



Catalytic Study of Iron, Aluminum, Vanadium and Cobalt Modified Titanium Silicalites-1 in the Hydroxylation of Benzene and Alkyl Benzene by Hydrogen Peroxide

Pornnapa Kasemsiri*, Kriangkrai Shenchunthichai, Patchanee Chammingkwan and Tharathon Mongkhonsi

Centre of Excellence on Catalysis and Catalytic Reaction, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, 10330, Thailand.

*Author for correspondence; e-mail: kae_en_39@hotmail.com

Received : 15 September 2007

Accepted : 17 November 2007.

ABSTRACT

This research studies catalytic properties of TS-1 modified Fe, Al, Co and V in the hydroxylation of benzene and alkyl benzene with hydrogen peroxide. The results show that adding Fe, Al, Co and V can increase the catalytic activity of TS-1 on the hydroxylation of benzene in the following order Co-TS-1 > V-TS-1 > Fe-TS-1 > Al-TS-1 > TS-1. Further investigation reveals that the added metals improve the performance of TS-1 by decreasing the adsorption of phenol on the TS-1 surface, thus prevent the blockage of the active site by the phenol formed. In addition, they also inhibit the decomposition of H_2O_2 , thus providing more H_2O_2 for the reaction. For the hydroxylation of toluene, it was found that the hydroxygroup can substitute at both ortho and para position producing o-cresol and p-cresol respectively.

Keyword: Titanium silicalite-1, hydroxylation, benzene, alkyl benzene.

1. INTRODUCTION

Phenol is a compound that has a hydroxyl group attaches directly to a benzene ring. Phenol is used to make chemical intermediates in pharmaceuticals, agricultural and chemicals plastics [1]. The main method used to manufacture phenol since the 1960s has been through the oxidation of 1-methylethylbenzene, commonly called cumene, which is made from benzene and propylene. The cumene process is combined with the fact that it is a three-stage process: (1) alkylation of

benzene with propylene to produce cumene, (2) oxidation of cumene to produce cumene hydroperoxide, and (3) decomposition of the hydroperoxide to phenol and acetone. This process has several shortcomings as follows: it is a multistage, the cumene hydroperoxide is explosive and the production rate of the co-product, acetone, exceeds market demand [2]. Therefore, a new route to produce phenol in one step is demanded. A potential route is the direct insertion of a hydroxyl group to

the benzene ring via the hydroxylation of benzene by hydrogen peroxide. Many researches have studied this reaction extensively and found that titanium silicalite-1 (commonly known in the name TS-1) is a potential catalyst since using TS-1 in the reaction can occur at a relative low temperature (i.e. 70-80°C), using H_2O_2 offers low cost per oxygen atom and the absence of by-products [3]. Despite the fact that TS-1 exhibits an excellent selectivity (near 100% to phenol), it suffers a major drawback i.e. its activity is quite low. Therefore, an improvement of its activity is needed. The present work introduces a method to enhance the catalytic activity of the TS-1 by adding a second metal to the TS-1. The selected metals are Fe, Al, Co and V.

Alkylbenzene is organic compound that has an alkyl group bound to a benzene ring. Theoretically, the alkyl group activates the ring and makes the ring of the alkylbenzene become more active than benzene ring. For the hydroxylation of alkylbenzene, fundamental theory suggests that a hydroxyl group should substitute a hydrogen atom at the ortho- or para- position [4]. For example, the hydroxylation of toluene by using molecule of oxygen can possibly gives o-cresol and/or p-cresol as products, both have a wide variety of usage including the manufacture of synthesis resins, insecticides and herbicides [5]. Despite the important of this reaction, the hydroxylation of alkyl benzenes gains little interest.

In a previous work investigated the hydroxylation of aromatic hydrocarbons (such as benzene, toluene and anisole) over TS-1/ H_2O_2 under triphase (catalyst-benzene- H_2O_2) and biphasic (catalyst-liquid (benzene- H_2O_2 -solvent)) conditions. The result obtained in the hydroxylation of toluene and anisole found the enhancement of reaction and para-hydroxy products were predominantly obtained under the triphase condition. For the

biphasic condition, the ortho-hydroxy product was preferred [6].

