การสังเคราะห์เบนซอลดีไฮด์โดยตรงจากปฏิกิริยาการออกซิไดซ์บางส่วนของโทลูอีนในเครื่องปฏิกรณ์แบบฟองแก๊ส

นางสาวภาวนา วงษ์บุญรอด

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DIRECT BENZALDEHYDE SYNTHESIS VIA THE PARTIAL OXIDATION REACTION OF TOLUENE IN A BUBBLE REACTOR

Miss Phawana Wongbunrod

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ภาวนา วงษ์บุญรอด: การสังเคราะห์เบนซอลดีไฮด์โดยตรงจากปฏิกิริยาการออกซิไดซ์บางส่วนของโทลูอีนในเครื่องปฏิกรณ์แบบฟองแก๊ส. (DIRECT BENZALDEHYDE SYNTHESIS VIA THE PARTIAL OXIDATION REACTION OF TOLUENE IN A BUBBLE REACTOR) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: รศ.ดร.ธราธร มงคลศรี, 84 หน้า.

งานวิจัยนี้ทำการศึกษาการเส้นทางใหม่ในการสังเคราะห์เบนซาลดีไฮด์โดยตรงจากโทลูอีนร่วมกับไฮโดรเจนเปอร์ออกไซด์ในเครื่องปฏิกรณ์แบบฟองแก๊สโดยมีตัวเร่งปฏิกิริยาไทเทเนียมซิลิกาไลต์-1 ที่ได้รับการปรับปรุงด้วยโลหะอะลูมิเนียมในปริมาณต่าง ๆ ปัจจัยที่ทำการศึกษาคือ ปริมาณโลหะอะลูมิเนียม ระยะเวลาการตกผลึก และความเข้มข้นของไฮโดรเจนเปอร์ออกไซด์ ผลการศึกษาพบว่าตัวเร่งปฏิกิริยาที่ได้รับการปรับปรุงทุกตัวให้ผลิตภัณฑ์หลักเป็นเบนซาลดีไฮด์โดยมีออโธ-ครีซอล และพารา-ครีซอลเป็นผลิตภัณฑ์ข้างเคียงในปริมาณเล็กน้อย ผลการทดลองแสดงให้เห็นว่าอะลูมิเนียมที่เติมเข้าไปในตัวเร่งปฏิกิริยาไทเทเนียมซิลิกาไลต์-1 จะเพิ่มการเกิดเบนซาลดีไฮด์ให้ดีขึ้น โดยมีค่าการเลือกเกิดเบนซาลดีไฮด์อยู่ในระดับร้อยละ 95-100 แต่ถ้าเติมอะลูมิเนียมในปริมาณที่มากเกินไปจะไปเร่งการสลายตัวของไฮโดรเจนเปอร์ออกไซด์ทำให้ได้ผลิตภัณฑ์ลดลง

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ลายมือชื่ออ.ที่ปรึกษาวิทยานิพนธ์หลัก......................

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PHAWANA WONGBUNROD: DIRECT BENZALDEHYDE SYNTHESIS VIA THE PARTIAL OXIDATION REACTION OF TOLUENE IN A BUBBLE REACTOR.
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This research studied a new route for the direct synthesis of benzaldehyde from toluene and hydrogen peroxide in a bubble reactor using titanium silicalite-1 catalysts modified with different amount of Al. The reaction is carried out at atmospheric pressure. Parameters investigated are amount of aluminium, crystallization time, and hydrogen peroxide concentration. The study found that all modified catalysts yield benzaldehyde as the major product with a small amount of o-cresol and p-cresol as by products. The experimental results also show that Al added into TS-1 promotes the formation of benzaldehyde and suppresses the formation of cresols. Too much Al added, however, will increase the decomposition of hydrogen peroxide which results in lower reaction products formed.

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Student's Signature:..ภาวนา...วงศ์บุญรอด
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Finally, I also would like to dedicate the achievement of this work to her parents (Ms. Mana Kornnum, Mr. Prasert Wongbunrod, Mr. Anurak Wongbunrod) who have always been the source of her suggestion, support and encouragement.

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CHAPTER I

INTRODUCTION AND IMPORTANCE OF RESEARCH

Benzaldehyde (C_6H_5CHO) is the simplest and the most industrially useful member of the family of aromatic aldehydes. More than 98% is used as an intermediate in production of pharmaceuticals, aromatic alcohols, photographic chemicals, dyes, benzoic acid and cinnamic acid. Purified benzaldehyde is used as an intermediate (60% on site and 38% off site) in closed systems and 1-2% is used as a solvent oil, resins, some cellulose ethers, cellulose acetate and nitrate.

The oldest benzaldehyde is produced by many processes such as the liquid phase oxidation of toluene, vapor phase oxidation of toluene, electrochemical and chlorination of toluene. The liquid phase oxidation and the vapor phase oxidation of toluene begin from reacting toluene with oxygen. The vapor phase oxidation more than seventy percent give main byproduct is CO_2. The both route different temperature in the reaction. The problem of both routes is that much of catalysts are used and used only in homogenous phase. The another disadvantage of this conventional process is the use of hazardous multi step use a large amount of energy in the separation process and give by product that is dissatisfied which is pass through the several of separation step. The electrochemical uses highly electricity. These processes have more expensive cost and much of catalysts are used. The chlorination of toluene is another way to produce benzaldehyde. First, the chlorine reacts with toluene and activated by photo catalysis. The product of this reaction is benzalchloride, then benzalchloride hydrolysis to benzaldehyde and byproduct is HCl which this way is complicated step.

