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APPENDICES

APPENDIX A

CALCULATION FOR CATALYST PREPARATION

The calculation is based on weight of Sodium Silicalite ($\text{Na}_2\text{O}\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$) in B1 and B2 solutions (Topic 4.1.2).

$$\text{Molecular Weight of Si} = 28.0855$$

$$\text{Molecular Weight of SiO}_2 = 60.0843$$

$$\text{Weight percent of SiO}_2 \text{ in sodium Silicate} = 28.5$$

Using Sodium Silicate 69 g with 45 g of water as B1 solution.

$$\begin{aligned} \text{mole of Si used} &= \text{wt.} \times \frac{(\%)}{100} \times \frac{(\text{M.W. of Si})}{(\text{M.W. of SiO}_2)} \times \frac{(1 \text{ mole})}{(\text{M.W. of Si})} \\ &= 69 \times (28.5/100) \times (1/60.0843) \\ &= 0.3273 \end{aligned}$$

MFI catalyst

For example , to prepare Si/Ti atomic ratio of 50 by using $\text{Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4$ for titanium source.

$$\text{Molecular weight of Ti} = 47.88$$

$$\text{Molecular weight of } \text{Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4 = 340.36$$

$$\text{Weight \% purities of } \text{Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4 = 97$$

Si/Ti atomic ratio = 50

$$\text{Mole of } \text{Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4 \text{ required} = 0.3273/50$$

$$= 6.546 \times 10^{-3} \text{ mole}$$

$$\text{amount of } \text{Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4 = (6.546 \times 10^{-3}) \times (340.36) \times (100/97)$$

$$= 2.2970 \text{ g}$$

For example, to prepare Si/Co atomic ratio of 150 by using $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ for cobalt source.

$$\begin{aligned}\text{Molecular weight of Co} &= 58.93 \\ \text{Molecular weight of } \text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} &= 291.03\end{aligned}$$

Si/Ti atomic ratio = 30

$$\begin{aligned}\text{Mole of } \text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} \text{ required} &= 0.3273/150 \\ &= 2.18 \times 10^{-3} \text{ mole} \\ \text{amount of } \text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} &= (2.18 \times 10^{-3}) \times (291.03) \\ &= 0.635 \text{ g}\end{aligned}$$

which used in A1 and A2 solutions.

APPENDIX B

DATA AND CALCULATION OF ACID SITE

Table B1 Reported total peak area from Micromeritics Chemisorb 2750

Catalysts	Reported total peak
TS-1	0.204749
Co-TS-1	0.232555
Al-TS-1	0.038862
V-TS-1	0.051934
Fe-TS-1	0.044416

Calculation of total acid sites

For example, TS-1, total acid site is calculated from the following step.

1. Conversion of total peak area to total peak volume

Conversion factor from Micromeritics Chemisorb 2750 is equal to 77.57016 ml/area unit. Therefore, total peak volume is derived from

$$\begin{aligned}
 \text{Total peak volume} &= 77.57016 \times \text{total peak area} \\
 &= 77.57016 \times 0.204749 \\
 &= 15.86838 \text{ ml}
 \end{aligned}$$

2. Calculation for adsorbed volume of 15% NH₃

$$\begin{aligned} \text{Adsorbed volume of 15\% NH}_3 &= 0.15 \times \text{total peak volume} \\ &= 0.15 \times 15.86838 \text{ ml} \\ &= 2.380356 \text{ ml} \end{aligned}$$

3. Total acid sites are calculated from the following equation

$$\text{Total acid sites} = \frac{(\text{Adsorbed volume, ml}) \times 101.325 \text{ Pa}}{\left(8.314 \times 10^{-3} \frac{\text{Pa} \cdot \text{ml}}{\text{K} \cdot \mu\text{mol}}\right) \times 298 \text{ K} \times (\text{weight of catalyst, g})}$$

For TS-1 sample, 0.2085 g of this one was measured, therefore

$$\begin{aligned} \text{Total acid sites} &= \frac{0.65826 \text{ ml} \times 101.325 \text{ Pa}}{\left(8.314 \times 10^{-3} \frac{\text{Pa} \cdot \text{ml}}{\text{K} \cdot \mu\text{mol}}\right) \times 298 \text{ K} \times (0.2085 \text{ g})} \\ &= 468 \mu\text{mol H}^+/\text{g} \end{aligned}$$

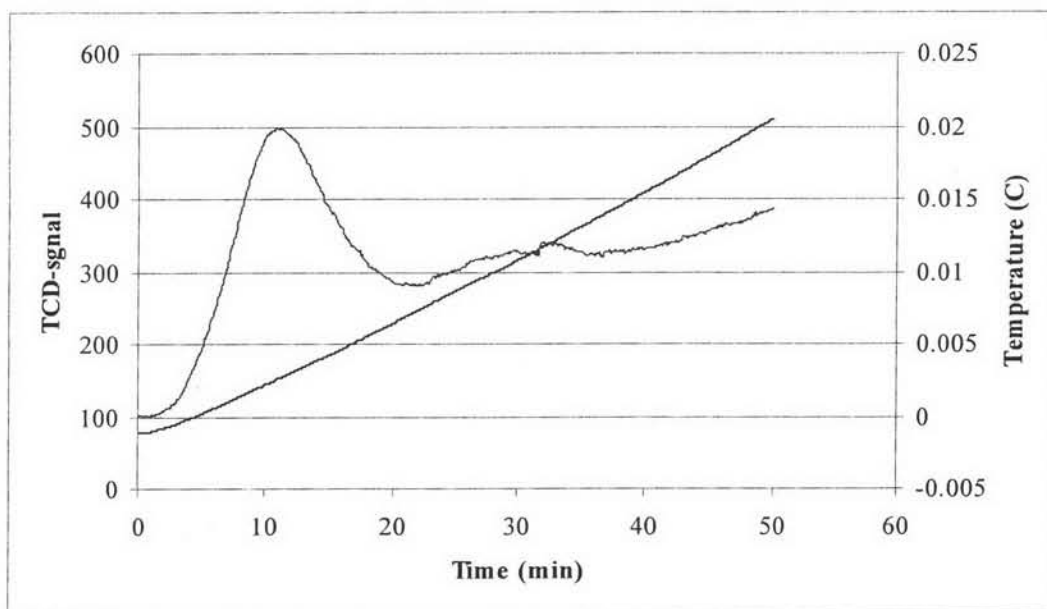


Figure B1 TCD signal and temperature versus time data of TS-1 from Micromeritics Chemisorb 2750

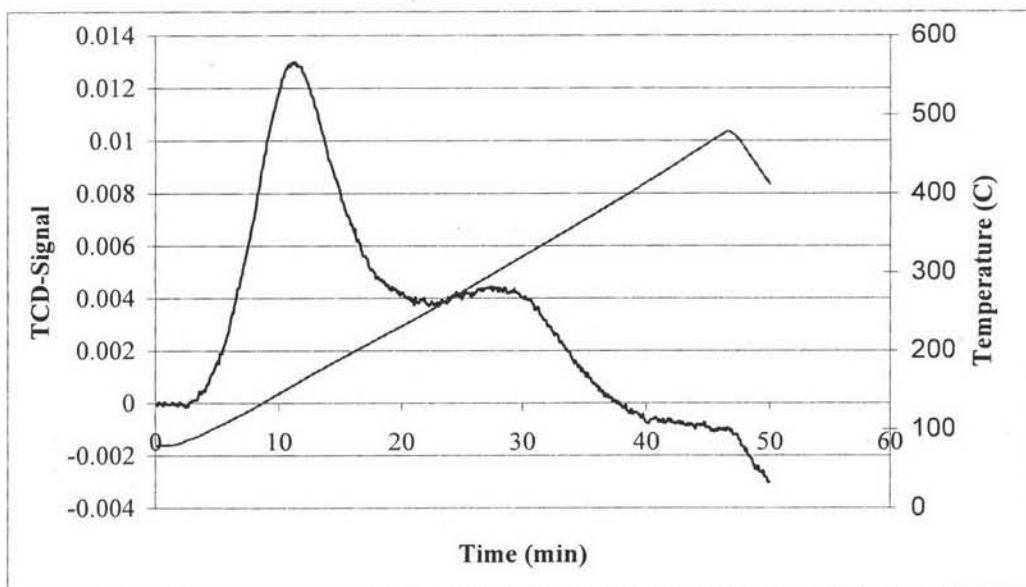


Figure B2 TCD signal and temperature versus time data of Co-TS-1 from Micromeritics Chemisorb 2750

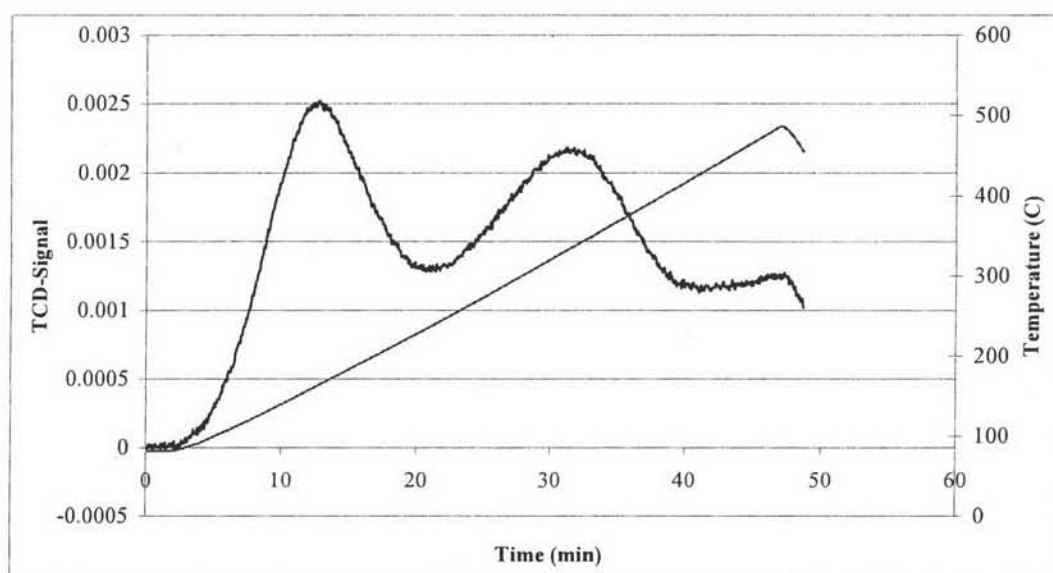


Figure B3 TCD signal and temperature versus time data of Al-TS-1 from Micromeritics Chemisorb 2750

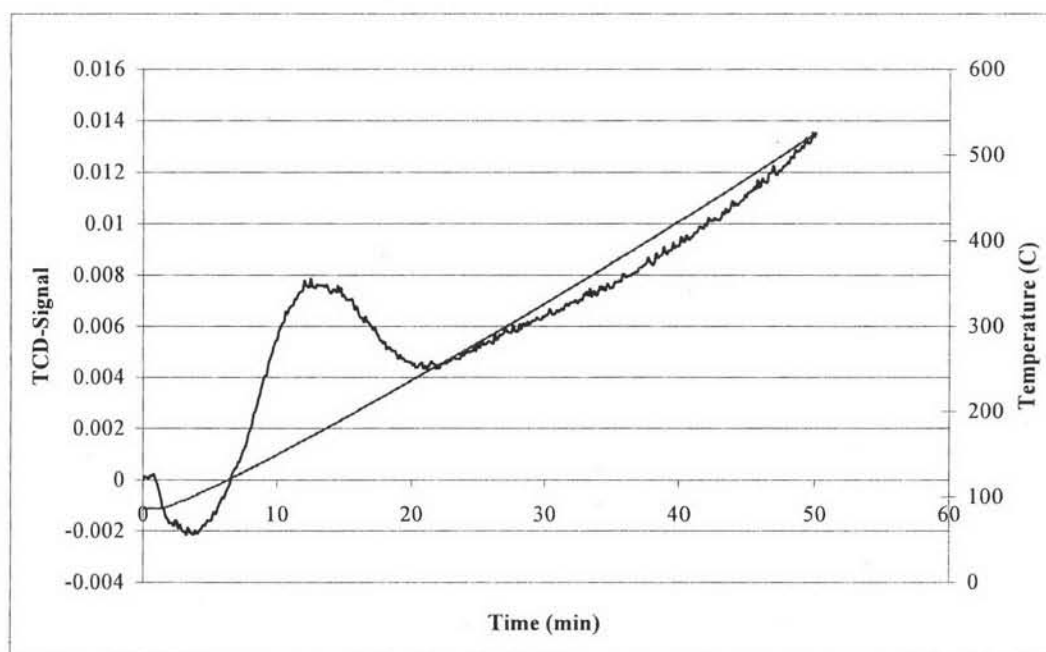


Figure B4 TCD signal and temperature versus time data of V-TS-1 from Micromeritics Chemisorb 2750

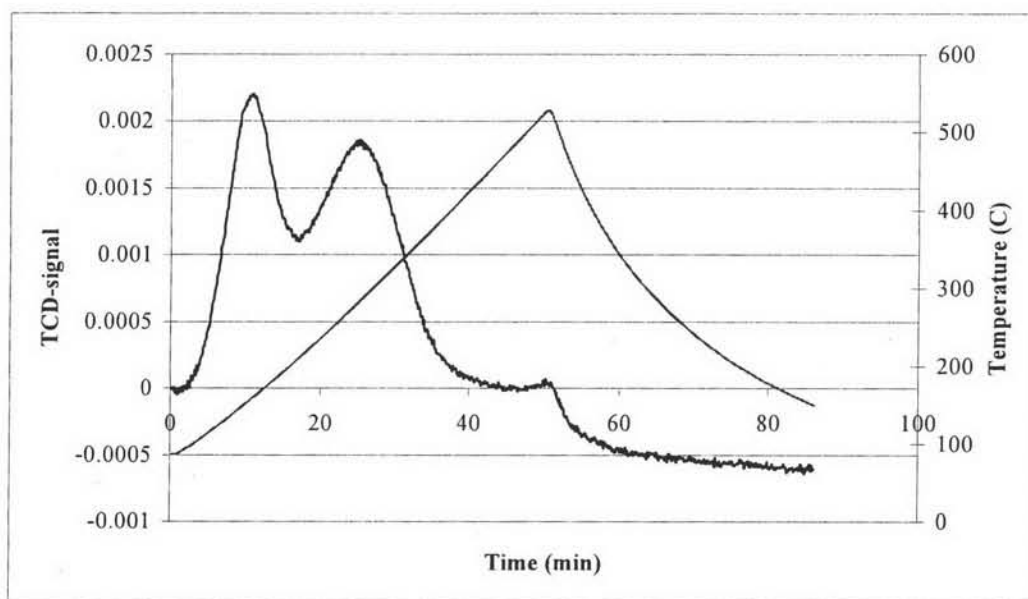


Figure B5 TCD signal and temperature versus time data of Fe-TS-1 from Micromeritics Chemisorb 2750

