temperature 70 and 95 °C.

The selectivity of product from the hydroxylation illustrated in Figure 5.14 and 5.15 present that benzaldehyde is the main product contained from of all catalysts. Particularly, Al-TS-1 is higher selectivity than other catalysts at 95 °C.

This point indicates that the catalysts used in reactions can also give a product obtained from the side chain oxidation although some catalysts have no strong acid sites as active site and in case the presence of strong acid site in catalyst, the benzaldehyde selectivity tends to increase. Therefore, the temperature increasing affects to the medium acid site and strong acid site which can promote the hydroxyl group substitution at both much benzene ring and alkyl side chain. Especially the side chain oxidation at 95 °C is much more preferred than the ring substitution and the side chain oxidation at 70°C. From the results of predominant side chain oxidation reveal that all of catalysts have both mechanisms presented in Figure 5.11 and 5.12 and their mechanisms are more influence than Figure 5.10.

Therefore, the temperature affects to average energy of reactant molecules is so low temperature, the reactant molecule with the highest energy still can not overcome the activation energy barrier. When temperature is increased the average molecular energy is raised up to a level that the portion of high energy molecule can overcome the activation energy barrier and convert to product. The reactants overcoming energy barrier exhibited in Figure 5.16.



**Figure 5.16** The activation energy barrier of reactant molecule at 70 °C and 95 °C.

### 5.2.1.3 Effect of second metals modified in TS-1

The role of second metals incorporated in TS-1 affects conversion of toluene at 70 °C and 95 °C will be discussed in this section. The total percentage conversion of toluene to products per mole of cation (Ti or Ti + M) and productivity of cresols and benzaldehyde at 70 °C are illustrated in Figures 5.17 and 5.18.

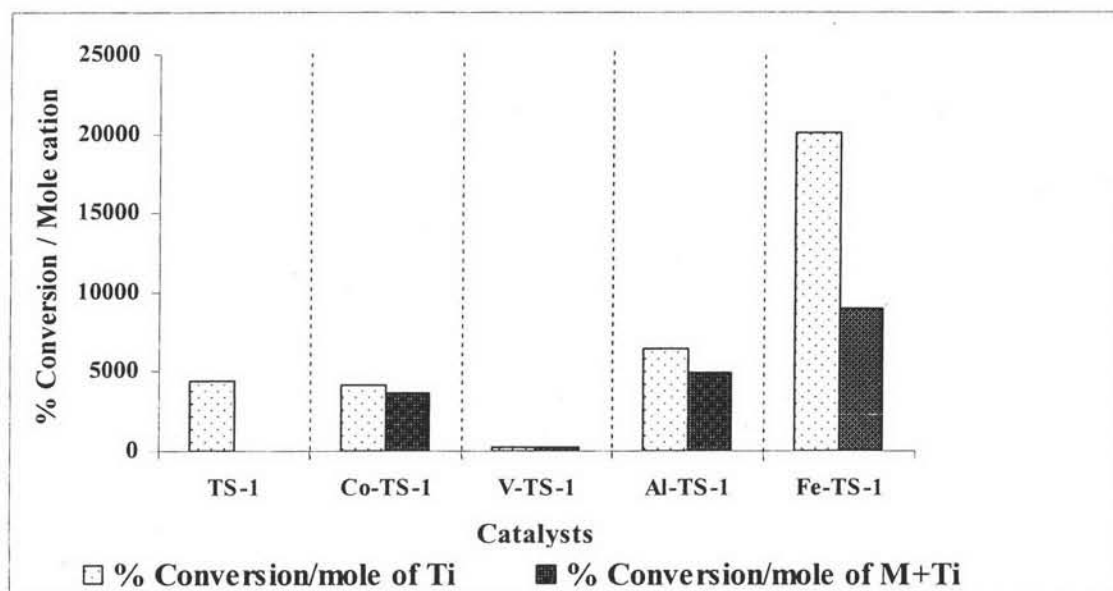


Figure 5.17 The total conversion of toluene to products per mole of cation at 70 °C.