The purpose of this work is to study the insertion of a hydroxyl group directly on the ring of benzene and alkyl benzene over various metal modified TS-1 catalysts (Co-TS-1, V-TS-1, Fe-TS-1 and Al-TS-1) using H_2O_2 a stirred slurry reactor under triphase condition. The aim of this research is to explore a new route for organic synthesis that can make the reactants more valuable.

2. MATERIALS AND METHODS

2.1 Catalyst preparation

The source of metals for preparation of decantation and gel solutions were $Co(NO_3)_2 \cdot 6H_2O$ for Co, $FeCl_3 \cdot 6H_2O$ for Fe, VCl_3 for V, $Al(NO_3)_3 \cdot 9H_2O$ for Al as the second metal, $Ti[O(CH_2)_3CH_3]_4$ for Ti, and sodium silicate for Si. TPABr (Tetra-n-propyl ammonium bromide $[(CH_3CH_2CH_2)_4N]Br$) was used as organic template. The atomic ratio of Silicon/Titanium and Silicon/Metal were set at 50, 150, respectively. The reagents are listed in table 1.

Firstly, a gel mixture was prepared by adding solution A-1 and solution B-1 into solution C-1 dropwise with vigorous stirring using a magnetic stirrer at room temperature. The pH of the gel mixture was maintained within the range 9-11. The gel mixture was separated from the supernatant liquid by a centrifuge. Secondly, a decantation solution was prepared by adding solution A-2 and solution B-2 into solution C-2, same as for the preparation of gel mixture.

Table 1. Reagents used for the preparation of TS-1 and M-TS-1.

Solution for the gel preparation	Solution for decant-solution preparation
<u>Solution A1</u>	<u>Solution A2</u>
Ti[O(CH ₂) ₃ CH ₃] ₄ 2.2085 g	Ti[O(CH ₂) ₃ CH ₃] 2.2085 g
TPABr 5.72 g	TPABr 7.53 g
NaCl 11.95 g	De-ionized water 60 ml
Second metal x g	Second metal x g
De-ionized water 60 ml	H ₂ SO ₄ (conc.) 3.4 ml
H ₂ SO ₄ (conc.) 3.4 ml	
<u>Solution B1</u>	<u>Solution B2</u>
Sodium silicate 69 g	Sodium silicate 69 g
De-ionized water 45 ml	De-ionized water 45 ml
<u>Solution C1</u>	<u>Solution C2</u>
TPABr 2.16 g	NaCl 26.27 g
NaCl 40.59 g	De-ionized water 104 ml
NaOH 2.39 g	
De-ionized water 208 ml	
H ₂ SO ₄ (conc.) 1.55 ml	

The colorless liquids from A-2, B-2 and C-2 was separated from the mixture by a centrifuge then mixed together with the milled gel mixture. The mixture of the milled gel mixture and colorless liquids was filled into a pyrex glass which was placed in a stainless steel autoclave. The atmosphere in the autoclave was replaced by nitrogen gas and pressurized up to 3 kg/cm² gauge. Then, the autoclave was heated from room temperature to 160°C with a heating rate of 2°C/min, and then heating up to 210°C with a heating rate of 12°C/h while being stirred at 60 rpm, followed by cooling the mixture to room temperature in the autoclave overnight. The temperature was programmed under the hydrothermal treatment to minimize the time which was necessary for the crystallization. The product crystals were washed with de-ionized water by a centrifuge. Then the crystals were dried in an oven at 110°C after that were calcined in an air stream at 550°C and held at

that temperature for 7 h, by heating them from room temperature to 550°C for burn off the organic template and leave the cavities and channels in the crystals. Before, catalysts which were used in reaction, pretreated with a nitric acid (5 M) at 80°C for 3 h. After, they were washed with distilled water until pH 7, dried at 110°C and calcined at 540°C for 7 h in static air.

2.2 Catalyst characterization

2.2.1 X-Ray Diffraction (XRD)

The crystallinity and X-ray diffraction patterns of the catalysts were performed by an X-ray diffractometer SIEMENS D5000 connected with a computer with Diffract ZT version 3.3 program for fully control of XRD analyzer. The experiments were carried out by using Cu K α radiation with Ni filter. Scans were performed over the 2 theta ranges from 6 to 40.