Titanium silicalite-1 was first reported by Taramasso et al. (1983). TS-1 is a silica rich molecular sieve with MFI structure in which isolated titanium species in the zeolite framework function as catalytic sites. The MFI structure is one type of ZSM-5 structure and 10 member ring channels by Wang et al. (2007). In the partial oxidation of many organic compounds, TS-1 zeolite is a very efficient catalyst for the oxidation of a variety of organic compounds with H_2O_2: alkane oxyfunctionalisation, hydroxylation of aromatic, olefin epoxidation, ammoximation of cyclohexanone by [Uguina et al. (2000)].

In a previous work, Sakullimcharoen (2007) has studied hydroxylation of alkyl benzenes in a bubble reactor over TS-1 and modified TS-1 (Al-TS-1, Co-TS-1, Fe-TS-1 and V-TS-1) catalysts using 3, 7.5 and 30 wt% hydrogen peroxide concentration as an oxidant. The hydroxylation of toluene gave cresol (ring oxidation) benzaldehyde (side chain oxidation). Al-TS-1 catalysts at Si/Al ratio is 122.85 (wt%Al is 0.77) for high 30 wt% hydrogen peroxide concentration give highest productivity with benzaldehyde. The selectivity benzaldehyde are much higher than that of cresol.

This present research has studys a new route for the synthesis of benzaldehyde from the partial oxidation of toluene in a bubble reactor using hydrogen peroxide as an oxidant over TS-1 and TS-1 modified with Al. The process should have the advantage that benzaldehyde can be produced in only one step. The investigation covers factor affecting product formation such as the aging time of the catalyst (1 and 3 days), the concentration of H_2O_2 and the effect of aluminium containing in TS-1 catalyst loaded by incorporation method.

This research possibly solve the problem of previous mention and give the new easily route to produce benzaldehyde.

The research has been scoped as follows:

1. Study about the synthesis TS-1 catalysts by hydrothermal method with titanium (IV) butoxide as titanium source, sodium-silicate as silica source and aluminium nitrate nanohydrate as aluminium source. The synthesis parameters that are studied.

2. Characterization of TS-1 and Al-TS-1 catalysts by using the following techniques.
   - X-ray Fluorescence Spectroscopy (XRF) to determine the composition of elements in the bulk of catalyst.
   - X-ray Diffractometry (XRD) to determine the structure of catalysts.
   - Fourier Transform Infrared Spectrometer (FT-IR) to determine the incorporation of Ti atoms as a framework element.
   - Ultraviolet-Visible Spectroscopy (UV-Vis) to determine coordination of Ti atoms in framework.
   - N_2 adsorption based on Brunauer-Emmett-Teller method (BET) and Barrett-Joyner-Halenda (BJH) to determine surface area pore size and pore volume.
   - Temperature Programmed Desorption of ammonia (NH_3-TPD) to determine the strong acid and weak acid sites of the catalyst.

3. Test catalytic reaction of Al-TS-1 catalysts various ratio Si/Al (200, 150, 100, 50) in a bubble reactor by hydroxylation of toluene with various 3, 7.5 and 30 wt% of hydrogen peroxide concentration as an oxidant to determine catalytic activity.

The present thesis is organized as follows:

Chapter I present the background and scopes of the research.

Chapter II presents the literature review, theory of reaction catalyst, information of modified TS-1 catalysts, information type reactor with TS-1, hydroxylation of toluene and comments on previous work.

Chapter III presents the experimental procedures of catalyst preparation, catalyst characterization and catalytic reaction in the hydroxylation of toluene.

Chapter IV presents the results and discussions of the hydroxylation of toluene over these TS-1 and Al-TS-1 catalysts in a bubble reactor.

Chapter V presents the conclusion from this research and some recommendations for future work.

Finally, the information of TS-1 catalyst, sample of calculation of catalyst preparation, acid site, conversion, calibration curves from area to mole of benzaldehyde, o-cresol and p-cresol this study research in appendix.

CHAPTER II

BACKGROUND AND INFORMATION

2.1 Theory of reaction

2.1.1 Reaction of H_2O_2 with TS-1 catalysts.

Hydrogen peroxide is a liquid made up of two atoms of hydrogen and two of oxygen (H_2O_2). As a molecule, it is similar in structure to water (H_2O), but less stable. It readily breaks down into water and oxygen when placed in contact with something it can react with. H_2O_2 is also formed by the action of sunlight on water, a natural purification system for our environment. Consequently, H_2O_2 has none of the problems of gaseous release or chemical residue that are associated with other chemical oxidants. And since H_2O_2 is totally miscible with water, the issue of safety is one of concentration. For chemical industrial using dilute H_2O_2 as an oxidant. H_2O_2 can often be made to oxidize one pollutant over another, or even to favor different oxidation products from the same pollutant. In addition to pollution control, H_2O_2 is used to bleach textiles and paper products, and to manufacture or process foods, minerals, petrochemicals, and consumer products (detergents).

Selective oxidation of aromatic compounds with hydrogen peroxide are known to occur in liquid phase using complexes of Mo, V, W, Pd, Fe, Mn, Pt, Re, etc. as homogeneous catalysts.

The role of hydrogen peroxide in organic synthesis has grown steadily over the years, as reflected by scientific and patent literature. The “active oxygen” content of hydrogen peroxide, 47% of its weight, is much higher than that of other oxidants. Water is the only byproduct.

The synthesis of titanium silicates TS-1 and TS-2, with MFI and MEL structure respectively, opened new opportunities in the oxidation with hydrogen peroxide, as heterogeneous catalysts. Titanium silicalite TS-1 is an efficient and selective catalyst for the oxidation of various organic molecules with H_2O_2: alcohols, olefins, aromatic hydrocarbons, alkyl aromatic hydrocarbons, alkanes, and sulfur and nitrogen compounds.