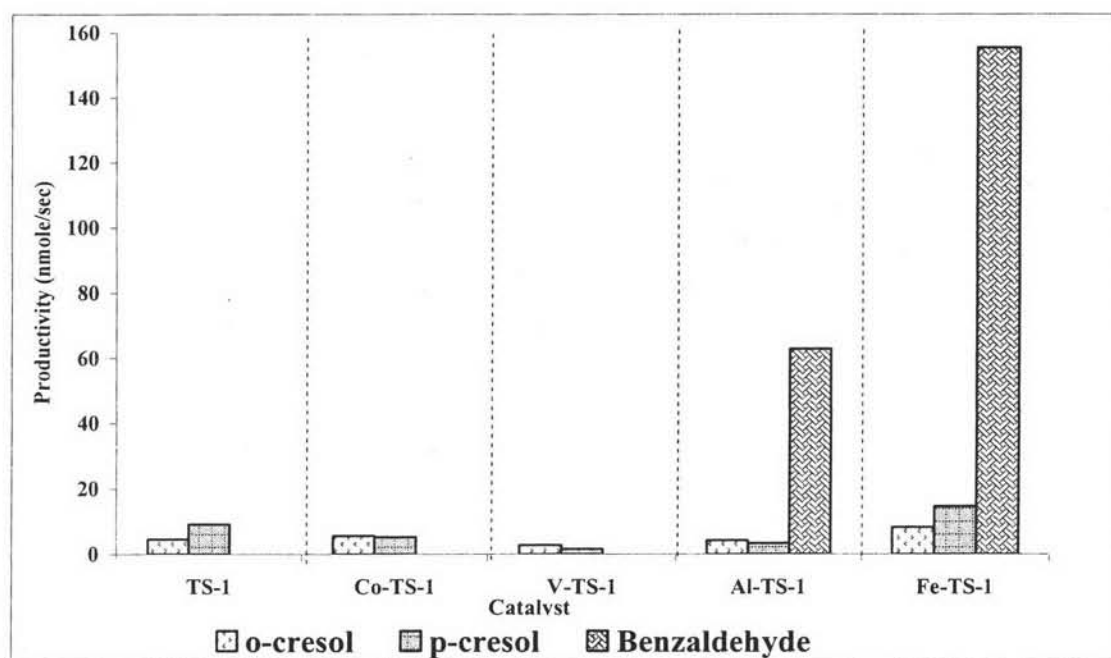
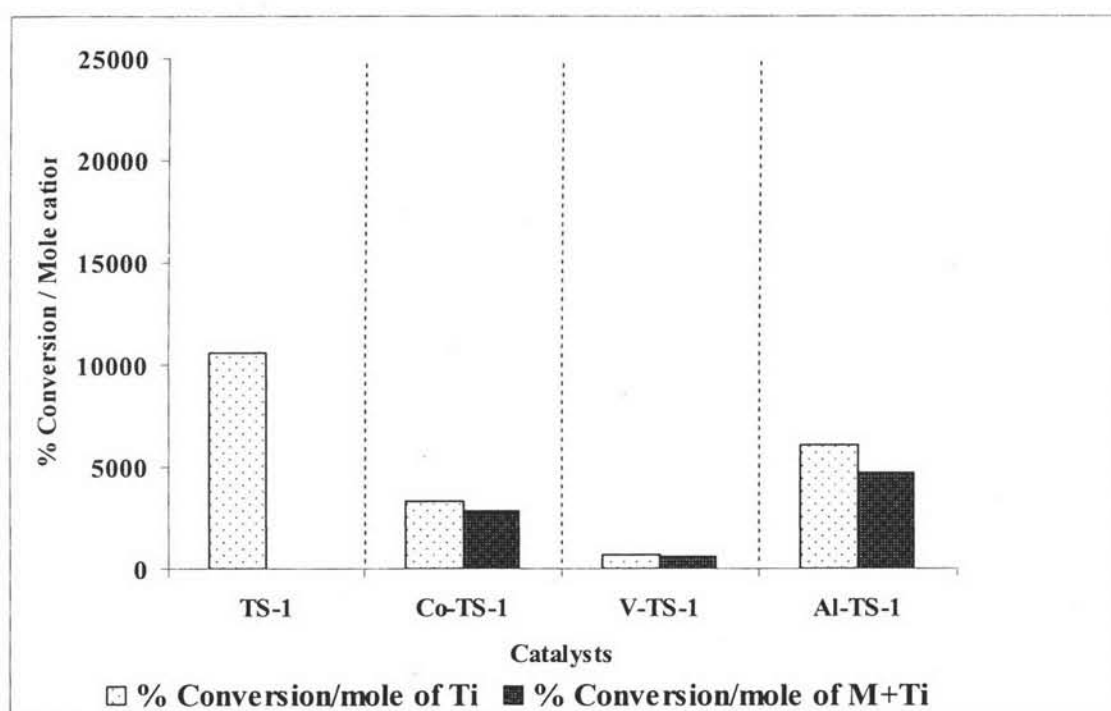