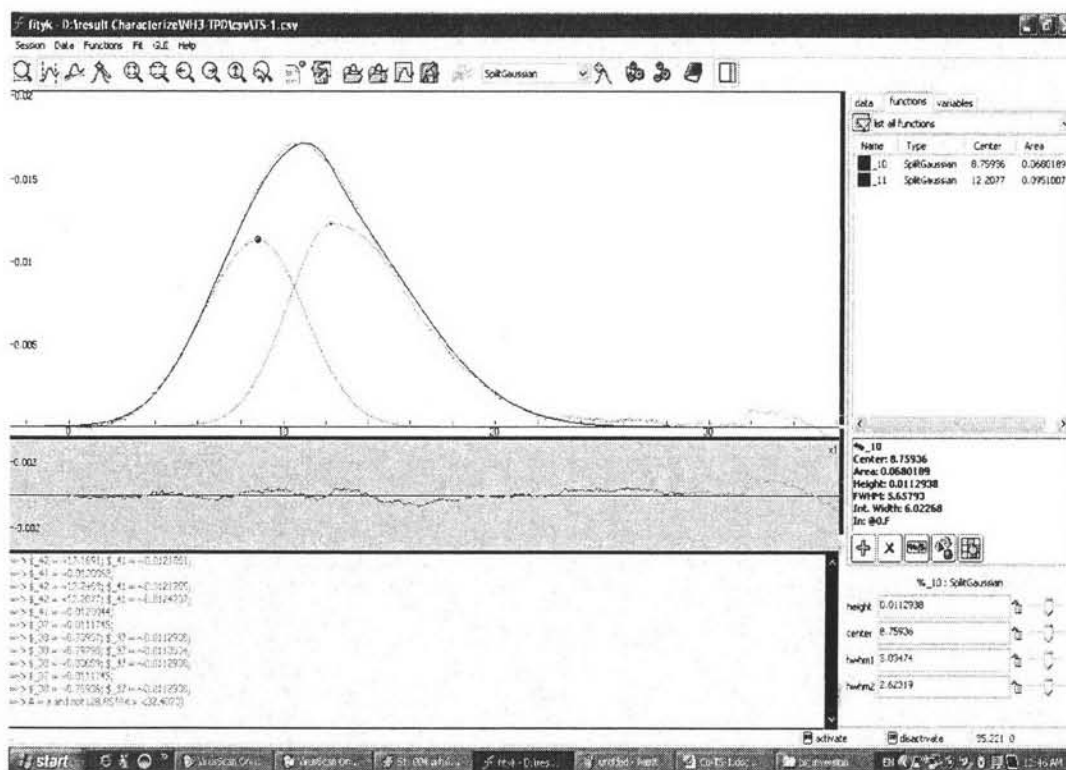


Figure B6 Data for calculating of acid site ratio of TS-1 from peak fitting program

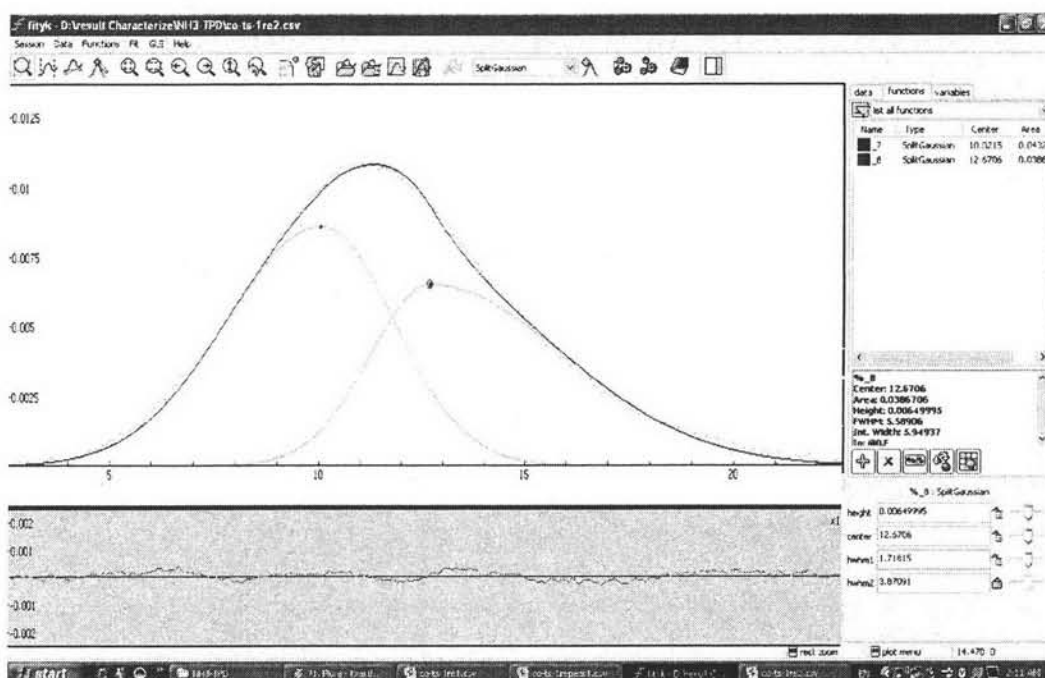


Figure B7 Data for calculating of acid site ratio of Co-TS-1 from peak fitting program

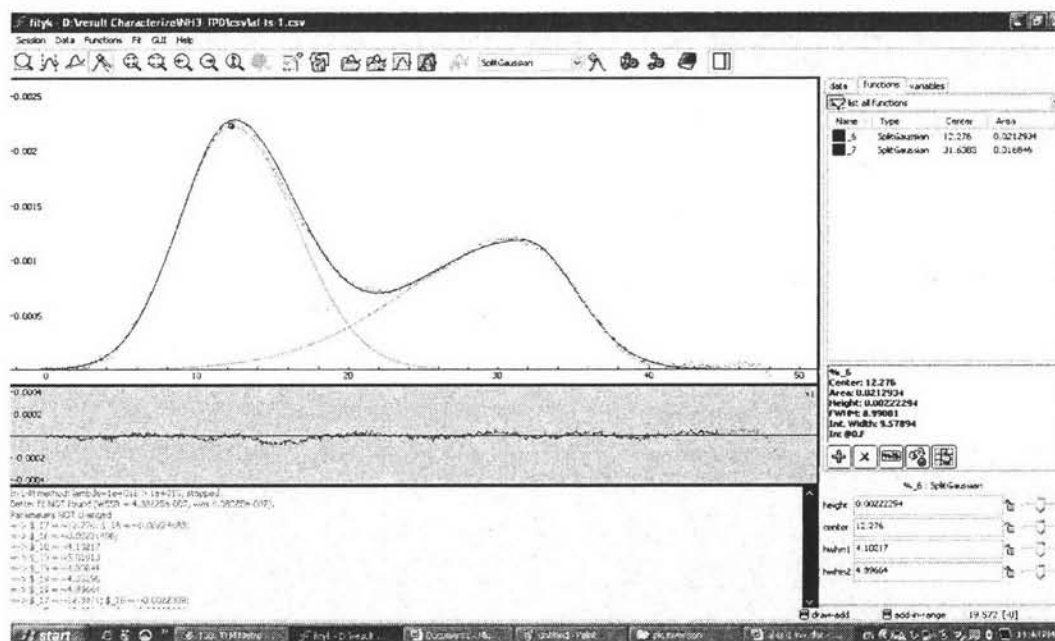


Figure B8 Data for calculating of acid site ratio of Al-TS-1 from peak fitting program

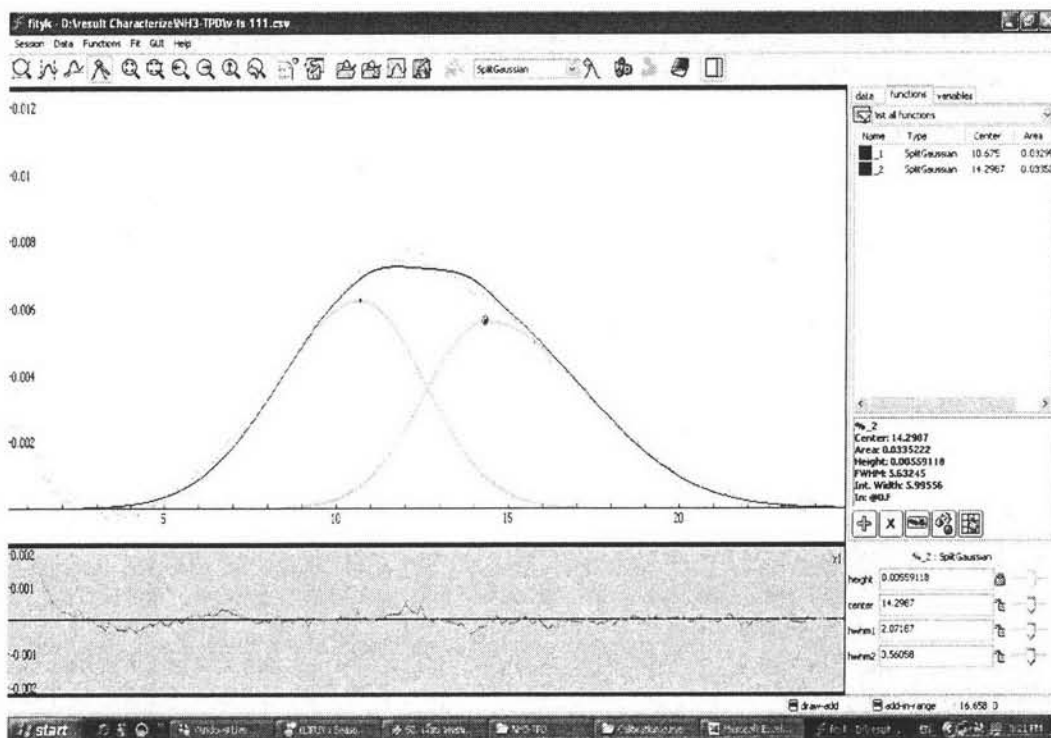


Figure B9 Data for calculating of acid site ratio of V-TS-1 from peak fitting program

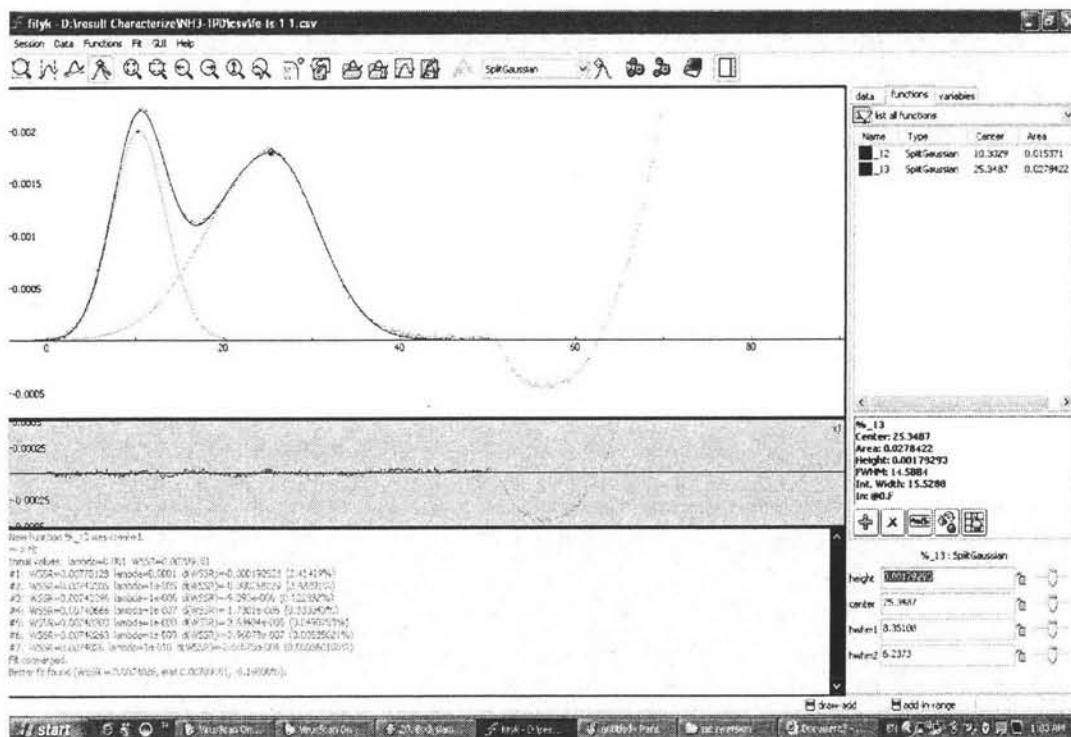


Figure B10 Data for calculating of acid site ratio of Fe-TS-1 from peak fitting program

Calculation of acid site ratio

To calculate acid site ratio, experiment data from Micromeritics Chemisorb 2750 are transferred to peak fitting program to separate peak. As known, the first peak of desorption process is indicated as weak acid, relative with another peak, and the second one is strong acid. Ratio of each acid site on the catalyst surface is calculated from peak areas reported by peak fitting program as shown above.

For example, TS-1, the ratio of each acid site on catalyst surface is calculated from the following equation.

$$\text{The ratio of weak acid} = \frac{1^{\text{st}} \text{ peak area}}{\text{summation of both peak areas}} \times 100 \%$$

From figure D10, 1st peak area and 2nd peak area are equal to 0.091673 and 0.061673, respectively.

$$\begin{aligned} \text{The ratio of weak acid} &= \frac{0.091673}{0.091673 + 0.061673} \times 100 \% \\ &= 59.92 \% \end{aligned}$$

$$\begin{aligned} \text{Therefore, the ratio of strong acid} &= 100 - 59.92 \% \\ &= 40.08 \% \end{aligned}$$

Note. Reported center values of both peaks from peak fitting program reveal times at the maximum of both peaks occur. Since, we know the relationship between time and temperature during desorption process from Micromeritics Chemisorb 2750, hence, the temperature at the maximum of both peaks as we state as desorption temperature of both acid sites can be located.

APPENDIX C

CALCULATION OF METAL QUANTITY

Example of the calculation of the metal quantity in VCl_3_A1 catalyst

The XRF results were reported in the amount of metal oxide as shown in table C1

Table C1 Data from XRF technique

Metal oxide	Concentration
K_2O	234 ppm
CaO	123 ppm
TiO_2	0.75 Wt%
V_2O_5	0.42 Wt%
Fe_2O_3	186 ppm
Cu_2O	83 ppm
ZnO	61 ppm
ZrO_2	33 ppm
MoO_2	2 ppm
SiO_2	98.75 Wt%
Br	45 ppm

Molecular weights of the metal oxides are shown as follow:

K_2O	94.196	Fe_2O_3	159.6922	MoO_2	127.9388
CaO	56.0794	Cu_2O	143.0914	SiO_2	60.0843
TiO_2	236.3818	ZnO	81.3894	Br	79.904
V_2O_5	181.88	ZrO_2	123.2228		

1. Convert concentration in unit ppm to weight%

For example, convert K_2O 234 ppm to weight%

$$K_2O \text{ 234 ppm} = \frac{234}{1,000,000} \times 100 = 0.0234 \text{ wt\%}$$

2. Mole of metal oxides

$$\text{Mole of } K_2O = \frac{\text{weight of } K_2O}{\text{molecular weight of } K_2O}$$

$$\text{Mole of } K_2O = \frac{0.0234}{94.196} = 2.484 \times 10^{-4} \text{ mole}$$

3. Mole of cation (e.g. potassium: K)

Mole of cation = (number of cation atom) \times (mole of metal oxide)

$$\begin{aligned} \text{Mole of K} &= (2) \times (2.484 \times 10^{-4}) \\ &= 4.968 \times 10^{-4} \text{ mole} \end{aligned}$$

4. Mole percent of cation (e.g. potassium: K)

$$\text{Mole \% of K} = \frac{\text{mole of K}}{\text{total mole of cations}}$$

$$\text{Mole \% of K} = \frac{4.968 \times 10^{-4}}{1.650} = 0.0301 \text{ mole\%}$$

Calculated weight%, mole of metal oxide, mole of metal and mole% of cation are illustrated in table C2.