Huang et al. (1999) studied of epoxidation with H_2O_2 was and reported that it an attractive topic in catalysis, because epoxides were extremely important intermediates for the chemical industrial and H_2O_2 was a green oxidant using TS-1 catalyst. The results of 1-pentene epoxidation with H_2O_2 over TS-1, TS-1 was observed to be a very active and selective catalyst for this reaction under mild conditions. Sasidharan et al. (1995) studied TS-1 and TS-2 catalyzed efficiently the selective oxidation of both linear and cyclic ethers into the corresponding acids and lactones respectively, using dilute H_2O_2 as the oxidant. Halasz et al. (2003) studied continuous monitoring the oxyfunctionalization of hexane by aqueous H_2O_2 over three TS-1 type catalysts at atmospheric pressure and at temperatures from 40 to 60^oC. They reported that the oxyfunctionalization of n-hexane by H_2O_2 can measure well the activity and selectivity of catalysts. TS-PQ-B performed below the level of the best published catalysts while TS-PQ-C was quite competitive with them and TS-PQ-A was superior with respect of both the reaction rate and the efficiency for utilizing H_2O_2. Hydrogen peroxide was the preferred oxidant as it only produced water as a by-product in an environmentally friendly reaction and has a high oxygen uptake (47%).

2.1.2 Reaction of toluene with TS-1 catalysts.

Toluene, an important volatile organic compound is used in many kinds of industries, such as painting, printing, coating, and petrochemical industries. The emission of toluene causes serious air pollution, odor problem, flammability problem and affects human health. Toluene is of great importance as a chemical intermediate and solvent. Toluene is used as a raw material in the organic synthesis of a large number of chemicals such as toluene benzoic acid, benzaldehyde, xylene, other derivatives of toluene used as dye intermediates, resin modifiers, germicides, etc.

Toluene produced in the form of a mixture is used to back-blend gasoline. Isolated toluene, on the other hand, is used in: (a) the production of other chemicals; (b) as a solvent carrier in paints, thinners, adhesives, inks, and pharmaceutical products; and (c) as an additive in cosmetic products.

Toluene reacts as a normal aromatic hydrocarbon towards electrophilic aromatic substitution. With other reagents the methyl side chain in toluene may react, undergoing oxidation. Reaction with potassium permanganate leads to benzoic acid, whereas reaction with chromyl chloride leads to benzaldehyde. Halogenation can be performed under free radical conditions. Industrial uses of toluene include dealkylation to benzene, and the disproportionation to a mixture of benzene and xylene in the BTX process.

Chipurici et al. (2007) studied the oxidation of benzene and toluene with hydrogen peroxide on zeolite catalysts. In the case of benzene oxidation, the phenol resulted was quickly oxidized in the first phase of reaction, resulting dihydroxyl benzene. In case of toluene oxidation, the main products reported were cresols. Pitz et al. (2002) studied chemical kinetic study of toluene oxidation. Toluene has one of the simplest molecular structures of the alkylated benzenes and is a reasonable starting point for the development of detailed chemical-kinetic reaction mechanisms for alkylated benzenes. There are quite a few experimental studies of toluene oxidation whose data are very useful for mechanism validation. The selective partial oxidation of toluene in the gas phase using catalysts based on vanadia-containing system. The result benzaldehyde selectivities of 50% are reached at relative low toluene conversions of approximate 10-20%. Therefore, the knowledge on reactant-catalyst interaction is very important to improve the catalytic performance of these catalysts.

2.2 Information of modified TS-1 catalysts.

2.2.1 Effect of the synthetic method of titanium silicalite-1 (TS-1).

Early research about the preparation and characterization of the TS-1 catalysts [Taramasso et al. (1983)]. The material was prepared by using a source of silicon oxide a source of titanium oxide and alkali free tetrapropylammonium hydroxide (TPAOH) was used as the template. TS-1 contained low levels (up to about 2.5 atom %) of titanium substituted into tetrahedral positions in the silicalite lattice and was produced under severe conditions and at high cost, which makes the synthesis difficult to be industrialized. In order to reduce the cost of TS-1, tetrapropylammonium bromide (TPABr) can be used as the template to synthesize TS-1 instead of using the expensive template TPAOH. Padovan et al. (1992) had synthesized the TS-1 by wetness impregnation method of SiO_2-TiO_2 co-precipitate. The dried SiO_2-TiO_2 co-precipitate is impregnated with a required quantity of TPAOH solution similar to the pore volume of the solid and the subsequent treatment leads to the formation of TS-1 without the formation of TiO_2 species. Li et al. (2001) reviewed the effect of titanium species in TS-1 prepared by hydrothermal method on the catalytic activity. They reported that the form of titanium atoms incorporate into the framework of titanium silicalite-1 (TS-1) synthesized using tetrapropylammonium bromide as template differed from that using the classical method. But the symmetry of TS-1 changed from monoclinic to orthorhombic with the increase of titanium content in both methods. Wang et al. (2002) studied titanium silicalite (TS-1) was successfully synthesized by using tetra-propylammonium bromide (TPABr) and n-butylamine as the template and the base. Their results showed that TS-1 had MFI structure with high crystallinity and large crystal size, and with two kinds of titanium species.