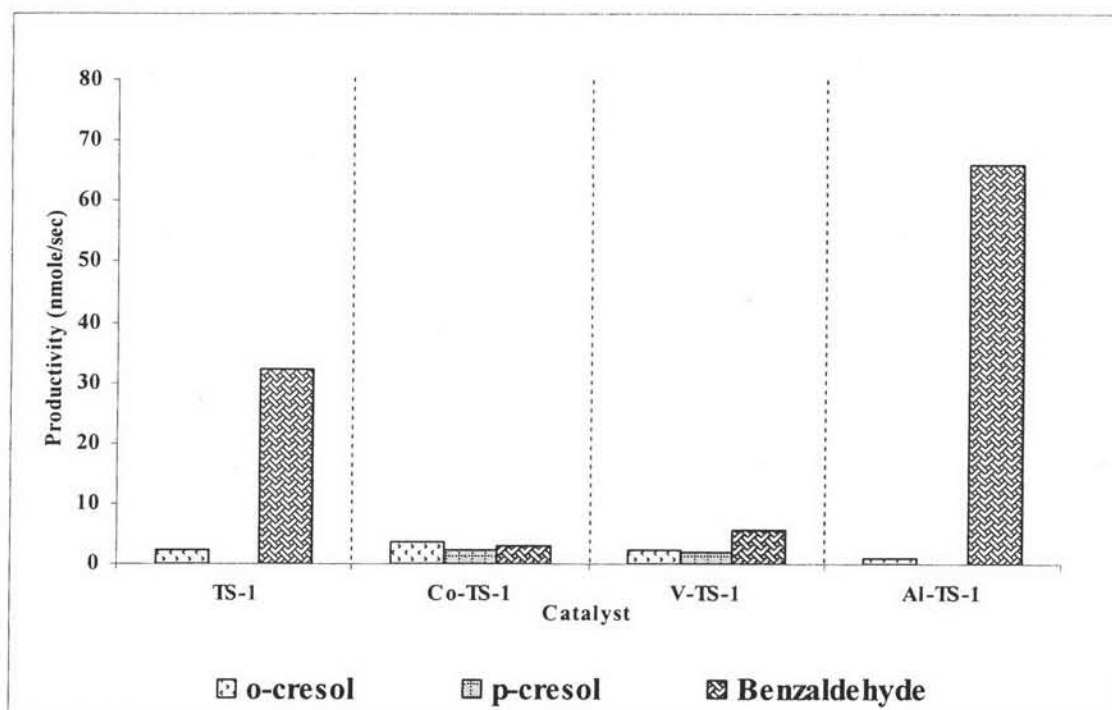