Table C2 Calculated weight%, mole of metal oxide, mole of metal

Metal oxides	Concentration	weight%	mole of metal oxide	mole of metal	Mole% of cation
K ₂ O	234 ppm	0.0234	2.484×10^{-4}	4.968×10^{-4}	0.0301
CaO	123 ppm	0.0123	2.193×10^{-4}	2.193×10^{-4}	0.0133
TiO ₂	0.75 Wt%	0.75	3.173×10^{-3}	3.173×10^{-3}	0.1920
V ₂ O ₅	0.42 Wt%	0.42	2.310×10^{-3}	4.620×10^{-4}	0.2795
Fe ₂ O ₃	186 ppm	0.0186	1.165×10^{-4}	2.329×10^{-4}	0.0141
Cu ₂ O	83 ppm	0.0083	5.800×10^{-5}	1.160×10^{-4}	0.0070
ZnO	61 ppm	0.0061	7.495×10^{-5}	7.495×10^{-5}	0.0045
ZrO ₂	33 ppm	0.0033	2.678×10^{-5}	2.678×10^{-5}	0.0016
MoO ₂	2 ppm	0.0002	1.563×10^{-5}	1.563×10^{-6}	0.0000945
SiO ₂	98.75 Wt%	98.75	1.644	1.644	99.4544
Br	45 ppm	0.0045	5.632×10^{-5}	5.632×10^{-5}	0.0034
Total		99.9967	1.6498	1.650	100

Sample: 503429 VTSL
 Tue 11/20/2007 at 3:02:37 PM
 Method Name: 503429 VTisi

V-TS-1

Analyte	Concentration	Intensity
CaO	657 ppm	25.0
TiO ₂	9.37 wt %	6196.1
V ₂ O ₅	0.49 wt %	29.0
Fe ₂ O ₃	1142 ppm	36.6
CuO	197 ppm	19.8
ZnO	130 ppm	18.3
ZrO ₂	90 ppm	19.1
SiO ₂	89.92 wt %	13655.2

Sample: 503196_Si Ti Co
 Fri 11/09/2007 at 2:29:21 PM
 Method Name: 503196

Co-TS-1

Analyte	Concentration	Intensity
SiO ₂	98.05 wt %	14139.4
CaO	148 ppm	21.1
TiO ₂	1.60 wt %	4066.3
Fe ₂ O ₃	358 ppm	32.6
CoO	0.25 wt %	358.6
CuO	73 ppm	19.6
ZnO	97 ppm	36.5
ZrO ₂	34 ppm	28.5

Sample: 503196_Si Ti
Fri 11/09/2007 at 2:37:58 PM
Method Name: 503196

TS-1

Analyte	Concentration	Intensity
SiO2	97.95 wt %	14069.8
CaO	223 ppm	34.0
TiO2	1.96 wt %	5256.1
Fe2O3	388 ppm	35.1
CoO	0.00 wt %	-1.8
CuO	51 ppm	14.3
ZnO	68 ppm	26.8
ZrO2	32 ppm	27.0

Sample: 510137 No.5
Tue 1/22/2008 at 1:35:23 PM
Method Name: 510137

Fe-TS-1

Analyte	Concentration	Intensity
SiO2	89.99 wt %	12474.1
CaO	468 ppm	15.0
TiO2	6.59 wt %	3737.4
Fe2O3	3.33 wt %	943.2
Cu2O	193 ppm	16.4
ZnO	129 ppm	13.8
ZrO2	102 ppm	19.1

Sample: 510137 No.6
Tue 1/22/2008 at 1:42:30 PM
Method Name: 510137

AI-TS-1

Analyte	Concentration	Intensity
Al2O3	0.65 wt %	43.5
SiO2	92.35 wt %	12094.4
CaO	543 ppm	21.1
TiO2	6.73 wt %	4654.5
Fe2O3	1172 ppm	35.4
Cu2O	187 ppm	19.6
ZnO	107 ppm	14.2
ZrO2	67 ppm	13.3

APPENDIX D

CALIBRATION CURVES

This appendix shows the calibration curves for calculation of composition of reactant and products in hydroxylation of benzene reaction. The reactant is benzene and the main product is phenol.

The flame ionization detector, gas chromatography Shimadzu model 9A was used to analyze the concentration of benzene and phenol by using GP 10% SP-2100 column.

Mole of reagent in y-axis and area reported by gas chromatography in x-axis are exhibited in the curves. The calibration curve of o-cresol is illustrated in the following figure.

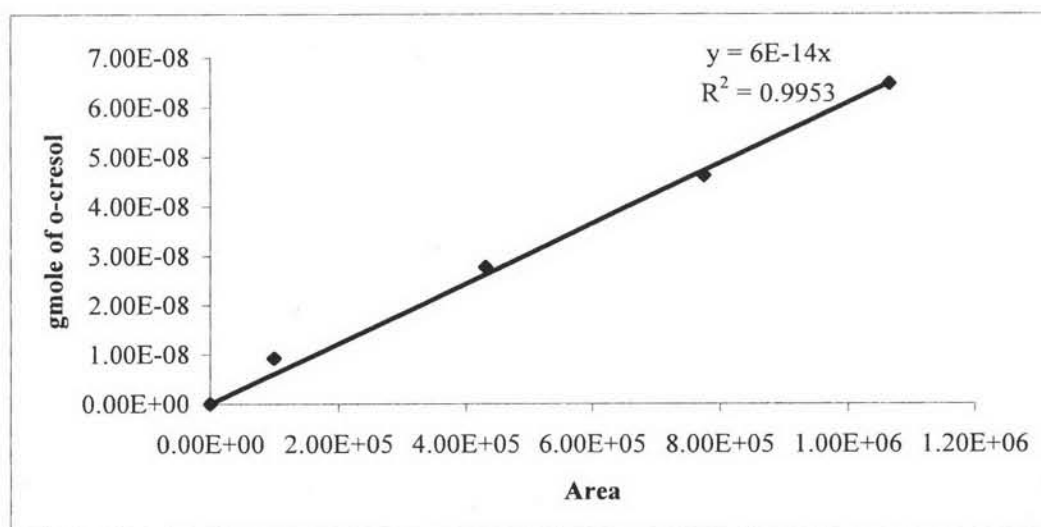


Figure D1 The calibration curve of o-cresol.

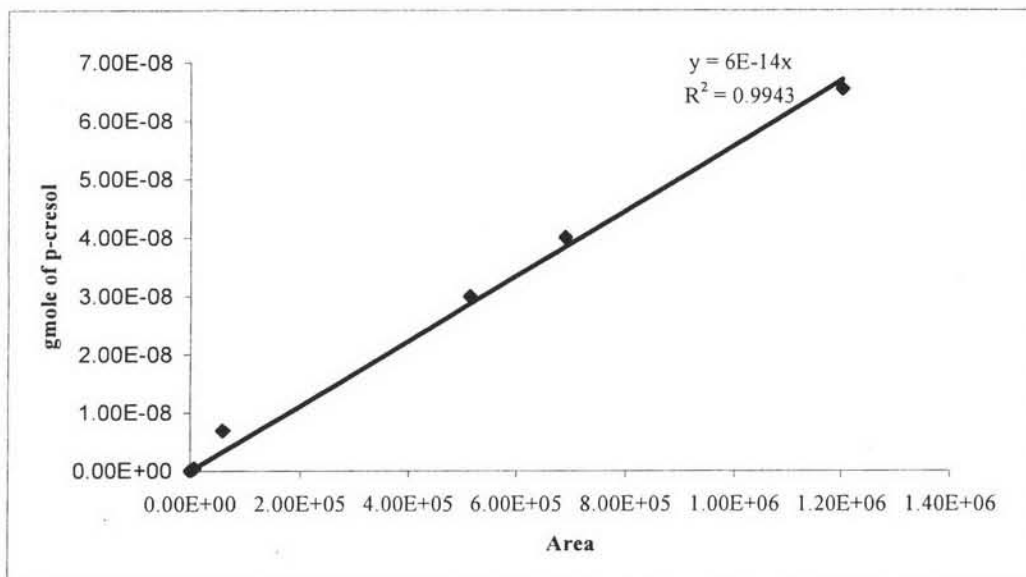


Figure D2 The calibration curve of p-cresol.

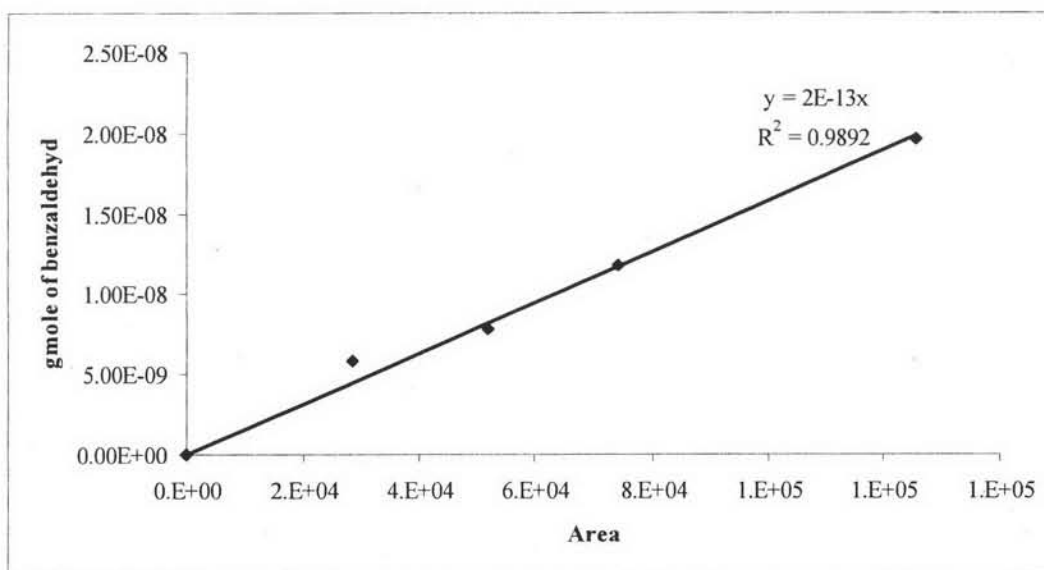


Figure D3 The calibration curve of benzaldehyd.

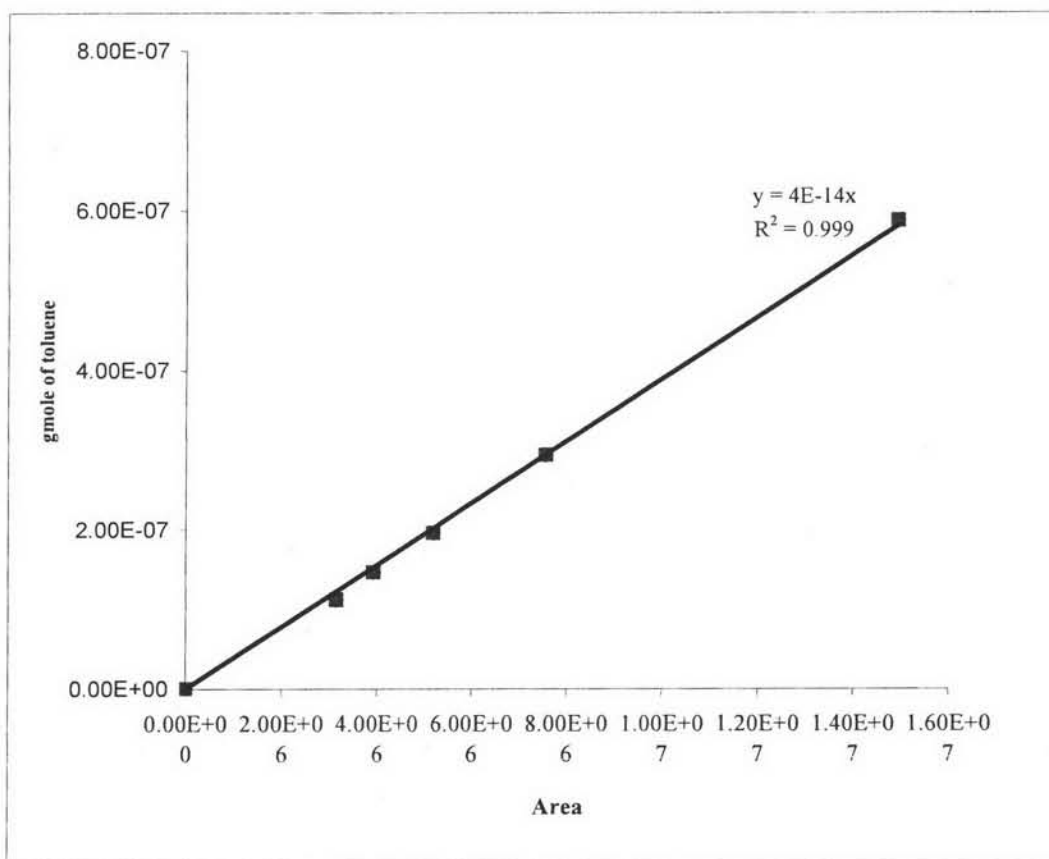


Figure D4 The calibration curve of toluene.

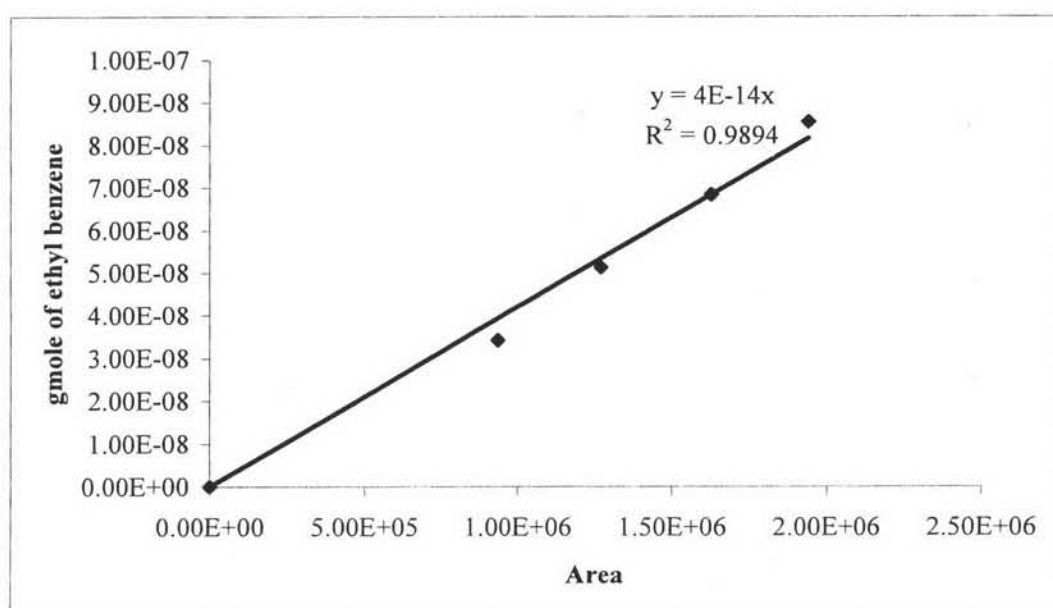


Figure D5 The calibration curve of ethyl benzene.

APPENDIX E

CALCULATION OF TOTAL CONVERSION OF REACTANTS

The amounts of toluene and ethyl benzene evaluated follow:

mole of sample adsorption = mole of blank sample – mole of non-adsorption

Where, mole of blank is mole of sample without catalysts in reactor and mole of non-adsorption is mole of sample analyzed by gas chromatography, they can be measured as follow:

$$\text{Mole of blank sample} = \frac{\text{Volume of benzene feeding} \times \text{Density of toluene}}{\text{Molecular weight of toluene}}$$

Mole of non-adsorption

$$= ((\text{area of phenol peak from integrator plot on GC-9A}) \\ \times \text{slope of graph sample in Appendix C})$$

APPENDIX F

CALCULATION OF PRODUCTIVITY AND SELECTIVITY

The productivity and selectivity for the hydroxylation of toluene and ethyl benzene was evaluated as example, selectivity and productivity of o-cresol

1. The productivity of o-cresol

$$\text{Productivity of o-cresol} = \frac{\text{Overall mole o-cresol}}{\text{Weighth catalyst (g)} \times 7200}$$

Where, the weight catalyst is amount of catalysts is used in reaction and over all mole of o-cresol can be determine from C2 in Appendix C.:

2. The selectivity of product

$$\% \text{ Selectivity of o-cresol} = \frac{\% \text{ Conversion of toluene to cresol}}{\% \text{ Total conversion of toluene to products}}$$

Where, the percentage total conversion of toluene to products and the percentage conversion of toluene to cresol can measured from E1 and E2 in Appendix E., respectively.