2.2.2 Fourier transform Infrared (FT-IR)

The functional group on the catalyst surface was determined by FT-IR using Nicolet model Impact 400. Each sample was measured in diffuse reflectance mode. Infrared spectra were recorded between 400 and 1300 cm^{-1} on a microcomputer

2.2.3 BET surface area measurement

The sample cell which contained 0.1 g of sample was placed into BET Micromeritics ASAP 2020. After degassing step, the surface area and pore volume of catalyst were measured.

2.2.4 X-Ray Fluorescence Spectrometer (XRF)

The chemical composition analysis of elements of the catalyst was performed by X-ray fluorescence (XRF) using Siemens SRS3400.

2.2.5 NH_3 Temperature Programmed Desorption (NH_3 -TPD).

Temperature programmed desorption of ammonia (NH_3 -TPD) was used to determine the acid properties of catalysts by measuring the areas of the desorption profiles obtained from the Micromeritics Chemisorb 2750 analyzer.

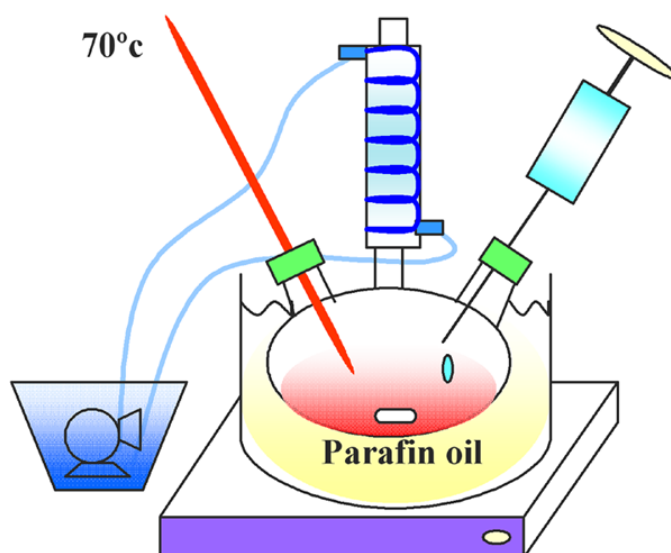


Figure 1. The hydroxylation reactor.

2.3 Reaction study in the hydroxylation of benzene

The hydroxylation of benzene and alkyl benzene (toluene) with H_2O_2 (30 wt% in water, Merk) was carried out in a 250 ml, water jacketed, three-necked, glass flask fitted with a condenser and a mechanical stirrer placed in a stirring block heater as shown in Figure 1. The reaction was performed at atmospheric pressure. Typically, 1 g of a catalyst was reacted with reactant as benzene

and alkyl benzene to H_2O_2 molar ratio equals to 1 to 1 (1.0 ml H_2O_2 , 0.9 ml C_6H_6 , 1.1 ml C_7H_8 and 50 ml of water). After reactant and H_2O_2 was added into reactor. For H_2O_2 was slowly injected drop-wise using a 1 ml syringe at 70 °C for 2 h. After the reaction has been stopped, 50 ml of ethanol was added into reactor to homogenize the aqueous phase and the organic phase. The products were analyzed by a gas chromatograph equipped with a FID detector (SHIMADZU GC9A).