Figure 5.18. The percentage of productivity of hydroxylation of toluene at 70 °C.

At 70°C, the total conversions of toluene to products per mole of (Ti+M) of TS-1, Co-TS-1, Al-TS-1 and Fe-TS-1 catalysts are in the same range. The exception is V-TS-1 which shows much lower total conversion per mole of (Ti+V). The productivity of cresols (Figure 5.18), however, gives different point of view. TS-1, Co-TS-1 and V-TS-1 have the same productivity of cresols. In contrast Al-TS-1 and Fe-TS-1 give higher productivity of cresols and also benzaldehyde, particularly Fe-TS-1 which has the highest productivity of both cresols and benzaldehyde. This point indicates that Co and V restrain benzaldehyde production while Al as well as Fe promotes the formation of benzaldehyde as main reaction product.



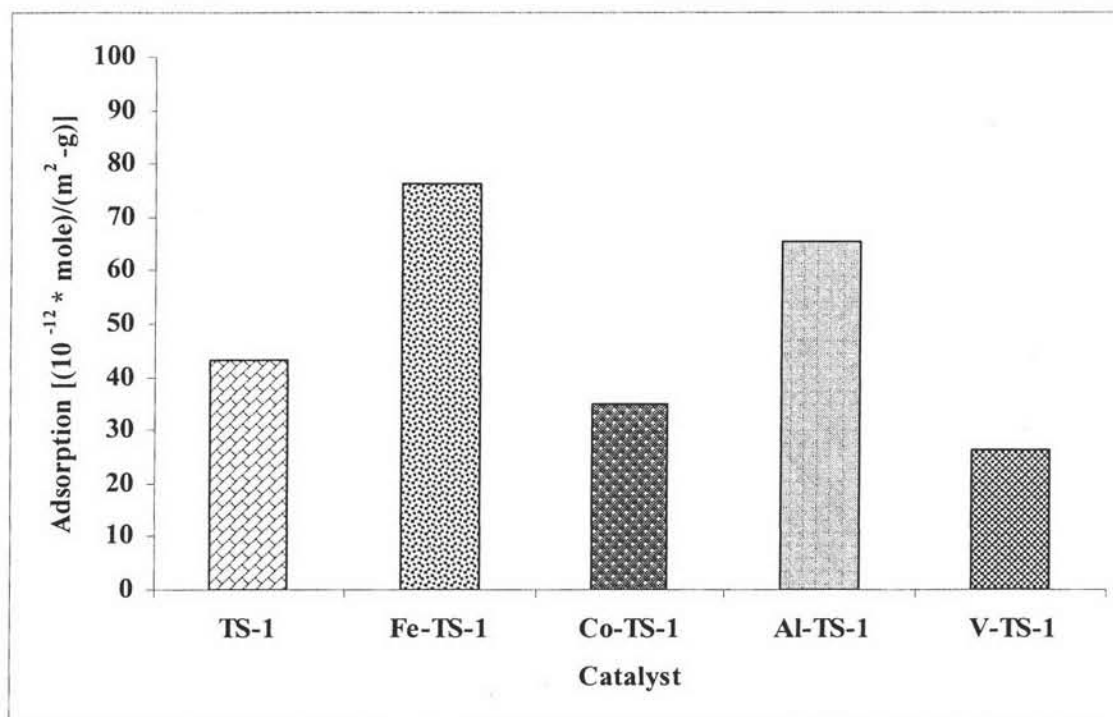
**Figure 5.19** The total conversion of toluene to products per mole of cation at 95 °C



**Figure 5.20** The productivity of hydroxylation of toluene at 95 °C.

The result in Figure 5.19 and 5.20 presents that the presence of V and Co cation in catalyst inhibit benzaldehyde production. This conclusion comes from the fact that V-TS-1 and Co-TS-1 have lower benzaldehyde productivity than TS-1 and Al-TS-1. On the other side, Al cation leads to enhancement benzaldehyde occurrence.

#### 5.2.1.4 Effect of adsorption toluene on catalyst



**Figure 5.21** The adsorption of toluene on TS-1 and M-TS-1.

Figure 5.21. reports that the ability of the catalyst surfaces to absorb toluene. The results present that TS-1 modified with Fe and Al have more capability to absorb toluene than TS-1, Co-TS-1 and V-TS-1. The amount of toluene adsorb by each catalyst follows the following order: Fe-TS-1 > Al-TS-1 > TS-1 > Co-TS-1 > V-TS-1. Since Fe-TS-1 and Al-TS-1 have the adsorption capability of toluene more than the other catalysts, this may be additional cause which can explain why they give the higher total conversion of toluene to products.

Furthermore, the result of toluene adsorption on catalyst relates the result in before section, i.e. although TS-1, Co-TS-1 and V-TS-1 have the same of amount reactant which adsorbs on them, they have district productivity at 70 °C (Figure 5.18) and 95 °C (Figure 5.20). This point suggests that the cations of second metal modified in TS-1 influence reaction that depend on the kind of cation.

### 5.2.2 Hydroxylation of ethyl benzene

The catalytic reaction of ethyl benzene was observed at two temperature same as toluene, 70 °C and 95 °C, and the reaction products obtained are analyzed by gas chromatography-mass spectrometry to determine kind of organic compounds. The products found are listed in Table 5.4 and raw data are summarized in Appendix.G.