APPENDIX G

CALCULATION OF ADSORPTION ON CATALYST

The amounts of toluene and ethyl benzene evaluated follow:

$$\text{mole of sample adsorption} = \frac{\text{mole of blank sample} - \text{mole of non-adsorption}}{\text{Surface area of catalyst (m}^2\text{/g)}}$$

Where, the surface area of catalyst are reported in table 5.1, the mole of blank is mole of sample without catalysts in reactor and the mole of non-adsorption is mole of sample analyzed by gas chromatography, they can be measured as follow:

$$\text{Mole of blank sample} = \frac{\text{Volume of benzene feeding} \times \text{Density of toluene}}{\text{Molecular weight of toluene}}$$

$$\begin{aligned} &\text{Mole of non-adsorption} \\ &= ((\text{area of phenol peak from integrator plot on GC-9A}) \\ &\quad \times \text{slope of graph sample in Appendix C}) \end{aligned}$$

APPENDIX H

DATA OF EXPERIMENTS

Table H1 Data of Figure 5.4

Catalyst	% Total toluene conversion conver to Products at 70°C		
	o-cresol	p-cresol	Benzaldehyde
TS-1	0.36554	0.725391	None
Co-TS-1	0.440328	0.407335	None
V-TS-1	0.217814	0.12636	None
Al-TS-1	0.330721	0.260084	4.799519
Fe-TS-1	0.619485	1.089819	11.53434

Table H2 Data of Figure 5.5

Catalyst	% Selectivity of Products at 70°C		
	o-cresol	p-cresol	Benzaldehyde
TS-1	33.50715	66.49285	None
Co-TS-1	51.94614	48.05386	None
V-TS-1	63.28599	36.71401	None
Al-TS-1	6.135461	4.82501	89.03953
Fe-TS-1	4.677603	8.228993	87.0934

Table H3 Data of Figures 5.13

Catalyst	% Total toluene conversion conver to		
	Products at 95°C		
	o-cresol	p-cresol	Benzaldehyde
TS-1	0.166267	0.173518	2.43289
Co-TS-1	0.278162	0.146526	0.220247
V-TS-1	0.189309	None	0.423367
Al-TS-1	0.085065	None	5.051356

Table H4 Data of Figures 5.14

Catalyst	% Selectivity of		
	Products at 95°C		
	o-cresol	p-cresol	Benzaldehyde
TS-1	6.396959	None	93.60304
Co-TS-1	41.3976	25.82396	32.77845
V-TS-1	26.58659	18.87543	54.53798
Al-TS-1	5.315002	None	94.685

Table H5 Data of Figures 5.15

Catalyst	% Selectivity of					
	Products (70°C)			Products (95°C)		
	o-cresol	p-cresol	Benzaldehyde	o-cresol	p-cresol	Benzaldehyde
	TS-1	33.50715	66.49285	None	6.396959	None
Co-TS-1	51.94614	48.05386	None	41.3976	25.82396	32.77844623
V-TS-1	63.28599	36.71401	None	26.58659	18.87543	54.53797773
Al-TS-1	6.135461	4.82501	89.03953	5.315002	None	94.68499785
Fe-TS-1	4.677603	8.228993	87.0934	None	None	None

Table H6 Data of Figures 5.17

Catalysts	% Conversion/mole at 70°C	
	Ti	Ti+M
TS-1	4441.464	None
Co-TS-1	4227.121	3623.646
V-TS-1	294.1604	269.4137
Al-TS-1	6421.291	4929.558
Fe-TS-1	20118.64	8989.99

Table H7 Data of Figure 5.18

Catalyst	Productivity (mole/sec) at 70°C		
	o-cresol	p-cresol	Benzaldehyde
TS-1	4.65E-09	9.22E-09	None
Co-TS-1	5.7E-09	5.28E-09	None
V-TS-1	2.82E-09	1.64E-09	None
Al-TS-1	4.33E-09	3.4E-09	6.28E-08
Fe-TS-1	8.34E-09	1.47E-08	1.55E-07

Table H8 Data of Figure 5.19

Catalysts	% Conversion/mole at 95°C	
	Ti	Ti+M
TS-1	10581.84	None
Co-TS-1	3350.765	2872.4
V-TS-1	648.879	594.2909
Al-TS-1	6118.825	4697.359

Table H9 Data of Figure 5.20

Catalyst	Pproductivity (mole/sec) at 95°C		
	o-cresol	p-cresol	Benzaldehyde
TS-1	2.19584E-09	None	3.21305E-08
Co-TS-1	3.60363E-09	2.24796E-09	2.85334E-09
V-TS-1	2.45252E-09	1.89827E-09	5.48478E-09
Al-TS-1	1.11263E-09	None	6.60704E-08

Table H10 Data of Figure 5.20

Catalyst	Toluene adsorption (mole abs/m ² -g)
TS-1	4.3251E-11
Fe-TS-1	7.63872E-11
Co-TS-1	3.48528E-11
Al-TS-1	6.54187E-11
V-TS-1	2.63103E-11

Table H11 Data of Figure 5.21

Catalyst	Ethyl benzene adsorption (mole abs/m ² -g)
TS-1	3.41645E-11
Fe-TS-1	3.44264E-11
Co-TS-1	2.27728E-11
Al-TS-1	4.23472E-11
V-TS-1	9.95273E-12

APPENDIX I

DATA AND REFERENCE OF GAS CHROMATRO SCOMETRY

The data obtained from by Gas Chromatography Mass Spectrometry (GC-MS, Agilent Technology 5973) are compare with the mass spectroscopy reference (the references are obtained from NIST MS version 2.0 program) in order to determine a king of compound.