2.2.2 Effect of the metal modified TS-1 for several reactions.

Many researches have tried to apply TS-1 catalysts. Klaewkla et al. (2006) studied effects of tin incorporation in the TS-1 on the kinetic modeling of phenol hydroxylation to dihydroxybenzenes with aqueous hydrogen peroxide. The kinetic analysis indicated that under the same reaction conditions, titanium-tin silicalite-1 (Ti-Sn-S-1) gave a higher phenol conversion rate than TS-1. Laufer and Hoelderich (2001) found that Pd/Pt/TS-1 catalyst could improve the selectivity of propylene oxide in the direct oxidation of propylene. Gas-phase epoxidation of propylene over small gold ensembles on TS-1 was investigated by Taylor et al. (2005). They found that low gold loadings resulted in an inherently small number of very active site and forcing the gold loading to higher values resulted in poor activity and stability. Ma et al. (2005) studied the transesterification of dimethyl oxalate with phenol over stannum modified TS-1 and found that the unmodified TS-1 but its catalytic activity was increased great by the interaction of Sn with Ti-O-SiO_3 weak Lewis acid centers although the Sn-modified TS-1. Russo et al. (2007) studied interaction of water vapor with Al-MCM-41, prepared by direct synthesis at ambient temperature and pressure, using tetraethoxysilane, aluminium sulfate, hexadecyltrimethylammonium bromide and ammonia, and its effect on the pore structure were studied in order to investigate the stability towards prolonged exposure to water vapor and the influence of the aluminium content. Upon prolonged exposure to water vapor, there is a small decrease in pore size (3-5%), pore volume (8-16%) and total surface area (3-7%). The stabilizing effect of the Al incorporated in the walls can result from a higher degree of condensation on the surface of the pore walls and from the mild acidity generated.

2.3 Information type reactor with TS-1

The improvement of productivity and yields of producing chemical plants is a constant goal of engineers and chemists who are engaged in production management, plant assistance, and technical service. Many of these technical people regard the subject of chemical reactor technology. This valuable field of technology is extremely useful to the chemists and engineers who are involved with plant operations and production problems. The principles of chemical reactor technology can be applied to process analysis and plant assistance to improve production and to lower operating costs. There are much type of reactor i.e. catalytic membrane reactor, fixed bed reactor, glass batch reactor, electrochemical cells reactor and bubble reactor. Selective oxidation of phenol to with hydrogen peroxide over TS-1 was performed using two types of catalytic microreactor by Yube et al. (2007) a packed bed microreactor and a catalytic wall microreactor. They reported that the reaction rates were markedly faster in both microreactors than in flasks due to improvement of the contact efficiency between reactant and catalyst. However, using a packed bed microreactor, phenol conversion and yields of benzenediols decreased gradually with time course. Therefore, they developed a catalytic wall microreactor in which catalyst elements could be exchanged easily. In addition, the regioselectivity of hydroxylation, i.e., the molar ratio of para-diol (hydroquinone)/ortho-diol (cetechol) changed remarkably. A higher degree of para-selectivity was achieved with the wall type reactor than the packed bed type reactor. Liu et al (2006) studied chemical kinetics of hydroxylation of phenol catalyzed by TS-1 on diatomite catalyst has good catalytic performance for the hydroxylation of phenol in the fixed-bed reactor operated continuously. The fixed-bed reactor continuous process had many advantages, such as to be free from tiresome operations of the catalyst filtration and makeup, and easy operation in large scale. The rate of hydroxylation of phenol increases with the increased of reaction temperature, phenol concentration and H_2O_2 concentration. Manit (2006) studied in the bubble reactor which are widely used in chemical industry where heterogeneous gas-liquid or gas-solid reaction take place, particularly, in which the liquid phase controls mass transfer processes due to the relative insolubility of gases.

Bubble column are widely used in the chemical industry where heterogeneous gas-liquid or gas-solid reactions take place, particularly, in which the liquid phase controls mass transfer processes due to the relative insolubility of gases. Important applications of bubble columns include oxidation, hydrogenation, ozonolysis, alkylation, column flotation, wastewater treatment. Structured catalytic bubble columns are new, very promising types of multiphase reactors. Their configuration lies basically between slurry reactors and trickle bed reactors. Multistage bubble column reactors are frequently used in chemical industry for relatively slow gas-liquid reactions. The main advantages of this reactor type with respect with the conventional slurry bubble column are: no problems for separating catalyst from the liquid, improved conversion and selectivity due to staging of the liquid phase and no scale up problems because the hydrodynamics is dictated by the size of the open channels of the catalytic structure. The main advantages over trickle beds are: lower pressure-drop even with 1 mm size particles, excellent radial dispersion, and possibility of counter-current operation without flooding. The bubble column reactor according to this invention provides advantages in that it can generate small bubble sizes, thus increase the residence time of the gas phase even under relatively high gas velocities and also relatively high viscosities of the liquid reactant, thereby improving the mass transfer performance of the reactor.

2.4 Hydroxylation of toluene

Purposal that the direct hydroxylation of toluene in an attractive route for the preparation of benzaldehyde show that in Figure 2.1, Although TS-1 has been used as catalyst for toluene hydroxylation in the presence of dilute H_2O_2 and an organic solvent. In the case of toluene there are two oxidation sites. One is primary carbon atom of the side chain methyl group and the other one is the ring.