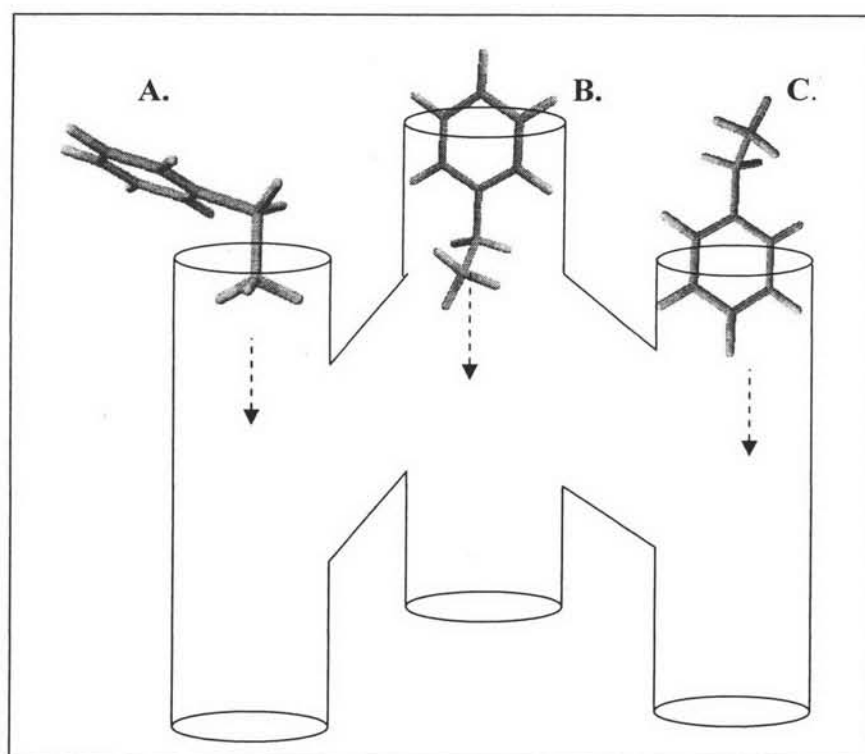
The majority products gained from using all catalysts at 70 °C and 95 °C are acetophenone and 1-phenethyl alcohol. In case using Co-TS-1 and Fe-TS-1 at 70 °C, another product, benzaldehyde, is observed. Moreover, Fe-TS-1 also has phenethyl alcohol and benzalacetaldehyde. The observed benzaldehyde is likely come from toluene contamination in ethyl benzene reactant. The reaction at 95 °C only gives products as acetophenone and 1-phenethyl ethanol. All products found indicate that the reaction between ethyl benzene and hydrogen peroxide is only occurred at the side chain ethyl group.

**Table 5.4** The products from hydroxylation ethyl benzene at 70°C and 95°C

Catalysts	Products at 70°C	Products at 95°C
TS-1	Acetophenone and 1-phenethyl ethanol	Acetophenone and 1-phenethyl ethanol
Co-TS-1	Acetophenone, 1-phenethyl ethanol and Benzaldehyde	Acetophenone and 1-phenethyl ethanol
V-TS-1	Acetophenone and 1-phenethyl ethanol	Acetophenone and 1-phenethyl ethanol
Al-TS-1	Acetophenone and 1-phenethyl ethanol	Acetophenone and 1-phenethyl ethanol
Fe-TS-1	Phenyl acetaldehyde, Acetophenone, Benzaldehyde, Phenethyl alcohol and 1-phenethyl ethanol	None