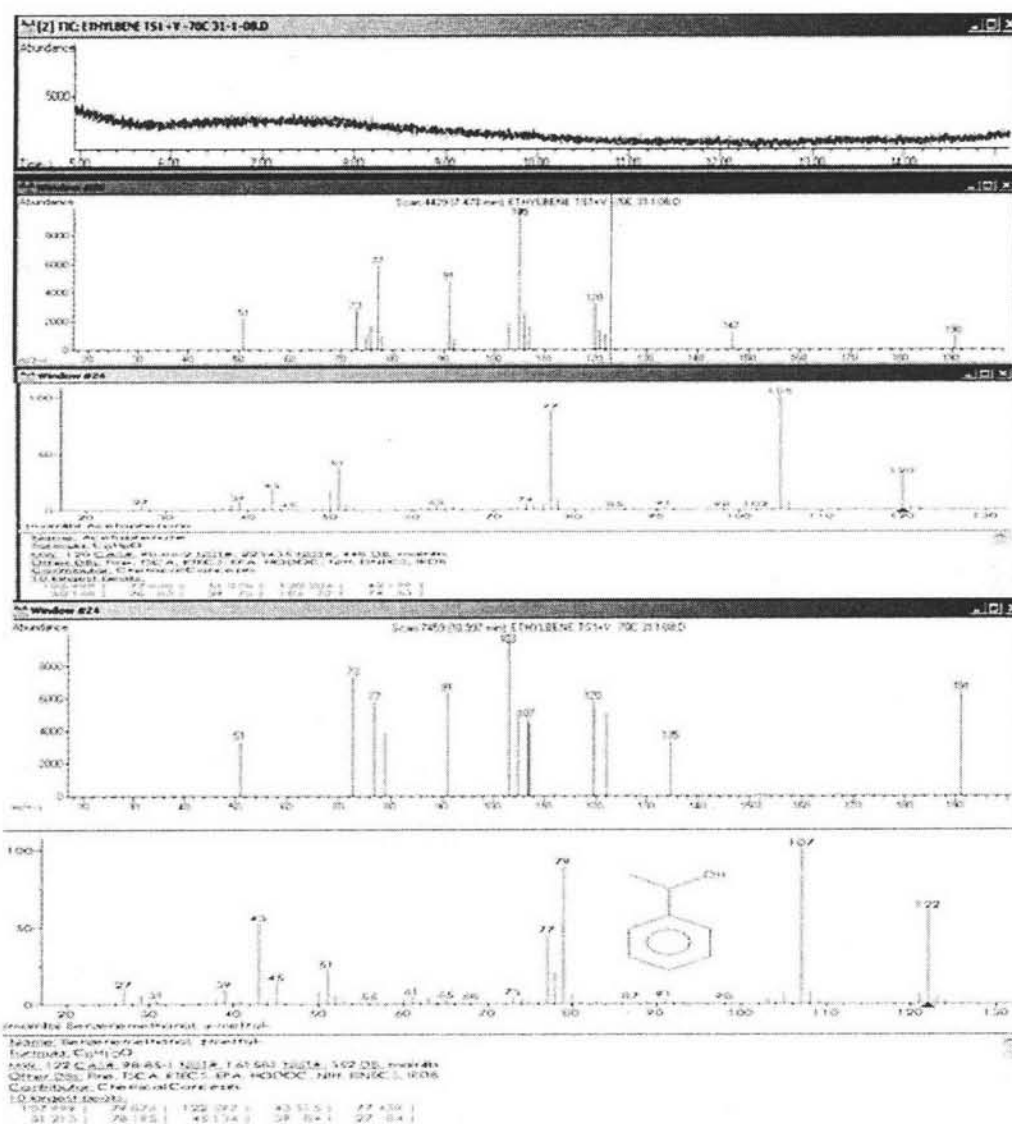


Figure 11 Products from hydroxylation with using TS-1 at 70°C

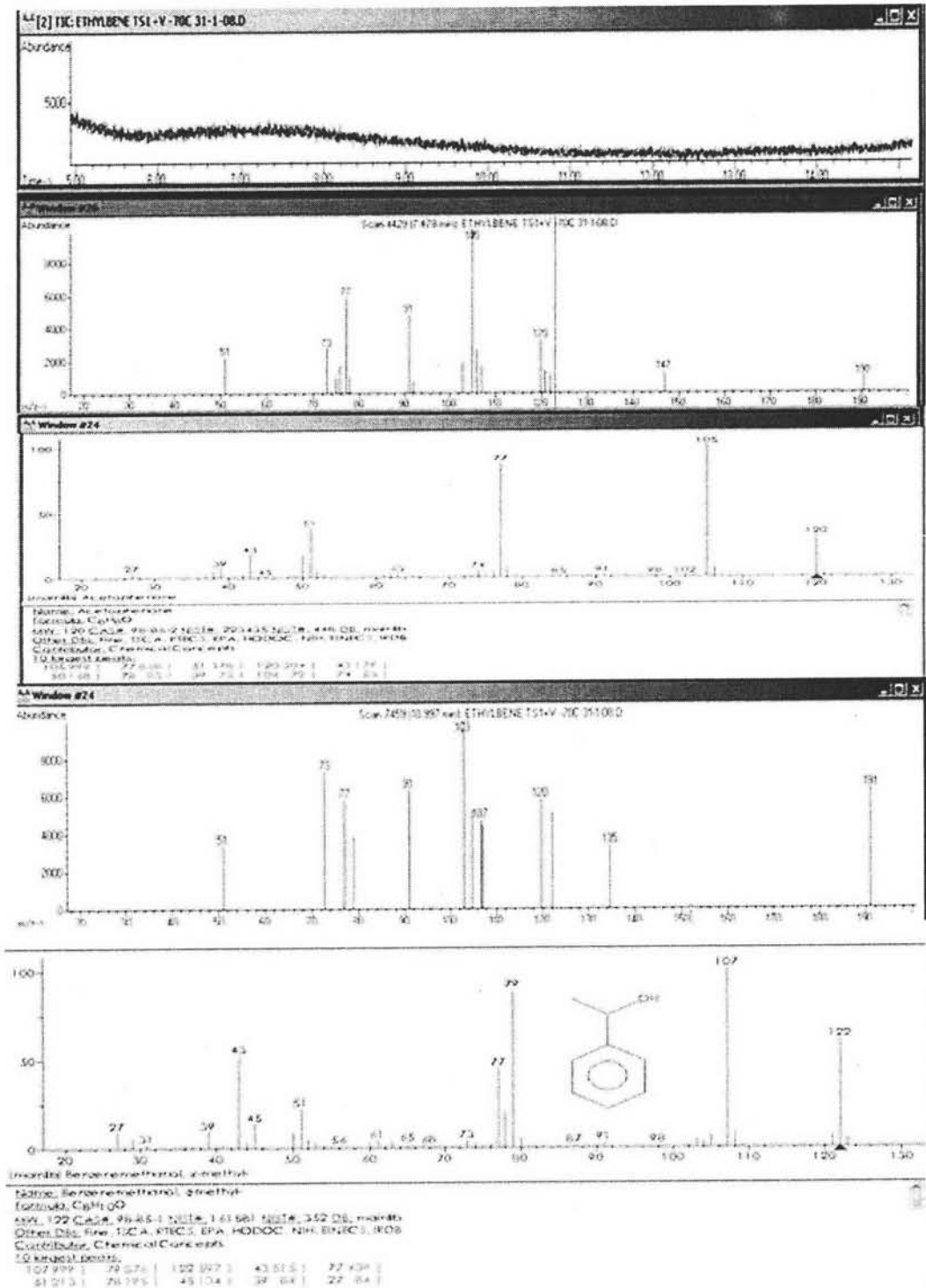


Figure I2 Products from hydroxylation with using Al-TS-1 at 70°C

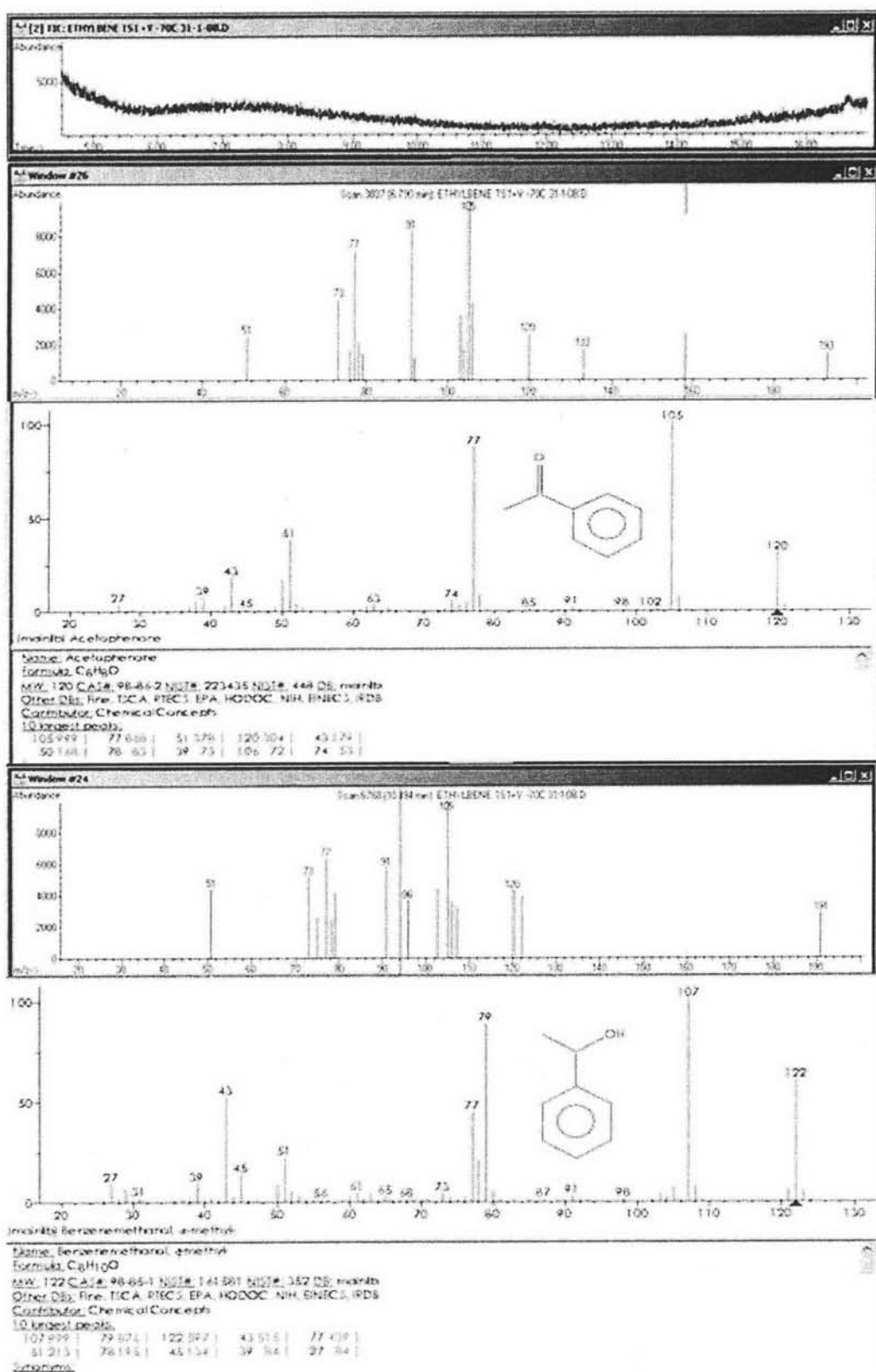


Figure I3 Products from hydroxylation with using V-TS-1 at 70°C



Figure I4 Products from hydroxylation with using Fe-TS-1 at 70°C

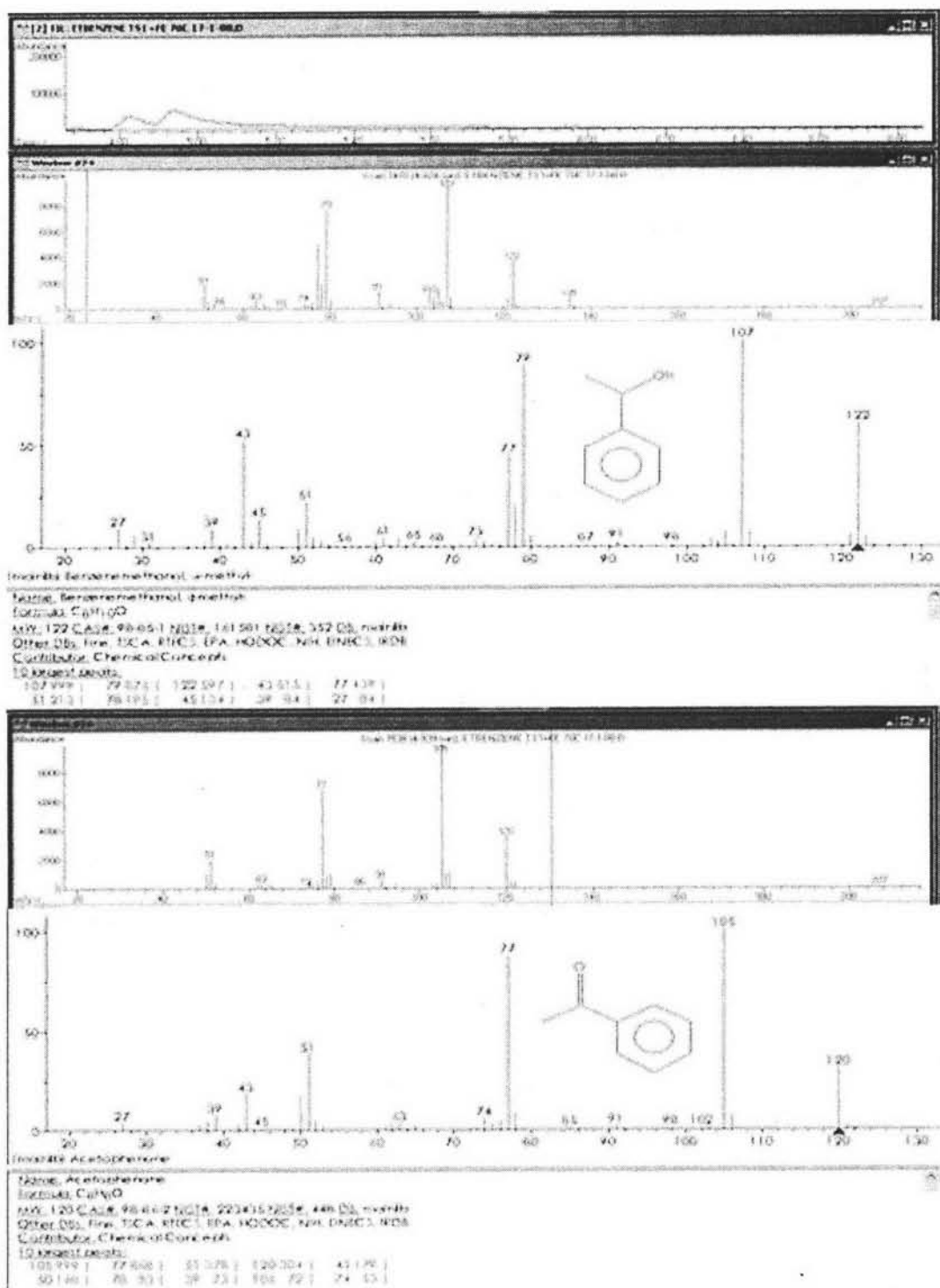


Figure I5 Products from hydroxylation with using Co-TS-1 at 70°C

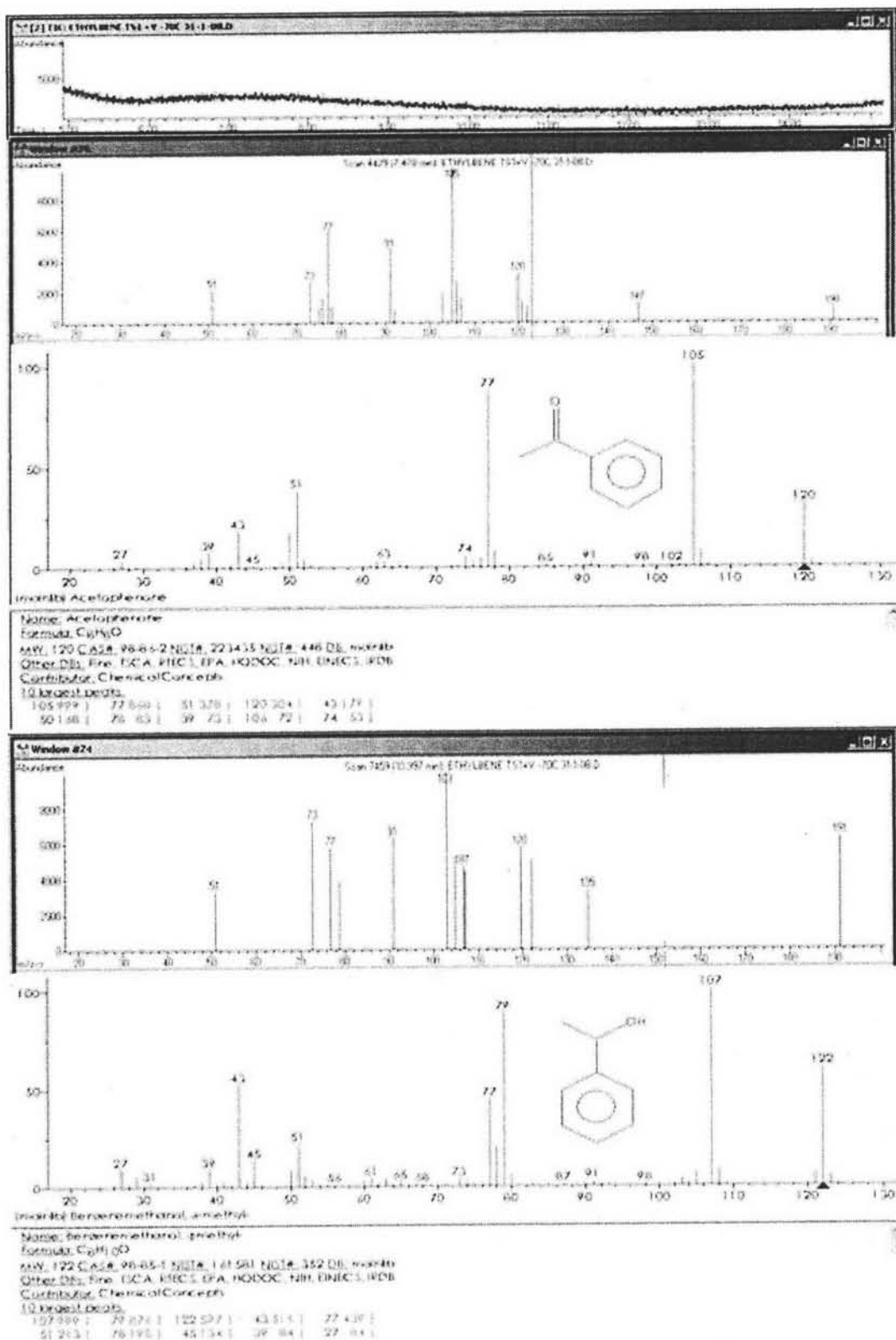


Figure I6 Products from hydroxylation with using TS-1 at 95°C

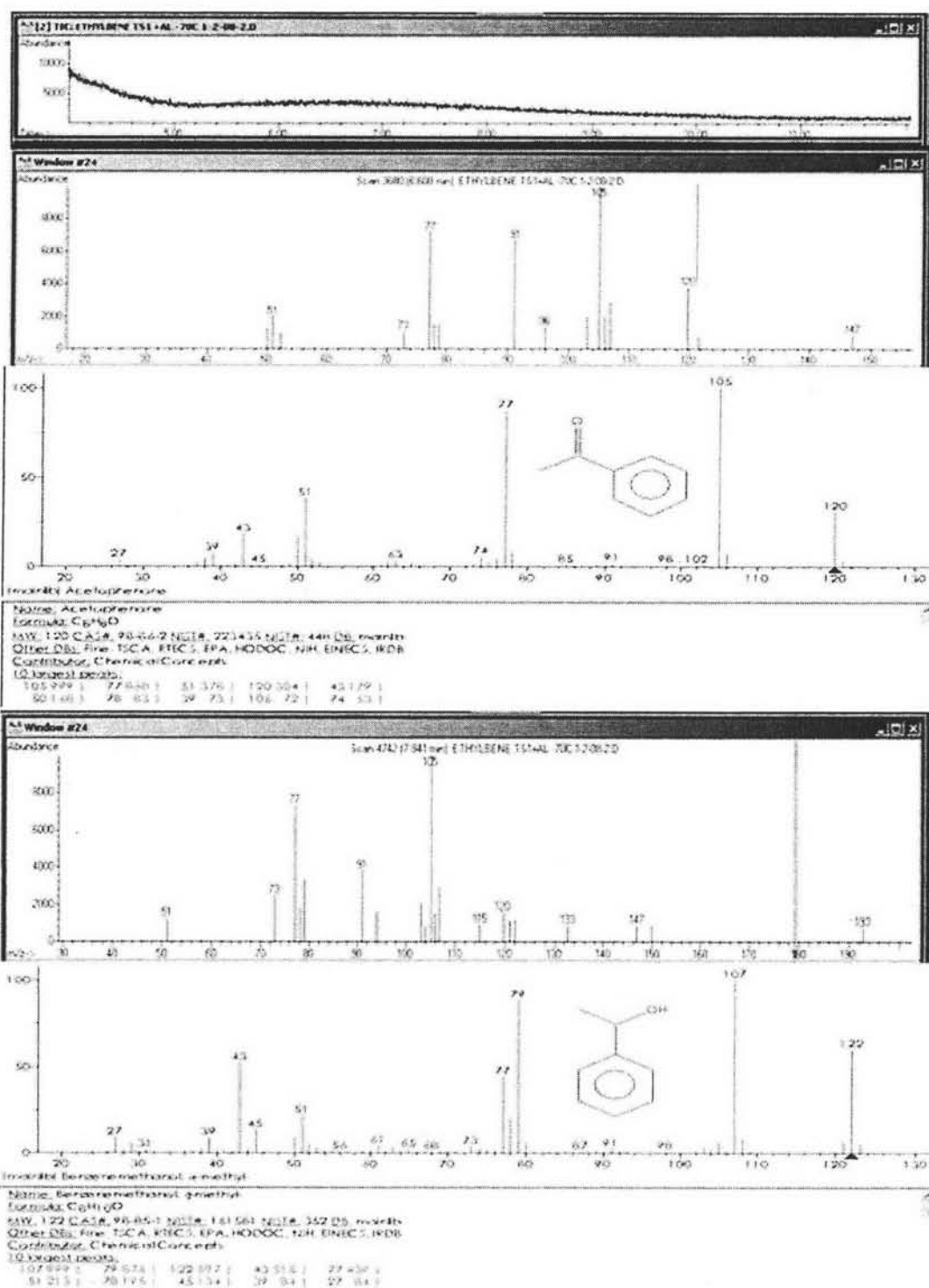


Figure I7 Products from hydroxylation with using Al-TS-1 at 95°C

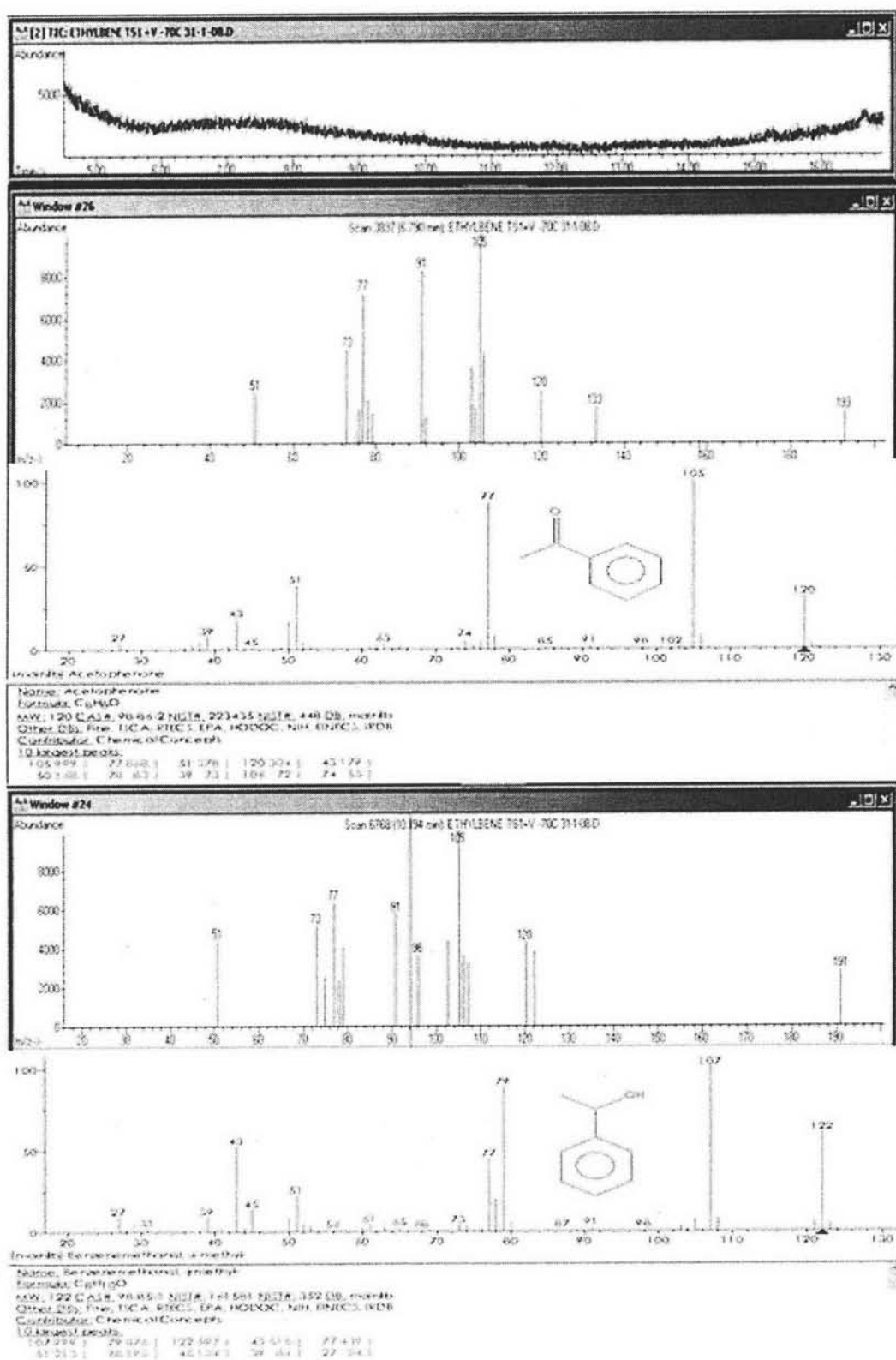


Figure I8 Products from hydroxylation with using V-TS-1 at 95°C

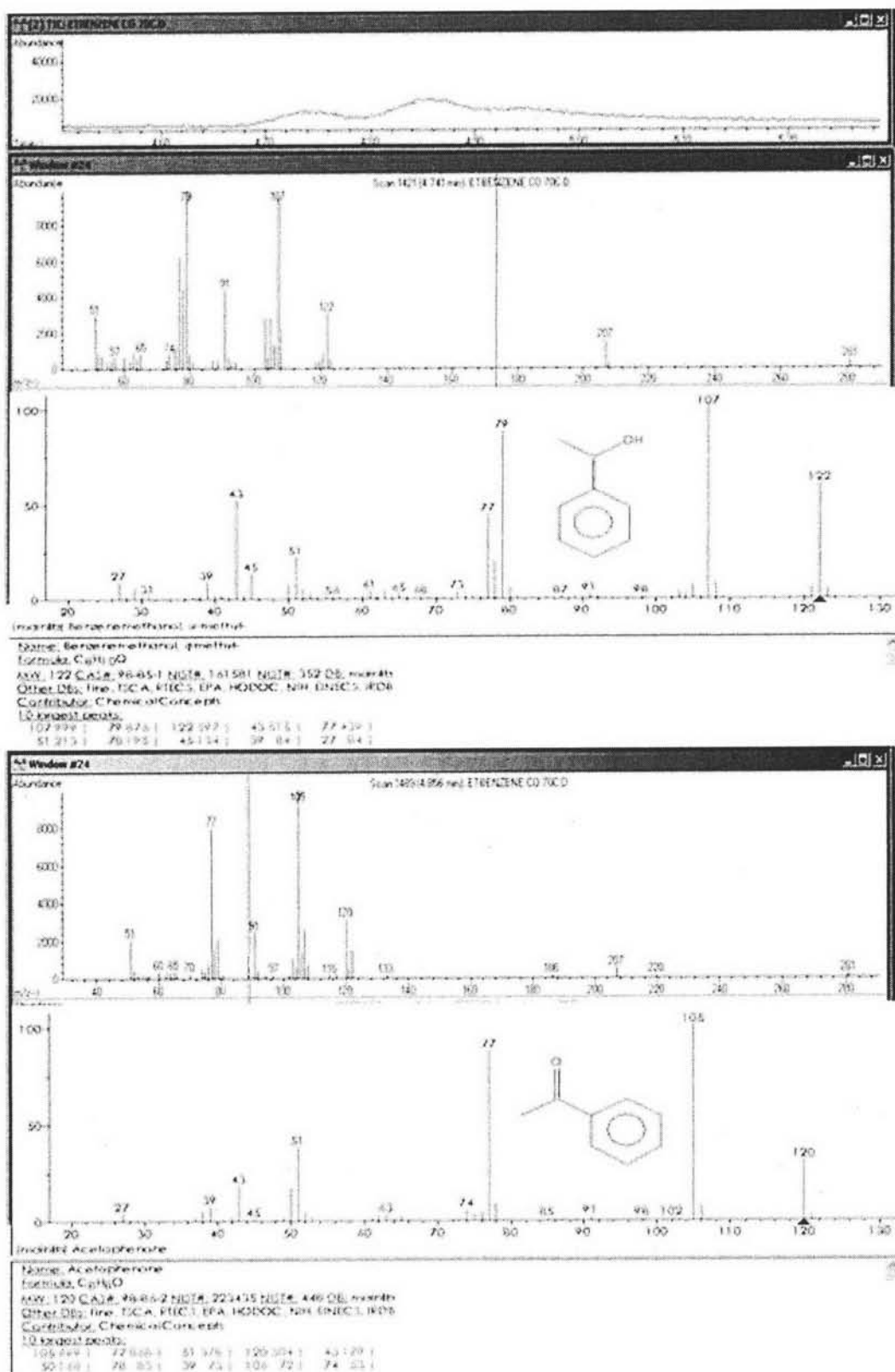


Figure I9 Products from hydroxylation with using Co-TS-1 at 95°C

APPENDIX J**MATERIAL SAFETY DATA SHEET****Ethyl benzene****Safety data for ethyl benzene****General**

Synonyms: phenylethane, EB, ethylbenzol, ethyl benzene

Molecular formula: C_8H_{10}

Physical data

Appearance: colourless liquid

Melting point: -95 C

Boiling point: 136 C

Vapour density: 3.7

Vapour pressure: 10 mm Hg at 20 C

Specific gravity: 0.867

Flash point: 15 C

Explosion limits: 1 % - 6.7 %

Autoignition temperature: 432 C

Stability

Stable. Incompatible with oxidizing agents. Flammable.

Toxicology

May be harmful by inhalation, ingestion or through skin contact. Causes severe eye irritation. Skin and respiratory system irritant. Experimental teratogen. Narcotic in high concentration.

Personal protection

Safety glasses. Good ventilation.

Toluene

Safety data for toluene

General

Synonyms: methylbenzene, phenylmethane, toluol, antisol 1A, CP 25, methacide, methylbenzol

Molecular formula: C_7H_8

Physical data

Appearance: Colourless liquid with a benzene-like odour (odour threshold 0.17 ppm)

Melting point: -93 C

Boiling point: 110.6 C

Specific gravity: 0.865

Vapour pressure: 22 mm Hg at 20 C (vapour density 3.2)

Flash point: 4 C

Explosion limits: 1% - 7%

Autoignition temperature: 536 C

Stability

Stable. Substances to be avoided: oxidizing agents, oxygen, moisture. Highly flammable. Hygroscopic.

Toxicology

Toxic by inhalation, ingestion or by absorption through skin. Serious irritant. Experimental teratogen.

Personal protection

Safety glasses. Good ventilation.

Hydrogen Peroxide, 30% solution**Safety data for hydrogen peroxide, 30% solution****General**

Synonyms: albone 30, albone 35, albone 50, albone 70, albone 35cg, albone 50cg, albone 70cg, interox, kastone, perone 30, perone 35, perone 50. Data also applies to solutions of similar strength.

Note: Typical concentrations lie in the range 3%-35%. Solutions of much higher concentration (e.g. 60% and above) present significantly increased risks, and should not be used unless such strength is absolutely essential.

Physical data

Appearance: colourless liquid

Melting point: ca. -28 °C

Boiling point: ca. 114 °C

Specific gravity: typically near 1.19

Vapour pressure: 23.3 at 30 °C

Stability

Unstable - readily decomposes to water and oxygen. Light sensitive. May develop pressure in the bottle - take care when opening. Forms potentially explosive compounds with ketones, ethers, alcohols, hydrazine, glycerine, aniline, sodium borate, urea, sodium carbonate, triethylamine, sodium fluoride, sodium pyrophosphate and carboxylic acid anhydrides. Materials to avoid include combustibles, strong reducing agents, most common metals, organic materials, metallic salts, alkali, porous materials, especially wood, asbestos, soil, rust, strong oxidizing agents.

Toxicology

Toxic. Corrosive - can cause serious burns. Eye contact can cause serious injury, possibly blindness. Harmful by inhalation, ingestion and skin contact. Typical OEL 1 ppm.

Personal protection

Safety glasses are essential; acid-resistant gloves are suggested. Suitable ventilation.

Acetophenone**Safety data for acetophenone****General**

Synonyms: acetylbenzene, methyl phenyl ketone, phenyl methyl ketone, 1-phenylethanone, MPK, PMK

Molecular formula: C_8H_8O

Physical data

Appearance: yellow liquid

Melting point: 19 C

Boiling point: 202 C

Vapour density: 4.1

Vapour pressure: 0.45 mm Hg at 20 C

Specific gravity: 1.03

Flash point: 82 C

Explosion limits:

Autoignition temperature: 570 C

Stability

Stable. Incompatible with strong oxidizing agents, strong bases, strong reducing agents. Combustible.

Toxicology

Harmful if swallowed. May be harmful by inhalation or if absorbed through skin. Skin irritant. Causes severe eye irritation. May act as a narcotic.

Personal protection

Safety glasses. Adequate ventilation.

Benzaldehyde**Safety data for bezaldehyde****General**

Synonyms: benzoic aldehyde, almond artificial essential oil, benzenecarbonal, benzene carboxaldehyde, artificial almond oil, NCI-C56133, oil of bitter almond

Molecular formula: C_6H_5CHO

Physical data

Appearance: colourless to yellow liquid with an almond-like odour

Melting point: -56 C