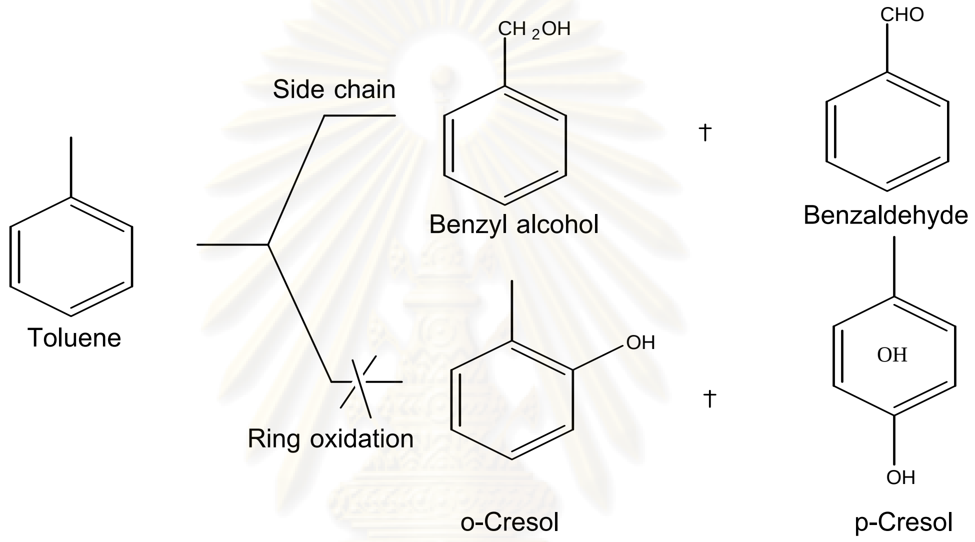


Figure 2.1 Hydroxylation of toluene

CHAPTER III

EXPERIMENTAL AND PROCEDURE

This research studies TS-1 and TS-1 modified with Al having various Si/Al ratio (200, 150, 100 and 50) and agings time (1 and 3 day). This chapter is dividul into three sections: The chemicals and catalyst preparation procedure are described in section 3.1. The structure, surface properties, composition and acidity of the catalyst characterized by various techniques such as XRF, XRD, FT-IR, UV-Vis, BET and NH_3-TPD are described in section 3.2. The final section 3.3, is the catalytic reaction of hydroxylation of toluene in a bubble reactor.

3.1 Catalyst preparation

The preparation of TS-1 and Al-TS-1 catalysts uses the incorporation method. The same amount of aluminium nitrate nanohydrate was added in both gel solution and decantation solution. Detail of chemicals used in the preparation of TS-1 and Al-TS-1 catalysts are shown in the Table 3.1. The recipies used are summarized in Table 3.2 and the preparation procedure is shown in Figure. 3.1.

Table 3.1 Chemicals used in the catalyst preparation

Chemical	Grade	Supplier
Titanium(IV) butoxide 97%	-	Aldrich
Tetrapropylammonium bromide 98%	-	Aldrich
Sodium chloride	Analytical	APS
Sodium hydroxide	Analytical	Merck
Sulfuric acid	Analytical	Aldrich
Sodium silicate solution	Extra pure	Merck
Aluminium(III)nitrate nonahydrate	Analytical	APS

Table 3.2 Reagents used for the preparation of TS-1, Al-TS-1: Si/Ti = 50, Si/Al = 200, 150, 100 and 50

Solution for the gel preparation			Solution for decant-solution preparation		
Solution A1			Solution A2		
$Ti[O(CH_2)_3CH_3]_4$	2.2970	g	$Ti[O(CH_2)_3CH_3]_4$	2.2970	g
TPABr	5.72	g	TPABr	7.53	g
NaCl	11.95	g	De-ionized water	60	ml
$Al(NO_3)_3.9H_2O$, Si/Al = 200	0.61	g	$Al(NO_3)_3.9H_2O$, Si/Al = 200	0.61	g
$Al(NO_3)_3.9H_2O$, Si/Al = 150	0.82	g	$Al(NO_3)_3.9H_2O$, Si/Al = 150	0.82	g
$Al(NO_3)_3.9H_2O$, Si/Al = 100	1.23	g	$Al(NO_3)_3.9H_2O$, Si/Al = 100	1.23	g
$Al(NO_3)_3.9H_2O$, Si/Al = 50	2.46	g	$Al(NO_3)_3.9H_2O$, Si/Al = 50	2.46	g
De-ionized water	60	ml	H_2SO_4 (conc.)	3.4	ml
H_2SO_4 (conc.)	3.4	ml			
Solution B1			Solution B2		
Sodium silicate	69	g	Sodium silicate	69	g
De-ionized water	45	ml	De-ionized water	45	ml
Solution C1			Solution C2		
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_2SO_4 (conc.)	1.55	ml			