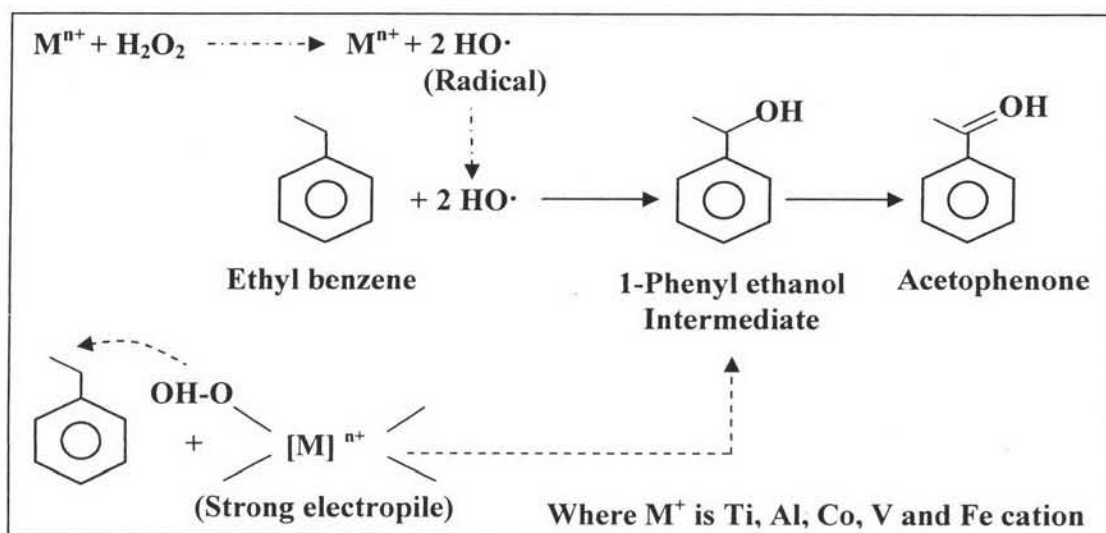


The low conversion ethyl benzene to products at 70 °C and 95 °C can be explained using the shape of ethyl benzene molecule. Ethyl benzene has large kinetic diameter, as presented in Figure 5.7, that can hindrance its molecule to enter the pore of catalyst. Therefore, ethyl benzene molecule can diffuse into the pore of catalysts if its molecule aligns appropriately with direction of the pore. Some example directions of ethyl benzene molecule entering to catalyst pore illustrated in Figure 5.22. In model (A) only the side chain enters the catalyst pore which results in the reaction at the ethyl group. Models (B) and (C) show how the entire ethyl benzene molecule can enter the catalyst pore which is not likely to occur due to nonlinearity of ethyl benzene structure. Therefore, the reaction at benzene ring does not occur.

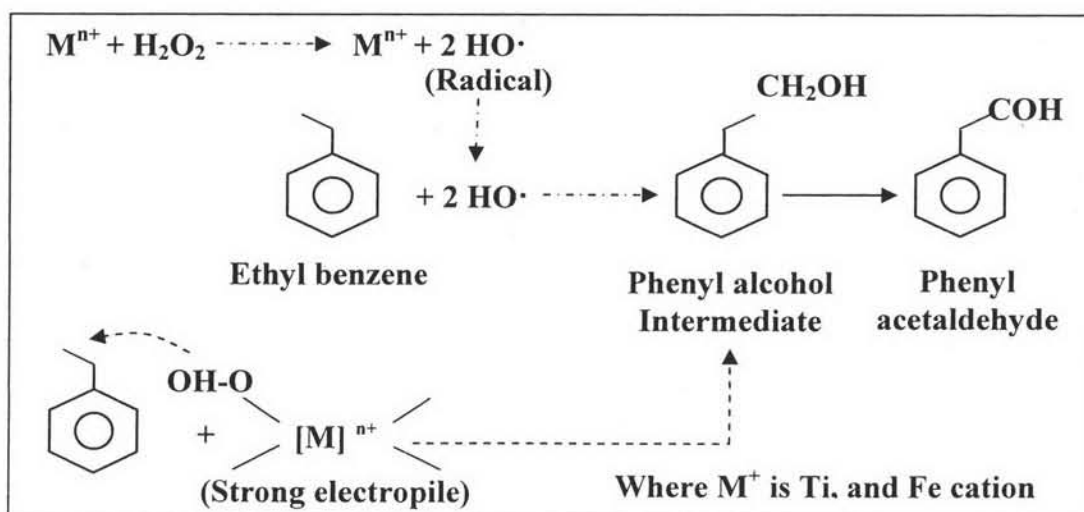


**Figure 5.22** The directions of ethyl benzene molecule enter pores catalyst

The mechanism of product formation of ethyl benzene hydroxylation is similar to benzaldehyde production (Figures 5.11 and 5.12), i.e. (i) ethyl benzene is attack with ( $\cdot\text{OH}$ ) radical or strong electrophilic of hydrogen peroxide and (ii) ethyl benzene is oxidized to intermediate compounds and then converts to products. This mechanism scheme is used to explain the formation of 1-phenethyl ethanol, acetophenone, phenethyl alcohol and phenyl acetaldehyde exhibited in Figures 5.23 and 5.24. For benzaldehyde, the formation has the similar mechanism as previously illustrated in Figures 5.11 and 5.12.