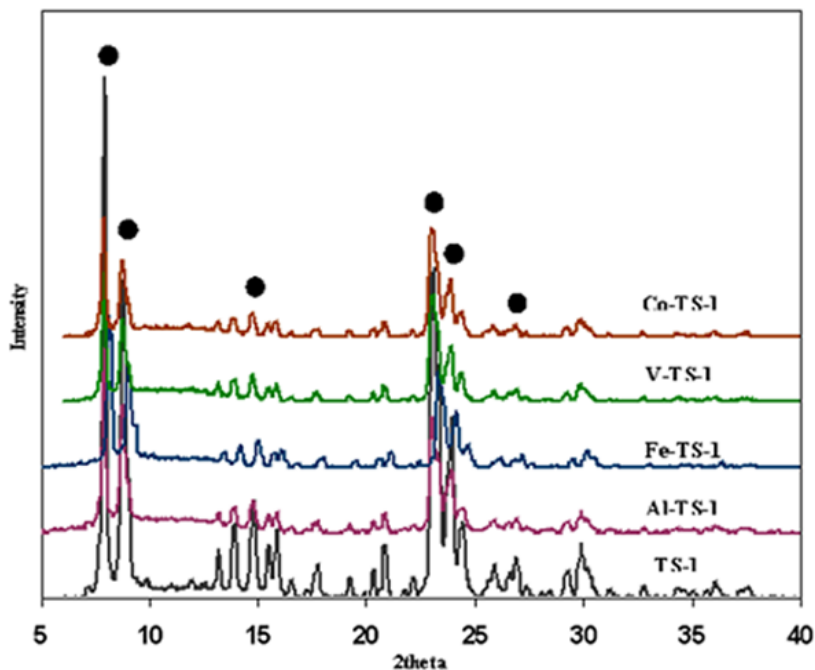


Figure 2. The XRD patterns of the modified TS-1.

3. RESULTS AND DISCUSSION

3.1 Catalyst characterization

3.1.1 X-ray diffraction (XRD)

Figure 2 shows the XRD patterns of TS-1 and modified TS-1. They present six main peaks at 2 theta as 8, 8.8, 14.8, 23.1 and 26.7. The pattern obtained as the especially pattern for a crystalline zeolite having a MFI structure [7]. They have no peak at 2 theta \approx 25.3, represents the anatase TiO₂ phase. Therefore, all TS-1 synthesized using TPABr as template

does not contain anatase. After the catalysts were pretreated with HNO₃, it is found that the structures are not destroyed by the pretreatment.

3.1.2 Determination of surface area by BET

The surface areas in Table 2, the correlation between BET surface area and average pore size diameter of each sample shows the microporous being a major contributor to area surface.

Table 2. Composition and surface area.

Sample	A _{BET} (m ² /g)	Poresize (Å ^o)
TS-1	321.72	28.76
Co-TS-1	361.62	26.99
V-TS-1	354.87	26.73
Fe-TS-1	344.27	25.62
Al-TS-1	331.71	26.96

3.1.3 Determination of composition by X-ray Fluorescence spectroscopy (XRF).

The compositions of TS-1 and modified TS-1 are shown in Table 3 below. 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 Ti^{4+} ion in the formation of TS-1 structure.

Table 3. XRF analysis TS-1 and modified TS-1.

Sample	%Si	%Ti	%M	%Si/Ti	%Si/M	%TiO ₂
TS-1	32.97	0.22	none	150.63	none	0.77
Co-TS-1	33.06	0.12	0.027	276.86	1220	0.47
V-TS-1	33.05	0.11	0.022	282.24	1535	0.43
Fe-TS-1	32.92	0.21	0.055	158.67	590	0.78
Al-TS-1	33.09	0.18	0.066	182.59	503	0.77

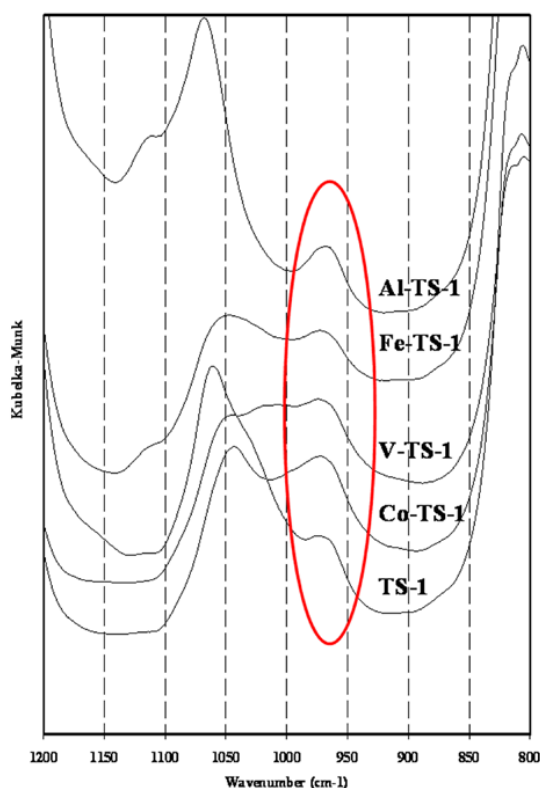


Figure 3. The wave number of the modified TS-1.

3.1.4 Fourier-transform infrared spectroscopy (FT-IR)

The stronger the band at 960 cm^{-1} the more titanium atoms incorporated into the framework. [8]. Besides, the research from reported the IR at the position 960 cm^{-1} that is band typical for tetrahedral group $Ti(OSi)_4$ appears in the silicalite spectrum [2, 9-10].