Boiling point: 179 C

Vapour density: 3.6 (air = 1)

Vapour pressure: 1 mm Hg at 26 C

Density (g cm⁻³): 1.04

Flash point: 63 C (closed cup)

Explosion limits: 2.1 - 13.5 %

Autoignition temperature: 192 C

Water solubility: slight

Stability

Stable. Combustible. Incompatible with strong oxidizing agents, strong acids, reducing agents, steam. Air, light and moisture-sensitive.

Toxicology

Eye irritant. Harmful by inhalation or ingestion. May be harmful by skin contact. May cause allergic reaction. Slight local anesthetic properties. There is limited evidence that this chemical may act as a carcinogen in laboratory animals. Narcotic in high concentration.

Transport information**Personal protection**

Safety glasses, adequate ventilation.

o-cresol**Safety data for o-cresol****General**

Synonyms: 2-cresol, o-cresylic acid, 1-hydroxy-2-methylbenzene, o-methylphenol, 2-methylphenol, o-toluol, 2-hydroxytoluene, o-hydroxytoluene

Molecular formula: C₇ H₈ O

Physical data

Appearance: colourless to light yellow liquid

Melting point: 32 - 34 C

Boiling point: 191 C

Vapour density: 3.72

Vapour pressure: 0.3 mm Hg at 20 C

Specific gravity: 1.048

Flash point: 81 C

Explosion limits:

Autoignition temperature: 598 C

Stability

Stable, but light and air sensitive. Combustible. Incompatible with oxidizing agents, bases.

Toxicology

Highly toxic. May be fatal if inhaled, swallowed or absorbed through skin. Experimental neoplastigen. Human mutagenic data. Readily absorbed through the skin. Very destructive of mucous membranes. Causes burns. Inhalation may cause spasm. Severe skin and eye irritant.

Personal protection

Safety glasses, gloves, good ventilation.

p-cresol**data for p-cresol****General**

Synonyms: 1-hydroxy-4-methylbenzene, 4-methylphenol, p-cresylic acid, 4-cresol, p-hydroxytoluene, 4-hydroxytoluene, p-methylphenol, para-cresol, p-tolyl alcohol, p-toluol

Molecular formula: $\text{CH}_3\text{C}_6\text{H}_4\text{OH}$

Physical data

Appearance: crystals

Melting point: 34 C

Boiling point: 202 C

Vapour density: 3.7 (air = 1)

Vapour pressure: 0.1 mm Hg at 20 C

Density (g cm^{-3}): 1.03

Flash point: 86 (closed cup)

Explosion limits:

Autoignition temperature:

Water solubility: moderate

Stability

Stable. Combustible. Incompatible with strong oxidizing agents. Light-sensitive.

Toxicology

Poison. May be fatal if swallowed. Readily absorbed through the skin. Harmful if swallowed or inhaled, and in contact with skin. Corrosive - causes severe burns. Experimental neoplastigen. May cause serious eye damage. Severe skin and eye irritant. Typical TLV/TWA 5 ppm. Typical PEL 5 ppm.

Personal protection

Safety glasses, gloves, adequate ventilation.

Penethyl alcohol**Safety data for phenethyl alcohol****General**

Synonyms: benzyl carbinol, 2-phenyl ethanol, 2-phenethyl alcoholethyl alcohol, rose oil, orange oil, beta-hydroxyethylbenzene

Molecular formula: $C_8H_{10}O$

Physical dataalcoh

Appearance: colourless liquid point: - 27 C

Boiling point: 219 - 221 C at 750 mm Hg

Specific gravity: 1.023

Vapour pressure: 1 mm Hg at 58 C

Flash point: 216 F

Explosion limits:

Autoignition temperature:

Stability

Stable. Substances to be avoided include strong acids and strong oxidizing agents. Combustible.

Toxicology

Harmful by inhalation, ingestion and through skin absorption. Irritant.

Personal protection

Safety glasses. Adequate ventilation.

Phenyl acetaldehyde**Safety data for phenyl acetaldehyde****General**

Synonyms: phenyl acetaldehyde, phenylacetic aldehyde, phenylethanal, phenyl ethanal, alpha-tolualdehyde, alpha-toluic aldehyde, hyacinthin

Molecular formula: C_8H_8O

Physical data

Appearance: colourless to slightly yellow liquid

Melting point: -10 C

Boiling point: 195 C

Vapour density:

Vapour pressure:

Density ($g\ cm^{-3}$): 1.08

Flash point: 87 C (closed cup)

Explosion limits:

Autoignition temperature:

Water solubility:

Stability

Stable. Combustible. Incompatible with strong oxidizing agents, strong bases.

Toxicology**Personal protection**

Safety glasses.

1-phenethyl ethanol**Safety data for 1-phenethyl ethanol****General**

Synonyms: alpha-methylbenzenemethanol, 1-phenethyl alcohol, 1-phenylethanol, styralyl alcohol, styrallyl alcohol

Molecular formula: $C_8H_{10}O$

Physical data

Appearance: liquid

Melting point: 9 - 11 C

Boiling point: 98 C

Vapour density:

Vapour pressure:

Density ($g\ cm^{-3}$): 1.012

Flash point: 86 C

Explosion limits:

Autoignition temperature:

Water solubility:

Stability

Stable. Flammable. Incompatible with strong acids, strong oxidizing agents.

Toxicology

Toxic. May act as a carcinogen. Irritant. Severe eye irritant.

Personal protection

Safety glasses, gloves, good ventilation. Treat as a possible carcinogen.

APPENDIX K

LIST OF PUBLICATION

Pornnapa Kasemsiri and Tharathorn Mongkhonsi, "Catalytic study of modified titanium silicalites-1 in the hydroxylation of Alkyl benzene by hydrogen peroxide ", 9th Nation Graduate Research Conference, Chonburi, Thailand, March, 2008, Ref. No.O-042-Physical Science and Technology (oral presentation).