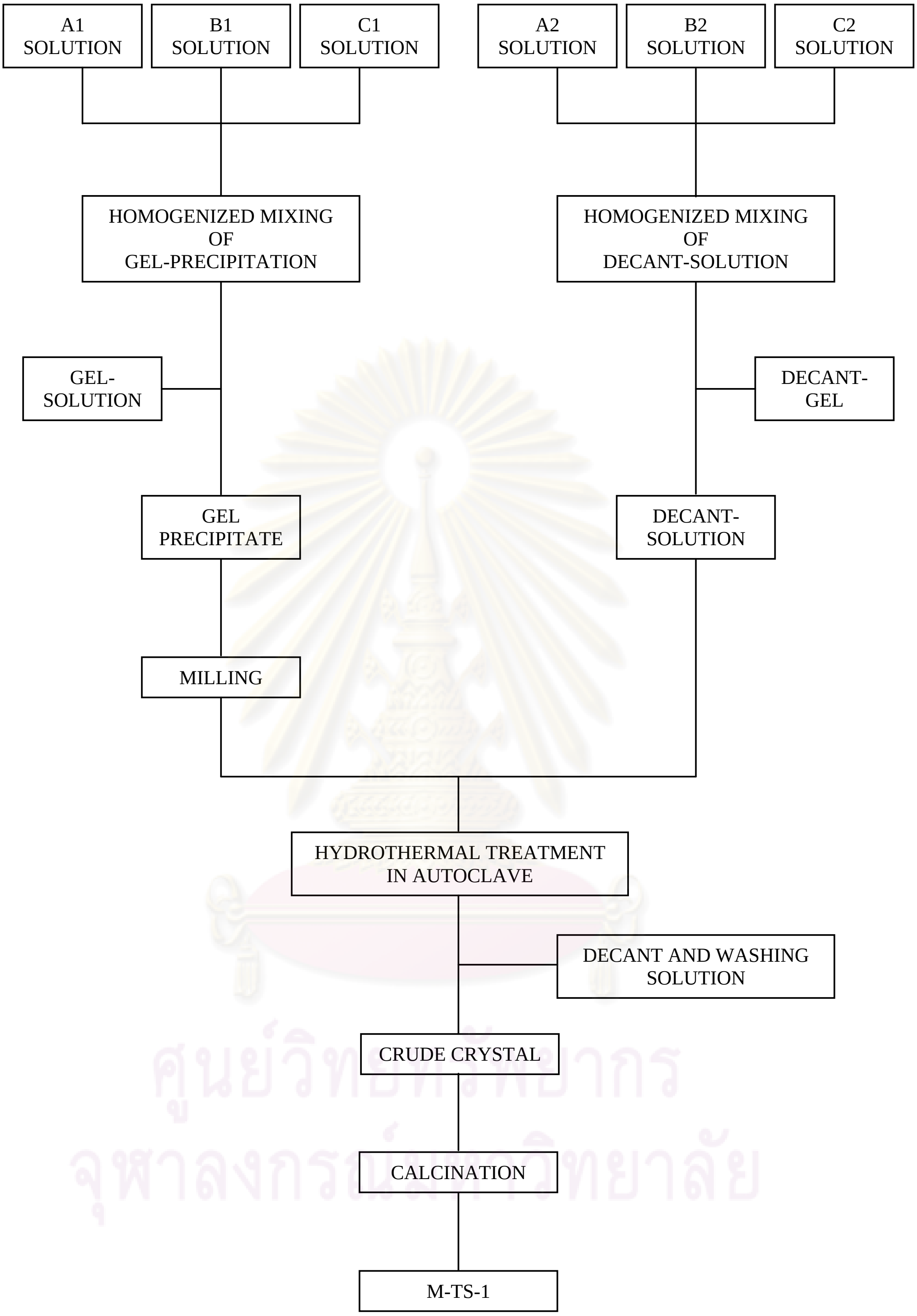


Figure 3.1 The preparation procedure of Al-TS-1 by rapid crystallization method.

Firstly, a gel mixture was prepared by adding solution A1 and solution B1 into solution C1, while stirring with a magnetic stirrer at room temperature. The pH of the gel mixture was maintained within the range 9-11. The mixed solution was further stirred for 2 h. The gel mixture was separated from the supernatant liquid by a centrifuge. Secondly, a decantation solution was prepared by adding solution A2 and solution B2 into solution C2, same as for the preparation of gel mixture. The supernatant liquids from A2, B2 and C2 were mixed together with the milled gel mixture. However, before mixing, the pH of solution was maintained to be in the range 9-11. The colorless supernatant liquid was separated from the mixture by centrifugation.

In the step of crystallization, the supernatant of solution C1 is mixed with the decant of solution C2 in a 500 ml. The pyrex glass container was placed in a stainless steel autoclave. The air in the autoclave is replaced with N_2 gas under pressure 3 kg/cm^2 gauge, after that the autoclave was heated from room temp to 180°C with a heating rate of 2°C/min. After that the hot mixture was cooled down to room temperature in the autoclave overnight. The temperature was programmed under the hydrothermal treatment for the crystallization.

The obtained product crystals were washed with de-ionized water decreased pH from about 10 to 7 by centrifugation in order to remove chloride out of the crystals. Then the crystals were dried in an oven at 110 ºC for at least 24 h. The dry crystals were calcined in an air stream at 550 ºC and held at that temperature for 7 h, by heating them from room temperature to 550 ºC at a heating rate at 10 ºC/min. The calcined crystals were finally cool down to room temperature.

The treatment TS-1 and Al-TS-1 catalysts were placed into a round bottom flask then 5M of HNO_3 aqueous solution was added. After reflux at 80 ºC for 3 h, the treatment catalyst was filtered, washed with distilled water until pH 7, dried at 110 ºC and calcined at 540 ºC for 24 h in static air. The powder is final product.

3.2 Catalyst characterization

The powder structure were characterized by using power X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD), Fourier Transform Infrared (FT-IR), Ultra Violet-Visible (UV-Vis), Brunauer-Emmett-Teller (BET) and Temperature Programmed Desorption of Ammonia (NH_3-TPD).

3.2.1 X-Ray Fluorescence Spectrometer (XRF)

The chemical composition analysis of elements of the catalyst was performed by X-ray fluorescence (XRF) using Siemens SRS3400 at the Nuclear Science and Technology Knowledge Center.

3.2.2 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 $K\alpha$ radiation with Ni filter. Scans were performed over the 2θ ranges from 6^{o} to 30^{o}.

3.2.3 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 mixed with KBr with ratio of sample: KBr equal to 1:100 and then pressed into a thin wafer. Infrared spectra were recorded between 400 and 4000 cm^{-1} on a microcomputer.

3.2.4 Ultra Violet-Visible (UV-Vis)

The Ultra Violet-Visible was used to confirm the titanium structure on a Perkin Elmer Lambda 650 spectrometer. The spectra in the wavenumber range 200 to 700 nm and absorbance axis.

3.2.5 BET surface area measurement

The total surface area, pore volume and pore size were calculate using BET Micremeritrics ASAP 2020. The sample cell which contained 0.2 g of sample was placed into BET Micromeritrics ASAP 2020. After degassing step, the surface area and pore volume of catalyst were measured.

3.2.6 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. NH_3-TPD was carried out using a flow apparatus. The catalyst sample (0.1 g) was treated at 550^oC in helium flow for 1h and then saturated with 15 %NH_3/He mixture after cooling to 80 ^oC. After purging with helium at 80 ^oC for 1 h to remove weakly physisorbed NH_3, the sample was heated to 550 ^oC at therate of 10 ^oC/min in a helium flow of 50 cm^3/min. The amount of acid sites on the catalyst surface was calculated from the desorption amount of NH_3. It was determined by measuring the areas of the desorption profiles obtained from the Micromeritics Chemisorb 2750 analyzer.