Figures 3 presents the characteristic absorption band of tetrahedral Ti^{4+} in the modified TS-1 and M-TS-1 which have the band at 960 cm^{-1} that indicates they have strong framework titanium species.

3.1.5 Temperature Programmed Desorption (TPD)

NH_3 -TPD was used to determine the strength and amount of the acid site of the catalysts. It is found that each NH_3 -TPD profile can be deconvoluted into two main peaks. The first peak, will be named here “the weaker acid site”, appears around $120\text{-}145^\circ\text{C}$.

The second peak, will be named here “the stronger acid site”, appears around 202-403°C. The result shows the increase of the stronger acid sites in the following order: TS-1 < Al-TS-1 < Fe-TS-1 < V-TS-1 < Co-TS-1. Therefore, the added second metals make catalysts which have more amount of the acid site.

3.2 Hydroxylation benzene

The result of benzene hydroxylation using TS-1 and M-TS-1 at 70°C for 3 hr, shows in the Figure 4, reveals that the catalytic activity is in the following order Co-TS-1 > V-TS-1 > Fe-TS-1 > Al-TS-1 > TS-1. The maximum benzene conversion was achieved with Co-TS-1 about 14.775 %.

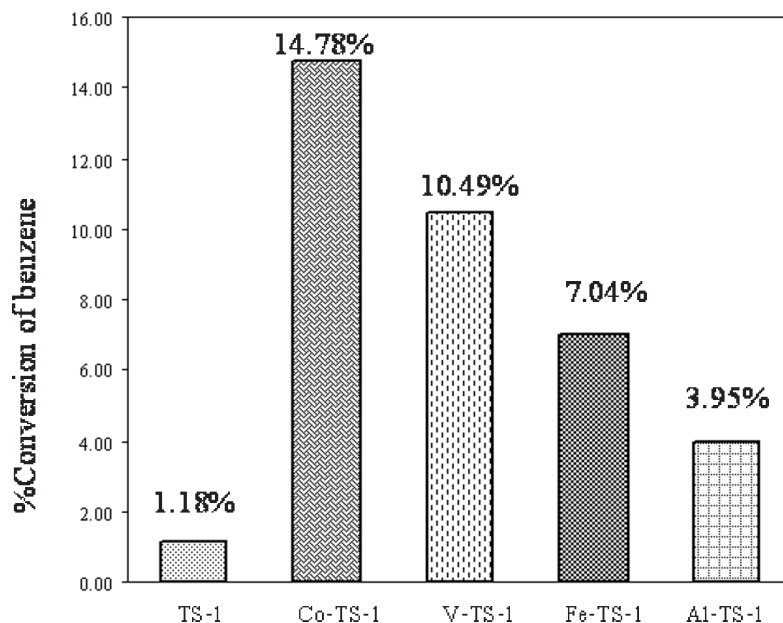


Figure 4. The hydroxylation of benzene with H_2O_2 using TS-1 and modified TS-1.

3.3 The decomposition of H_2O_2 and the adsorption of phenol formed on the catalyst surface

It is hypothesized that the enhanced catalytic activity of the modified catalysts relates to the ability of the catalyst in inhibiting (a) the decomposition of H_2O_2 and (b) the adsorption of phenol formed on the catalyst surface. To verify the above hypotheses, two more experiments were performed.

To quantify the decomposition of H_2O_2 , 1 g of catalyst with 1.27 g of aqueous H_2O_2 (1 ml) is mixed at 70°C for 3 hr and then titrate with the standard $KMnO_4$ solution. The titration is carried out until the colour of the solution became purple (all H_2O_2 was

consumed). The more the $KMnO_4$ solution used, the more H_2O_2 remained. The results are shown in the Figure 5. It is found that the decomposition of H_2O_2 is in the following order Co-TS-1 < V-TS-1 < Fe-TS-1 < Al-TS-1 < TS-1 which shows that the catalyst with higher activity decomposed lower amount of H_2O_2 . Therefore, more H_2O_2 is provided for the reaction.