Pornnapa Kasemsiri, Kriangkrai Shenchunthichai, Patchanee Chammingkwan and Tharathon Mongkhonsi, "Catalytic study of iron, aluminum, vanadium and cobalt modified titanium silicalites-1 in the hydroxylation of benzene and alkyl benzene by hydrogen peroxide", Proceedings of Thai 16th Thailand Chemical Engineering and Applied Chemistry Conference, Chaing Mai, Thailand, Oct, 2007, Ref. No.KCF-016 and Chaing Mai Journal of science., Vol 35, No.1 (2008) 178-187.

การประชุมวิชาการวิศวกรรมเคมีและ เคมีประยุกต์แห่งประเทศไทย ครั้งที่ 17



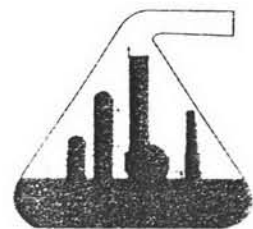
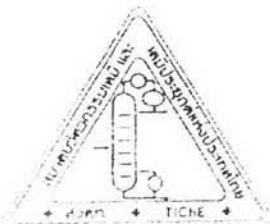
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จ.เชียงใหม่

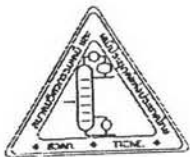
จัดโดย

ภาควิชาเคมีอุตสาหกรรม คณะวิทยาศาสตร์ มหาวิทยาลัยเชียงใหม่

ร่วมกับ

สมาคมวิศวกรรมเคมีและเคมีประยุกต์แห่งประเทศไทย





บทคัดย่อฉบับขยาย
(Extended Abstracts)
การนำเสนอแบบบรรยาย

การประชุมวิชาการวิศวกรรมเคมีและเคมีประยุกต์แห่งประเทศไทย
ครั้งที่ 17
ประจำปี 2550

ระหว่างวันที่ 29-30 ตุลาคม 2550
ณ โรงแรมดิเอ็มเพรส อำเภอเมือง จังหวัดเชียงใหม่

จัดโดย
ภาควิชาเคมีอุตสาหกรรม คณะวิทยาศาสตร์ มหาวิทยาลัยเชียงใหม่
ร่วมกับ
สมาคมวิศวกรรมเคมีและเคมีประยุกต์แห่งประเทศไทย

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

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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 hydroxy group 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] ₄ 2.2085g
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 centrifugation. 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 NH₃ Temperature Programmed Desorption (NH₃-TPD)

Temperature programmed desorption of ammonia (NH₃-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.

2.3 Reaction study in the hydroxylation of benzene

The hydroxylation of benzene and alkyl benzene (ethyl benzene and toluene) with H₂O₂ (30 wt% in water, Merck) 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 H₂O₂ molar ratio equals to 1 to 1 (1.0 ml H₂O₂, 0.9 ml C₆H₆, 1.1 ml C₇H₈ and 50 ml of water). After reactant and H₂O₂ was added into reactor. For H₂O₂ 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).

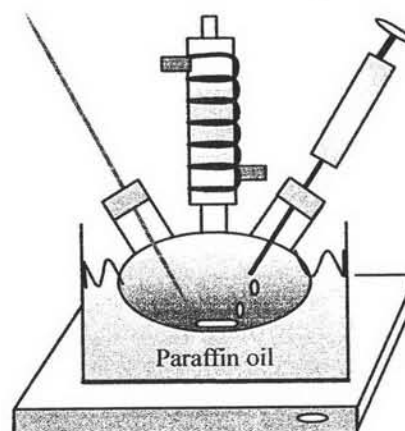


Figure 1 The hydroxylation reactor.

3. Result and discussion

3.1 Catalyst characterization

3.1.1 X-ray diffraction (XRD)

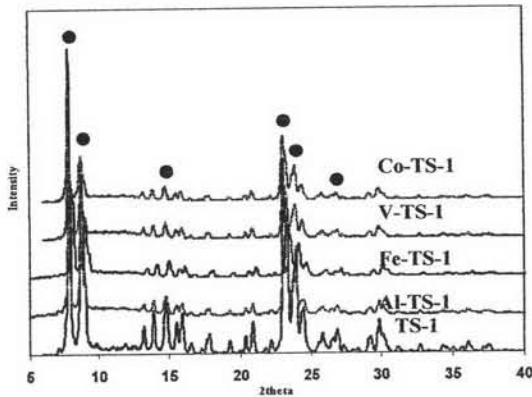


Figure 2 The XRD patterns of the modified TS-1.

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 is 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 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].

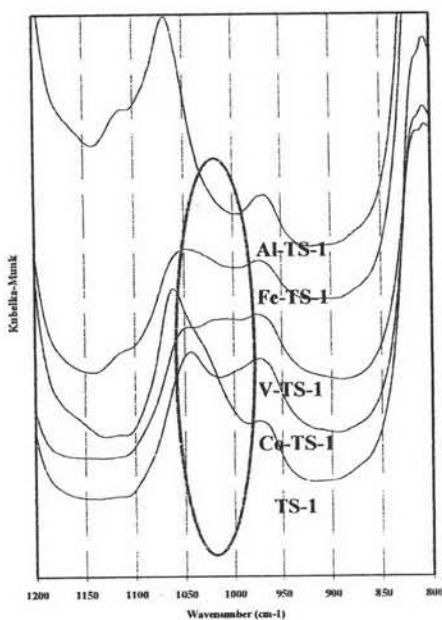


Figure3 The wave number of the modified TS-1.

Figure 3 presents the characteristic absorption band of tetrahedral Ti⁴⁺ 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.

3.1.3 Determine 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

3.1.4 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 Ti⁴⁺ ion in the formation of TS-1 structure.

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

Sampl	%Si	%T	%M	%Si/T	%Si/	%TiO
TS-1	32.9	0.22	none	150.63	none	0.77
Co-TS-	33.0	0.12	0.02	276.86	1220	0.47
V-TS-	33.0	0.11	0.02	282.24	1535	0.43
Fe-TS-	32.9	0.21	0.05	158.67	590	0.78
Al-TS-	33.0	0.18	0.06	182.59	503	0.77

3.1.5 Temperature Programmed Desorption (TPD)

NH₃-TPD was used to determine the strength and amount of the acid site of the catalysts. It is found that each NH₃-TPD profile can be deconvoluted into two main peaks. The first peak, will be named here "the weaker acid site", appears around 120-145°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 %.

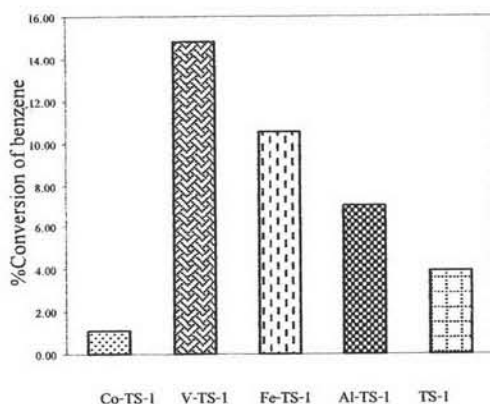


Fig 4. The hydroxylation of benzene with H_2O_2 using TS-1 and modified TS-1.

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 divide 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.

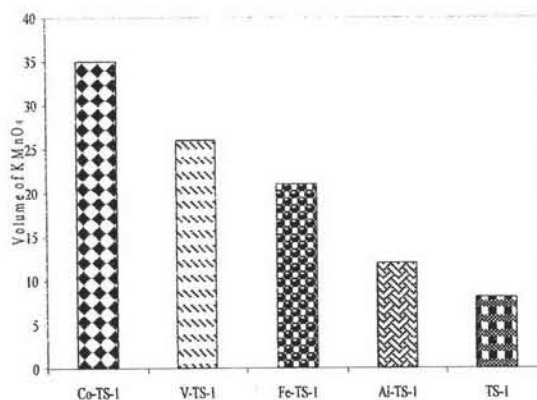


Fig 5. The titration of hydrogen peroxide solutions with standardize $KMnO_4$

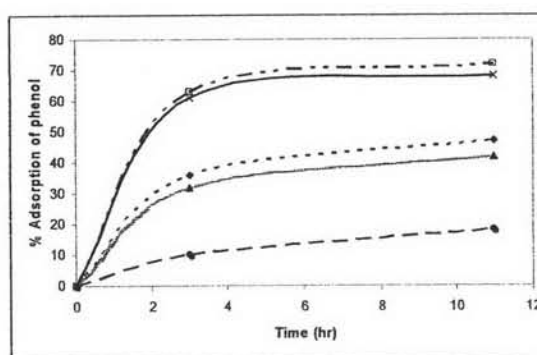


Fig 6. The adsorption of phenol of Co-TS-1(●), V-TS-1 (▲), Fe-TS-1(◆), Al-TS-1(×) and TS-1(□) catalysts.

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 h at 70°C under triphase condition is reported in Table 3. The product obtained from benzene hydroxylation is phenol while the 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.

Table 4 Products of hydroxylation.

Reactants	Product	conversion ^a	Product selectivity ^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 ($\mu\text{mol}/\text{sec}$)

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 is 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 present 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.

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PREFACE

This Special Issue of the Chiang Mai Journal of Science comprises selected papers which were presented at

The 17th Annual Conference of the Thai Institute of Chemical Engineering and Applied Chemistry (TICHE 17)

held at the Empress Hotel in Chiang Mai, Thailand, from 29-30 October 2007. The Conference was organized by the Department of Industrial Chemistry, Faculty of Science, Chiang Mai University, in association with the Thai Institute of Chemical Engineering and Applied Chemistry.

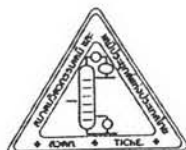
Over 360 participants attended the Conference. In addition to the 209 oral presentations (Plenary, Invited and Technical Papers), there was also an extensive and very lively poster session in which most of the 70 poster presentations were by postgraduate students.

The Conference covered most of active fields in chemical engineering and applied chemistry including fundamental of chemical engineering and applied chemistry, process and control engineering, kinetics and catalysts, energy and fuel technology, environmental and safety technology, nano-materials and powder technology, polymer and petrochemical technology, ceramic technology and metallurgy.

This Conference therefore provided a timely opportunity for chemical engineers, chemists and technologists to exchange ideas relating to the current state of research and development in these fields. By general consensus, the Conference was highly successful and this Special Issue now makes available to a wider audience some of the research work that was presented.

The Editorial Board of the Chiang Mai Journal of Science would like to thank the organizers of the Conference for submitting this collection of papers for publication. Covering a wide range of applications, they reflect the exciting developments that are taking place in these dynamic fields of research.

Surin Khanabsakdi
Editor



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Vol. 35 No. 1 January 2008

ISSN 0125 - 2526

Preface

- Synthesis of Nanosized Anatase Particles from Commercial Rutile Powder by Using Hydrothermal Method
Ubomwan Chutipunphinyo, Siriporn Larпкиattaworn and Pornapa Sutaridworakun 1-5
- The Preparation of Cordierite-Mullite Composite for Thermal Shock Resistance Material
Phatthamon Kiattisaksophon and Sukdiphon Thiansem 6-10
- Influence of pH, Electrolytes and Polymers on Flocculation of Kaolin Particle
Nongkhran Chaiwong and Apinon Nuntiya 11-16
- Effect of Flocculation of Alumina Slip on the Pore Size Distribution of Cast Alumina by Polyacrylamide (PAM)
Piamchit Silakate, Apinon Nuntiya and Siriporn Larпкиattaworn 17-22
- Production Methyl Esters from Palm Fatty Acids in Supercritical Methanol
Akaraphol Petchmala, Duangkamol Yujaroen, Artiwan Shotipruk, Motonobu Goto and Mitsuru Sasaki 23-28
- Hydrodynamics of Mixture Between PVC Resin and Anti-static Powder in Circulating Fluidized Bed
Thiti Saichua and Suchaya Nitivattananon 29-34
- Combustion of Moist Coal Briquettes
Prodpran Siritheerasas, Chomthida Chunnuyom and Piyaporn Sethabunjong 35-42
- Development of Fuel Briquettes from Biomass-Lignite Blends
Suparin Chaiklangmuang, Suwit Supa and Prattana Kaewpet 43-50
- Feasibility Survey of Fuel Briquette Demands in Roasting Food Restaurants in Chiang Mai Province, Thailand
Suparin Chaiklangmuang, Yaowaluck Chotchaitanakorn and Sanguansak Sri-phalang 51-55
- Adsorption Equilibrium of Zinc Ions from Aqueous Solution by Using Modified Clinoptilolite
Achanai Buasri, Phetcharat Yongbut, Nattawut Chaiyut and Kittiya Phattarasirichot 56-62
- Degradation of Congo Red Dye by Ozonation
Thirachitra Tapalad, Arthit Neramittagapong, Sutasinee Neramittagapong and Mallika Boonmee 63-68
- Biosorption of Lead (II) and Copper (II) from Aqueous Solution
Woranart Jonglertjunya 69-81



Chiang Mai Journal of Science

Faculty of Science, Chiang Mai University

Vol. 35 No. 1 January 2008

ISSN 0125 - 2526

- Feasible Use of Electrical Conductivity for Optimizing Polymer Dosage and Mixing Time Requirement in Sludge Conditioning
Tongchai Sriwiryarat, Kreethaphon Siriphrom, Nut Kaewpanao, and Anucha Puansuchjar 82-88
- Scaleup Effect on Performance of Proton Exchange Membrane Fuel Cell
Hong Leelasapakorn, Amaraporn Kaewchada, Watcharapon Traisantikul, Withawin Tiengtrakarnsuk, Sunun Limtrakul and Terdthai Vatanatham 89-94
- Comparison of Sludge Granule and UASB Performance by Adding Chitosan in Different Forms
Boonyarit Nuntakumjorn, Wuthichok Khumsalud, Naret Vetsavas, Thoranin Sujjaviriyasup and Chantaraporn Phalakornkule 95-102
- Subcritical Water Extraction of Polyphenolic Compounds from *Terminalia chebula* Fruits
Rangsriwong P., Rangkadilok N., and Shotipruk A. 103-108
- Experiments and Statistical Analysis of Supercritical Carbon Dioxide Extraction
Wipawee Yothipitak, Praiyya Thana, Motonobu Goto and Artiwan Shotipruk 109-115
- Value Added Products from By-products of Rice Bran Oil Processing
Wasinee Kaewboonnum, Ketmanee Wachararuji and Artiwan Shotipruk 116-122
- Extraction of Phenolic Compounds from Fruits of Bitter Melon (*Momordica charantia*) with Subcritical Water Extraction and Antioxidant Activities of These Extracts
Parichat Budrat and Artiwan Shotipruk 123-130
- 3-D Simulation of Particle and Gas Flow Behavior in a Riser with Venturi Pipe Inlet
Parinya Khongprom, Sunun Limtrakul and Terdthai Vatanatham 131-140
- Effect of Filler Loading on Curing Characteristics and Mechanical Properties of Thermoplastic Vulcanizate
Chayanoot Sangwichien, Panita Sumanatrakool and Orusa Patarapaiboolchai 141-149
- A New Analytical Expression of the Gas Conversion for TAP Experiments with Bimodal-Pore-Structure Catalyst
Wisuthchai Boonwatcharapunsakul and Phungphai Phanawadee 150-155
- Effect of Cerium Oxide and Zirconium Oxide to Activity of Catalysts
Akkarat Wongkaew 156-162



Chiang Mai Journal of Science

Faculty of Science, Chiang Mai University

Vol. 35 No. 1 January 2008

ISSN 0125-2526

- Catalytic Activity of TS-1 on the Hydroxylation of Benzene and Toluene with Hydrogen Peroxide in a Bubble Reactor
Suchitraporn Sakullimcharoen, Panus Manit and Tharathon Mongkhonsi 163-170
- Acetaldehyde Production from Ethanol over Ni-Based Catalysts
Arthit Neramittagapong, Wiphada Attaphaiboon and Sutasinee Neramittagapong 171-177
- 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 178-187
- Application of Polyethylene Glycol and Polymethyl Methacrylate as a Binder for Powder Injection Moulding of Hardmetals
Nutthita Chuankrerkkul, Peter F. Messer and Hywel A. Davies 188-195
- Applying of Aluminium Deoxidation in Iron Roll Casting
Teerapong Harnwirojkul, Mana Polboon, John Pearce and Thanaporn Korud 196-198
- The Effect of Surfactant Concentration on the Interlayer Structure of Organoclay
Apinon Nuntiya, Supachai Sompech, Suparerk Aukkaravittayapun and Jantrawan Pumchusak 199-205
- Preparation of Nanosilica Powder from Rice Husk Ash by Precipitation Method
Nittaya Thuadaij and Apinon Nuntiya 206-211
- Estimation of Water Content in PEM Fuel Cell
Chinnavat Thawornkuno and Chanin Panjapornpon 212-220
- Nonlinear Model-Based Control for Parabolic Partial Differential Equations Systems
Atthasit Tawai and Chanin Panjapornpon 221-228



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

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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 H₂O₂ 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/H₂O₂ under triphase (catalyst-benzene-H₂O₂) and biphasic (catalyst-liquid (benzene-H₂O₂-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 H₂O₂ 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(NO₃)₂.6H₂O for Co, FeCl₃.6H₂O for Fe, VCl₃ for V, Al(NO₃)₃.9H₂O for Al as the second metal, Ti[O(CH₂)₃CH₃]₄ for Ti, and sodium silicate for Si. TPABr (Tetra-n-propyl ammonium bromide [(CH₃CH₂CH₂)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.