The deconvlution of NH_3-TPD peak was carried out with the “fityk” curve fitting programme. The peaks were assumed to be Gaussian with showness shape (using parameter ‘SplitGaussian’ in the programme).

3.3 Reaction study in hydroxylation of toluene in a bubble reactor

3.3.1 Chemicals

The reactants used for the reaction study are shown in Table 3.3.

Table 3.3 The chemicals used for the reaction study.

Chemical	Grade	Supplier
Toluene	Analytical	Fisher Scientific
Hydrogen peroxide 30%	Analytical	Merck
Ethanol	Analytical	Merck

3.3.2 Apparatus

The catalytic test was performed in a flow system shown diagrammatically in Figure 3.2. The reaction system consists of a reactor, a gas controlling system, an evaporating system, an oil bath and a gas chromatography. The instruments used in this system are listed and explained as follows:

3.3.2.1 Reactor

The reaction was performed in a conventional glass tubular reactor (inside diameter = 4 cm), at atmospheric pressure. The reactor consists of two parts (tube part and head part). The gas mixture entered to the reactor from the head part which is jointed with glass tube immersing in the mixture of catalyst and hydrogen peroxide in order to allow gaseous toluene flows upward from the bottom of the reactor.

3.3.2.2 The evaporating system

The evaporating system consists of a 1 m tube bending in spiral shape. The entrance of the tube was installed with a three way valve which is connected to the gas controlling system in one side. Another side was adapted and used as the injection port. This tube was immersed in an oil bath which heated temperature at 150 °C and used as the evaporator for liquid toluene. The hot plate was used for heating up the oil bath. Liquid toluene was evaporated into gaseous phase before entering to the reactor by pulse injecting to the system via the injection port using a 1 ml syringe in order to control the accuracy of reactant amount.

3.3.2.3 Oil Bath

This instrument supplies the required heat to the reactor for the reaction. The reactor was operated at 70 °C.

3.3.2.4 Gas controlling system

The gas supplying system consists of a cylinder of ultra high purity nitrogen that equipped with a pressure regulator (0-120 psig), an on-off valve and a mass flow control was used for adjusting the flow rate.

3.3.2.5 Gas chromatography

The feed and products were analyzed by a gas chromatograph equipped with a FID detector (SHIMADZU GC9A). The operating conditions of the GC are listed in Table 3.4.

3.3.3 Reaction procedure

The hydroxylation of toluene with hydrogen peroxide was carried out by using a conventional flow shown in Figure 3.2 under the following condition atmospheric pressure.

Table 3.4 Operating conditions for gas chromatograph

Gas chromatograph	SHIMADZU GC9A
Detector	FID
Packed column	GP 10% SP-2100
Carrier gas	N_2 (99.999%)
Injector temperature (°C)	250
Detector temperature (°C)	250
Initial column temperature (°C)	80
Initial hold time (min)	5
Program rate (°C/min)	2
Final column temperature (°C)	230
Final hold time (min)	15
Analyzed chemicals	Toluene, Benzaldehyde and cresol

The procedures are described in the detail below.

1) 1 g of catalyst powder, hydrogen peroxide and a magnetic bar were filled in the glass tube reactor. Then, the reactor was heated up by raising the oil bath temperature to 70 °C.

2) Heat up the temperature of oil bath of the evaporating system to 150 °C.

3) Adjust the outlet pressure of nitrogen to 1.5 bars and turn on the on-off valve to allow nitrogen gas to pass through the evaporating system. The flow rate was adjusted to 60 ml/min by a mass flow controller. The outlet gas flow rate can be rechecked by using a bubble flow meter.

4) Start the reaction by injecting certain an amount of liquid toluene to the evaporating system. Upon entering the hot spiral tube, the liquid toluene was evaporated immediately to gaseous toluene and was flushed to the reactor by using N_2 as the carrier gas.

5) The gas mixture passes through the mixture containing the catalyst and hydrogen peroxide, where the hydroxylation of toluene reaction to took place.

6) The next period, the equivalent liquid toluene was injected into the toluene feed tube again.

7) Analyze the product sample by placing the reactor into the cool bath in order to stop the reaction.

8) Mix the liquid mixture with 40 ml of ethanol and stir until the liquid mixture became a homogeneous phase. After that, centrifuge the mixture in order to separate the catalyst from the liquid solution.

9) The liquid product was analyzed by the FID gas chromatography. The chromatogram data were converted into mole of products using a calibration curve (Appendix C).