**Figure 5.23.** The mechanism of 1-phenethyl-ethanol and acetophenone formation.

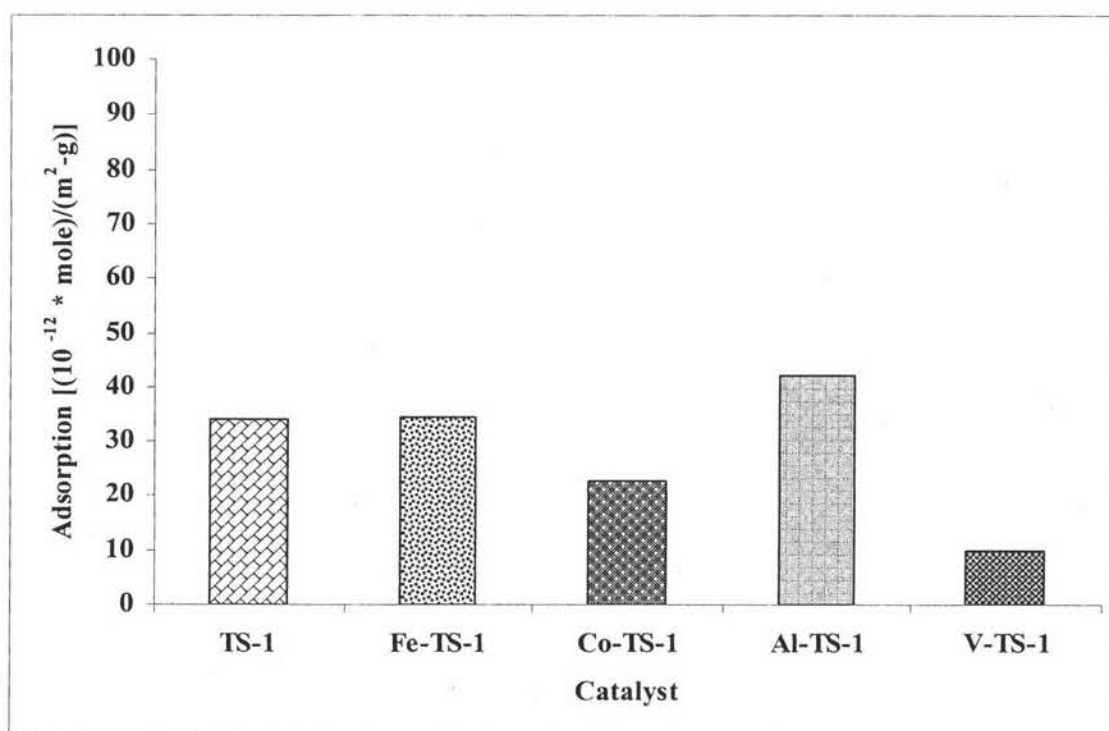


**Figure 5.24** The mechanism of phenyl alcohol and phenyl acetaldehyde formation.

The presence of 1-phenethyl ethanol and phenyl alcohol as intermediate in the system suggests the formation of the ketone (acetophenone) and the aldehyde (phenyl acetaldehyde) should be carried out via the formation of respective alcohols. This observation can support the conclusion in section 5.2.1 that benzaldehyde should form via an alcohol intermediate, benzyl alcohol. It is generally known that secondary alcohol (1-Phenethyl ethanol in this case) has higher resistance to oxidation than primary alcohol. In addition, a larger primary alcohol (like phenethyl alcohol) also has higher resistance to oxidation than a smaller primary alcohol (like benzyl alcohol). This can explain why the alcohol intermediates are found in the hydroxylation of ethyl benzene but absent from the hydroxylation of toluene.

### 5.2.2.1 Effect of ethyl benzene adsorbed on surface catalysts

The results of ethyl benzene adsorption on catalyst surfaces are reported in Figure 5.25.



**Figure 5.25** The adsorption of ethyl benzene on TS-1 and M-TS-1.

Compare with toluene adsorption (Figure 5.21) the amount of ethyl benzene adsorbed on surface catalysts are much lesser. This cause is ethyl benzene conversion lower than toluene as the same reaction condition.