To determine the phenol adsorption capacities of the catalysts, a phenol solution is prepared and divides into 6 tubes which are blank, added with Co-TS-1, V-TS-1, Fe-TS-1, Al-TS-1 and TS-1. The amount of phenol remained in each solution was measured at 3 and 11 hours.

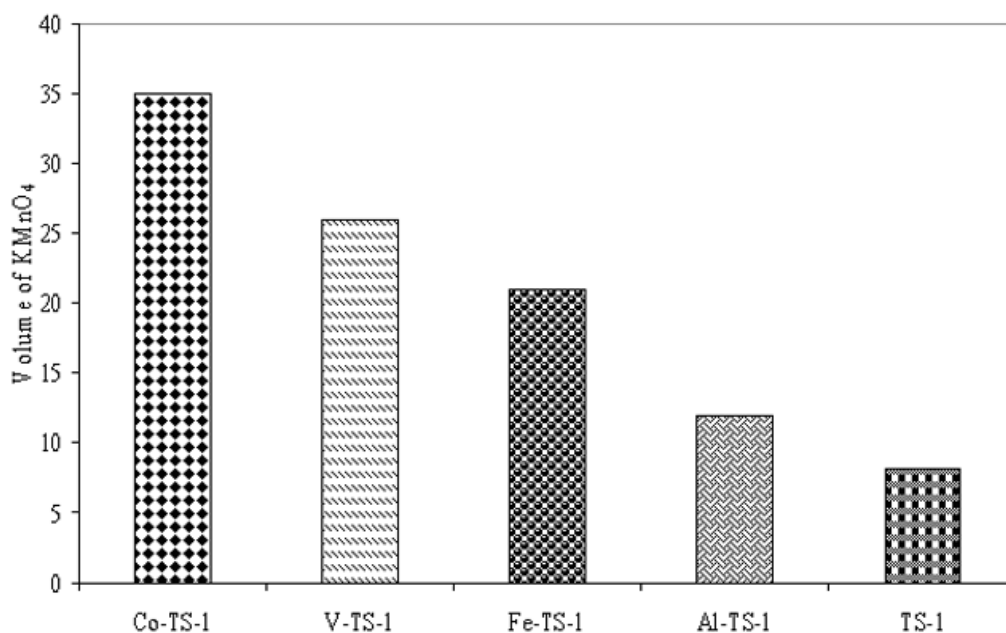


Figure 5. The titration of hydrogen peroxide solutions with standardize KMnO_4

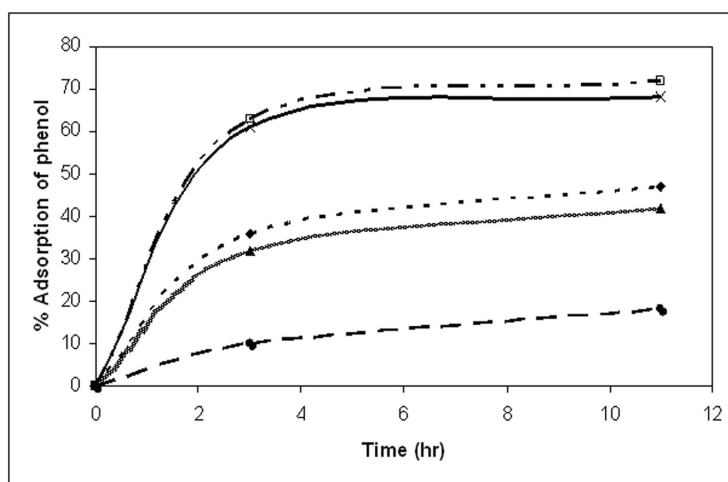


Figure 6. The adsorption of phenol of Co-TS-1(●), V-TS-1 (▲), Fe-TS-1(◆), Al-TS-1(×) and TS-1(□) catalysts.

The lower the concentration of phenol in the liquid phase the higher the amount of phenol on the catalyst surface. The results are shown in Figure 6. The graphs show that the catalyst with higher activity can adsorb less phenol, thus having more number of active site available for the reaction.

3.4 Pre-study on toluene hydroxylation

The results obtained from benzene and toluene hydroxylation by using reactants to H_2O_2 molar ratio 1:1 and 1.0 g of TS-1 for 2 hr at 70°C under triphase condition is reported in Table 3. The product obtained from benzene hydroxylation is phenol while the

Table 4. Products of hydroxylation.