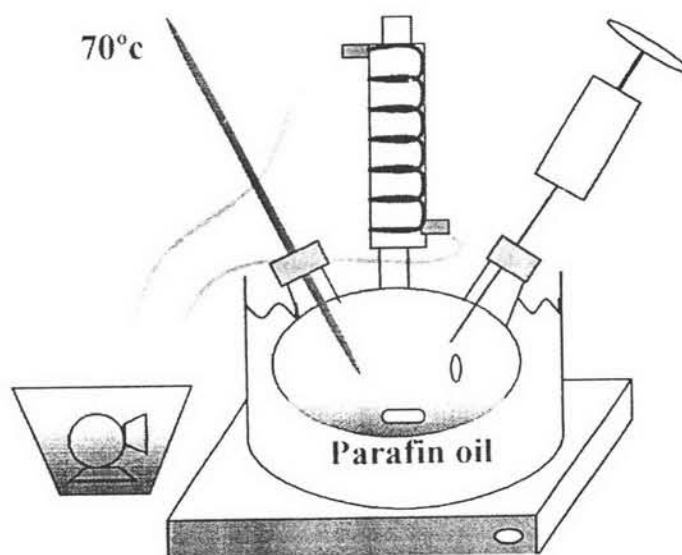


Figure 1. The hydroxylation reactor

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).

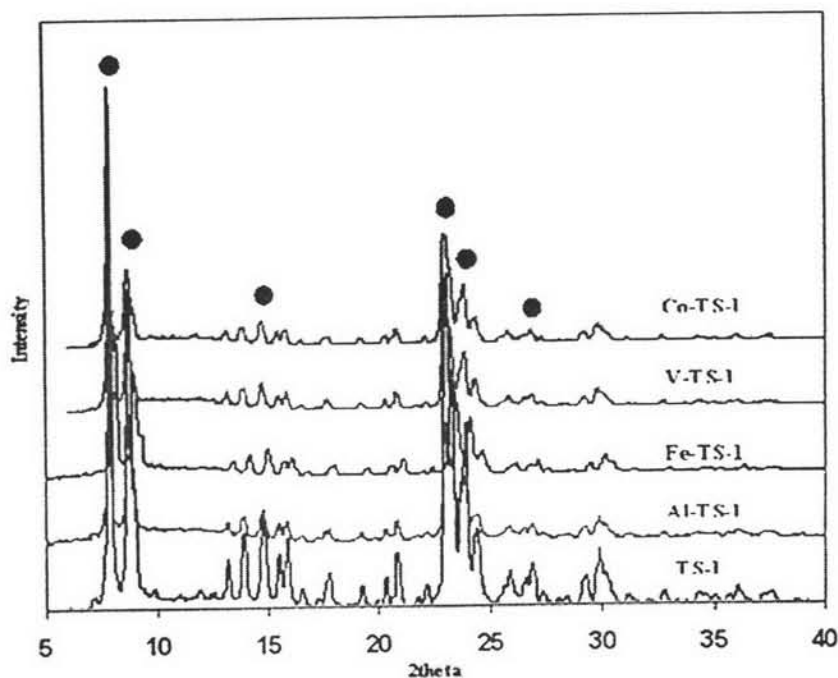


Figure 2. The XRD patterns of the modified TS-1.

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

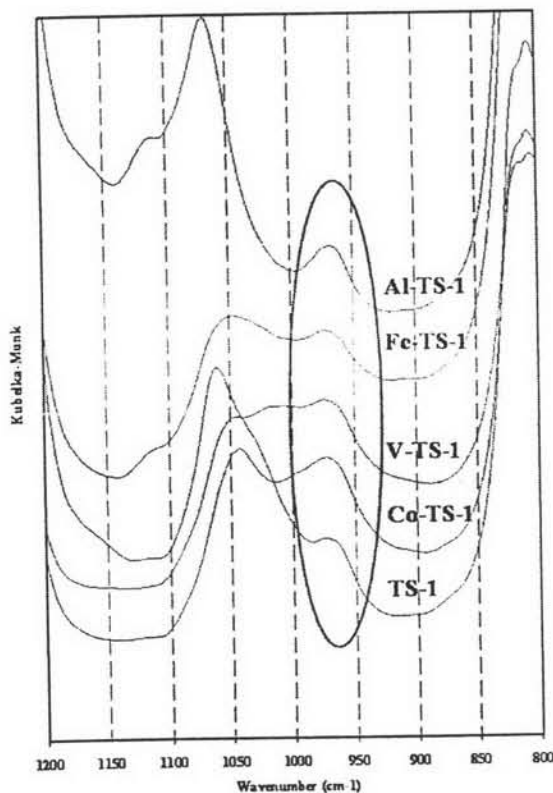


Figure 3. The wave number of the modified TS-1.

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 %.

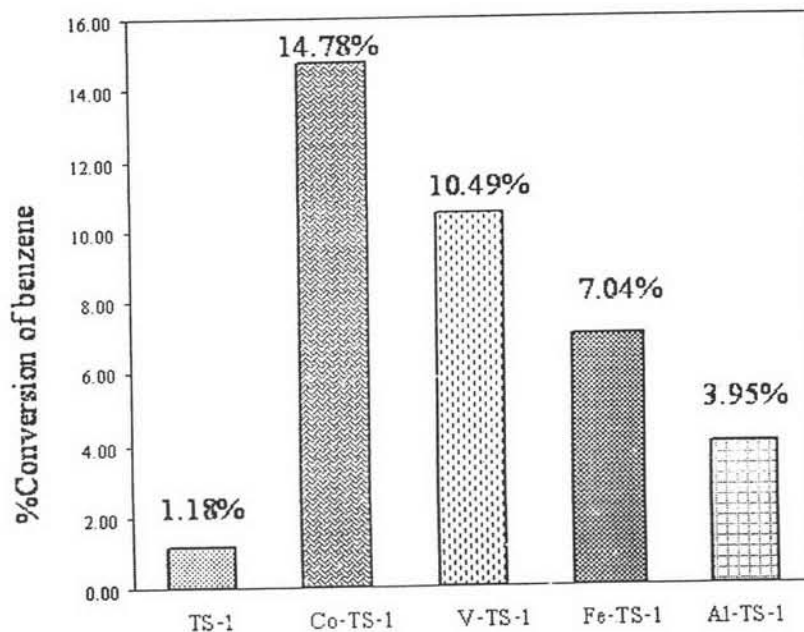


Figure 4. The hydroxylation of benzene with H_2O_2 using TS-1 and modified TS-1.

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.

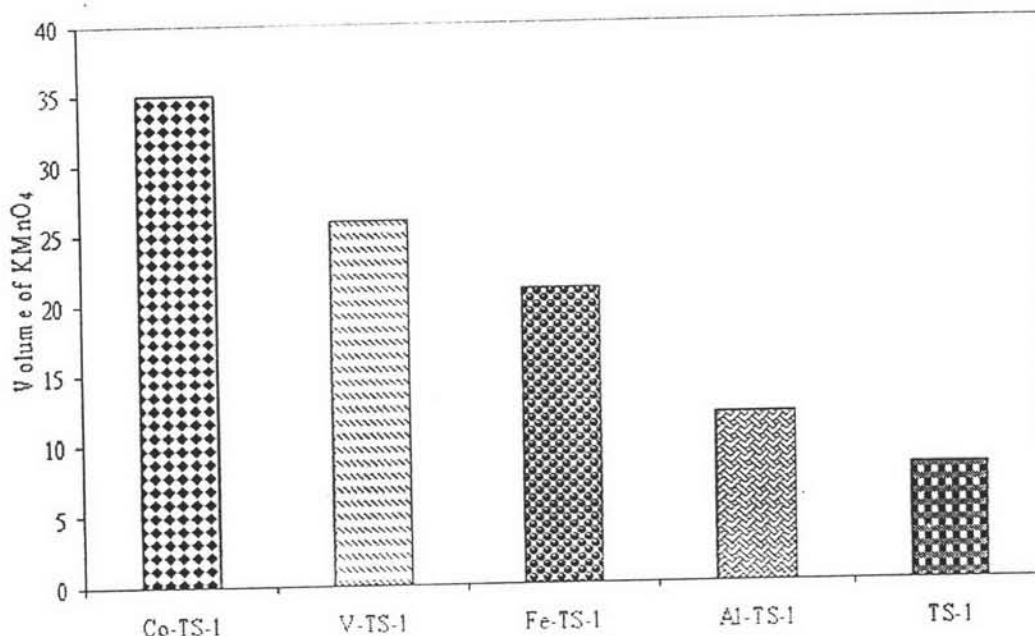


Figure 5. The titration of hydrogen peroxide solutions with standardize KMnO_4

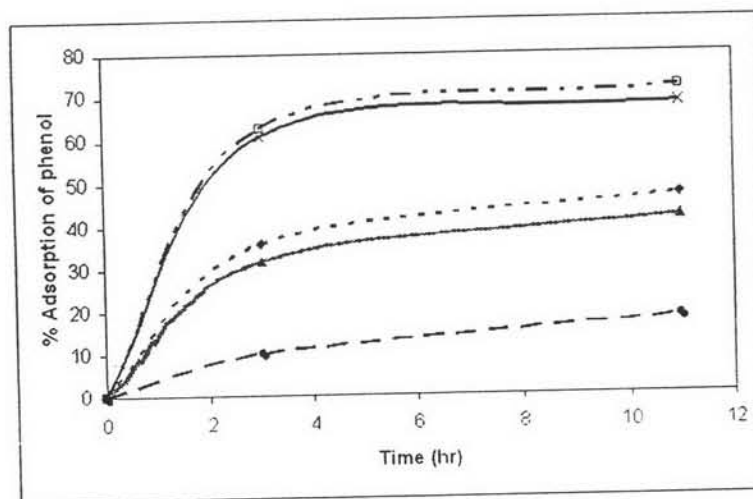


Figure 6. The adsorption of phenol of Co-TS-1(●), V-TS-1 (▲), Fe-TS-1(◆), Al-TS-1(×) and TS-1(□) catalysts.

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 is 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.

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รวมบทคัดย่อ (Abstracts)

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The 9th National Grad Research Conference

บัณฑิตวิทยาลัย มหาวิทยาลัยบูรพา

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ร่วมกับ

ที่ประชุมคณบดีบัณฑิตวิทยาลัย มหาวิทยาลัยของรัฐ (ทคปร.)

The Deans of Graduate School of Public Universities (DGPU)

Oral Presentation Schedule
Disciplinary Group : Physical Science and Technology
March 14, 2008
Venue: Room GS 302 Graduate School Building, Burapha University

NO.	TIME	PRESENTER	ABSTRACT	Page No.
O-037	14.15-14.30	ศุภวิรัช ปุณณานนท์ SUPAWAT PUNNANON	MICROWAVE RADIATION EFFECT ON POLYISOPRENE FILM FORMATION ON SILICA SURFACE BY ADMICELLAR POLYMERIZATION	67
O-038	14.30-14.45	นริศรา อยู่ประเสริฐ NARISSARA YOOPRASERT	POLYISOPRENE FILM FORMATION ON SILICA SURFACE BY ADMICELLAR POLYMERIZATION WITH VARIOUS γ -RAY DOSES FOR REACTION INDUCTION	68
O-039	14.45-15.00	สุวิชา นุ่มมีชัย SUWICHA NUMMEECHAI	INFLUENCE OF INITIATOR DECOMPOSITION ON POLYISOPRENE FILM FORMATION BY ADMICELLAR POLYMERIZATION	69
O-040	15.00-15.15	ปิยะวิทย์ โภคาเสริมส่ง PIYAVIT POKASERMSONG	COMPARATIVE STUDY OF ZIEGLER-NATTA CATALYST SYNTHESIS FOR ETHYLENE POLYMERIZATION	70
O-041	15.15-15.30	สุภาพร วิไลลักษณ์ SUPAPORN WILAILAK	PERFORMANCE EVALUATION OF HEAT INTEGRATED AND CONTROL STRUCTURES OF BUTANE ISOMERIZATION PLANT	71
O-042	15.30-15.45	พรนภา เกษมศิริ PORNNAPA KASEMSIRI	CATALYTIC STUDY OF MODIFIED TITANIUM SILICALITES-I IN THE HYDROXYLATION OF ALKYL BENZENE BY HYDROGEN PEROXIDE	72
O-043	15.45-16.00	พงษ์นรินทร์ จำรักษ์ PONGNARIN JAMRAK	COMPARING WATER VAPOR ADSORPTION OF MOLECULAR SIEVE 3A WITH LOCAL MATERIALS BY USING FIXED BED ADSORBER IN ANHYDROUS ETHANOL PROCESS	73
O-044	16.00-16.15	วีราภรณ์ คารมณ VERAPORN KAROM	ENVIRONMENTAL IMPACT COMPARISON OF LIQUEFIED NATURAL GAS (LNG) USING LIFE CYCLE ASSESSMENT TECHNIQUE	74

O-042**CATALYTIC STUDY OF MODIFIED TITANIUM SILICALITES-1 IN THE HYDROXYLATION OF ALKYL BENZENE BY HYDROGEN PEROXIDE****Pornnapa Kasemsiri* and Tharathon Mongkhonsi**

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This research studies catalytic properties of TS-1 modified Al, Co and V in the hydroxylation of alkyl benzene, i.e. toluene, with hydrogen peroxide. The results of the hydroxylation at 70°C for 2 h show that the additions of Co and V give ortho cresol (o-cresol) and para cresol (p-cresol) as main products but when using Al-TS-1, benzaldehyde also appears. At 95°C, however, benzaldehyde is more predominant than o-cresol and p-cresol. These indicate that the hydroxyl group can substitute at several positions on the benzene ring and at the methyl group. Moreover, the reactions of TS-1 modified with second metals make the adsorptions of hydrophobic molecule at the outside of catalyst pore more favorably than at the inside of the pore. These results in the selective of substitutions at ortho and methyl group positions are more prevalent than the para position.

Keywords:

Titanium silicalite-1/ Hydroxylation/ Alkyl benzene and toluene

VITA



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