Reactants	Product	conversion ^a	Productivity ^b
Benzene	Phenol	4.67	0.075
Toluene	o-cresol	0.41	0.005
	p-cresol	0.89	0.011

a: the conversion of reactants (mol%) and b: the productivity of products ($\mu\text{mol}/\text{sec}$)

hydroxylation of toluene produced o-cresol and p-cresol as the only observed products. Table 3 indicates that p-cresol is more predominant than o-cresol which means that the presence of the methyl group hinders the substitution at the ortho-position. The higher conversion of the hydroxylation of benzene is likely due to the higher diffusivity of benzene, compared to toluene, because of the absence of a branch substitution group on the ring.

4. CONCLUSIONS

The hydroxylation of benzene gives phenol as the main product with trace amount of di-substitution products. The effect of adding a second metal to catalyst shows catalytic activity in the following order Co-TS-1 > V-TS-1 > Fe-TS-1 > Al-TS-1 > TS-1. It has been demonstrated that the catalytic activity relates to the ability of the catalyst in inhibiting (a) the decomposition of H_2O_2 and (b) the adsorption of phenol formed on the catalyst surface. The hydroxylation of toluene produces two main products i.e. o-cresol and p-cresol with the latter as the major product. The fact that the reaction occurs mainly at the para position indicates that the presence of the alkyl group hinders the insertion of a hydroxyl group at the ortho position, i.e. steric effect. For the same reaction time and same mole ratio of reactants, the observed benzene conversion is higher than the observed toluene conversion. This suggests that the reaction is

controlled by pore diffusion of the organic reactant.

REFERENCES

- [1] Manit P., Hydroxylation of benzene to phenol using hydrogen peroxide in a bubble reactor, Master Thesis, Chulalongkorn University, Thailand, 2006
- [2] Pirutko, L. V., Uriarte, A. K., Chernyavsky, V. S., Kharitonov, A. S., and Panov, G. I., Preparation and catalytic study of metal modified TS-1 in the oxidation of benzene to phenol by N_2O , *Micropor. Mesopor. Mater.*, 2001; 48: 345-353.
- [3] Shenchunthichai K., Catalytic study of iron, aluminium, cobalt and vanadium modified titanium silicalites-1 in the hydroxylation of benzene to phenol by hydrogen peroxide, Master Thesis, Chulalongkorn University, 2004.
- [4] Robert C. Atkins and Francies Carey A., *Organic chemistry: a brief course* 3rd ed., McGraw-Hill, New York, 1944.
- [5] Mita S., Sakamoto, Yamada S., Sakaguchi S. and Ishii Y., Direct hydroxylation of substituted benzenes to phenols with air and CO using molybdovanadophosphates as a key catalyst, *Tetrahedron Letters.*, 2005; 46: 7729-7732.
- [6] Kumar R., Mukherjee P. and Bhaumik A., Enhancement in the reaction rates in the hydroxylation of aromatics over TS-1/

- H₂O₂ under solvent-free triphase condition, *Cat.Today.*, 1999; 49: 185-191.
- [7] Zhao, Q., Bao, X.H., Han, X.W., Liu, X.M., Tan, D.L., Lin, L.W., Guo, X.W., Li, G. and Wang, X.S., Studies on the crystallization process of titanium silicalite-1 (TS-1) synthesized using tetrapropylammonium bromide as a template, *Material Chemistry and Physics.*, 2000; 66: 41-50.
- [8] Li, G., Wang, X., Guo, X., Liu, S., Zhao, Q., Bao, X. and Lin, L., Titanium species in titanium silicalite TS-1 prepared by hydrothermal method. *Mater, Chem. Phys.*, 2001; 71: 195-201.
- [9] Zecchina, A., Spoto, G., Bordiga, S. Padovan, M. and Leofanti, G., Catalysis and absorption by zeolites, *Stud. Surf. Sci. Catal.*, 1991;30: 67.
- [10] Bolis, V., Bordiga, S., Lamberti, C., Zecchina, A., Carati, A., Rivetti, C., Spano, G. and Petrini, G., A calorimetric, IR, XANES and EXAFS study of the adsorption of NH₃ on Ti-silicalite as a function of the sample pre-treatment, *Micropor. Mesopor. Mater.*, 1999;30: 67-76.