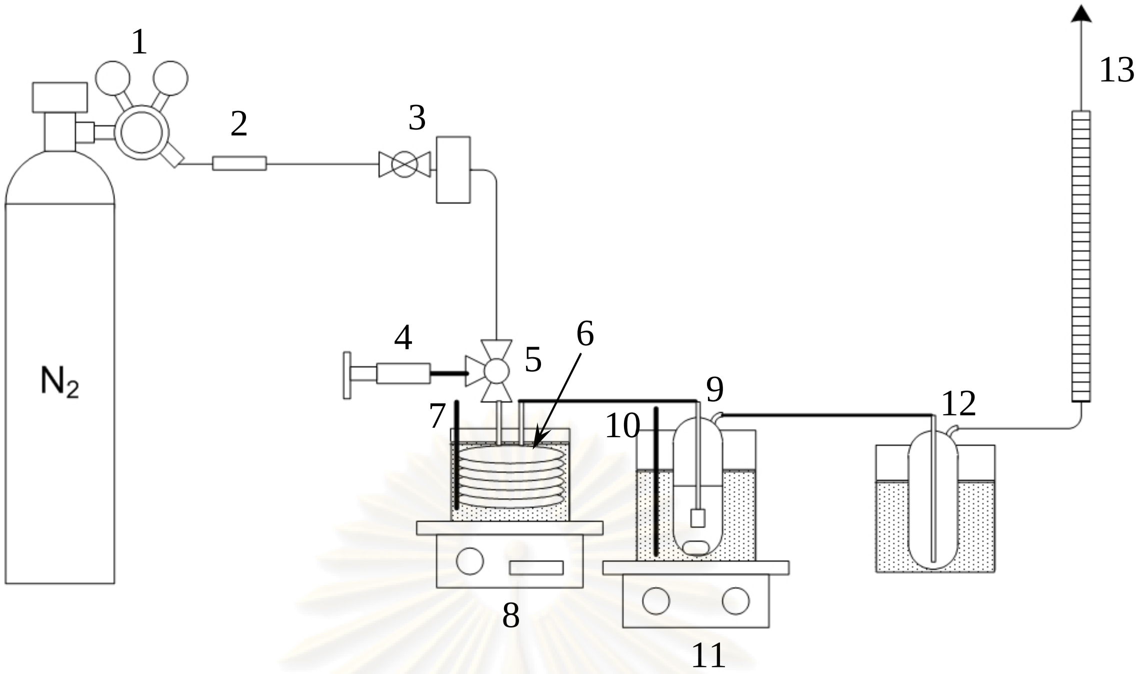


Figure 3.2 Schematic diagram of the reaction apparatus for the hydroxylation of toluene with hydrogen peroxide.

1. Pressure Regulator
2. Gas Filter
3. Gas Controlling System
4. Reactant Syringe
5. Three Way Connector
6. Evaporator
7. Thermometer
8. Oil Bath
9. Reactor
10. Thermometer
11. Oil Bath
12. Gas Trap
13. Vent Gas

CHAPTER IV

RESULTS AND DISSCUSSIONS

This chapter reports the characterization of TS-1 and Al-TS-1 catalysts prepared by hydrothermal method. The characterization comprises of XRF to measure the catalyst compositions, XRD to identify crystal structure, FT-IR to indicate the location of titanium cation, UV-Vis used to confirm the titanium structure, BET to measure the surface area, and NH_3-TPD to determine the strength and number of acid site of the catalysts. Physical characters and chemical properties are summarized in section 4.1. The study of hydroxylation of toluene is reported in section 4.2 as percentage of hydrogen peroxide converted to organic products, selectivity, yield and productivity of organic products.

4.1 Catalyst characterization

4.1.1 X-Ray Fluorescence (XRF)

The XRF technique is used for quantitative determination of Si, Ti and Al contents. Table 4.1 reports %Si, %Ti, %Al, Si/Ti and Si/Al. Amount titanium and metal loading are very low when compared with amount of silicon.

The results show that the amount of aluminium cation that can be incorporated in the MFI structure increases with the amount of aluminium added into the solutions A1 and A2. Due to Al^{3+} has similar diameter to Si^{4+}, the substitution of Si^{4+} by Al^{3+} should not be too difficult. In reality, the technique used to prepare TS-1 in the present work is modified from the rapid crystallization technique developed for the preparation of ZSM-5, an aluminosilicate zeolite.

The appearance of Al in TS-1 is possibly due to the contamination from the pyrex glass.

Table 4.1 Chemical compositions (%by mole) of TS-1 and TS-1 modified with aluminium (Al-TS-1).

Catalysts	%Si	%Ti	%Al	Si/Ti	Si/Al
TS-1(1D)[1]	93.87	4.21	0.25	22.30	375.48
Al-TS-1(1D), Si/Al=200[2]	95.73	2.99	0.62	32.02	154.40
Al-TS-1(1D), Si/Al=150	97.01	1.13	0.69	85.85	140.59
Al-TS-1(1D), Si/Al=100	95.31	2.7	0.88	35.30	108.31
Al-TS-1(1D), Si/Al=50	95.67	2.06	1.96	46.44	48.81
TS-1(3D)[1]	96.86	2.04	0.19	47.48	509.79
Al-TS-1(3D), Si/Al=200	90.00	1.91	0.59	47.12	152.54
Al-TS-1(3D), Si/Al=150	96.12	2.25	0.71	42.72	135.38
Al-TS-1(3D), Si/Al=100	96.62	1.87	1.01	51.67	95.66
Al-TS-1(3D), Si/Al=50	94.18	2.61	1.69	36.08	55.73

[1] Aging time: 1D – 1 day, 3D – 3 days

[2] Si/Al ratio used in preparation

4.1.2 X-Ray Diffraction (XRD)

The crystalline structures of TS-1 and Al-TS-1 are determined by XRD technique. The XRD patterns of TS-1 and Al-TS-1 prepared from 1 day aging and prepared from 3 day aging are showed in Figures 4.1 and 4.2 respectively. Figures 4.1 and 4.2 show that all catalysts have six main characteristic peak at $2\theta \approx 8.0$, 8.8, 14.8, 23.1, 24.0 and 29.5 that are the characteristic peak of the MFI structure. The major difference between the catalysts obtained from 3 day aging (Al-TS-1(3D)) and the catalysts from 1 day aging (Al-TS-1(1D)) is the catalysts obtained from 3 day aging have shaper and stronger peaks. This indicates that the catalysts obtained from 3 day aging have more perfect crystal structure than the catalysts obtained from 1 day aging. However, it can be concluded that the variation of aging time from 1 day to 3 days does not significantly affect the main crystalline structure of the catalyst.

In addition, the incorporation of aluminium into TS-1 catalyst does not affect significantly the MFI structure. After the catalysts were treated, it is found that the structures are not destroyed by the treatment with HNO_3.

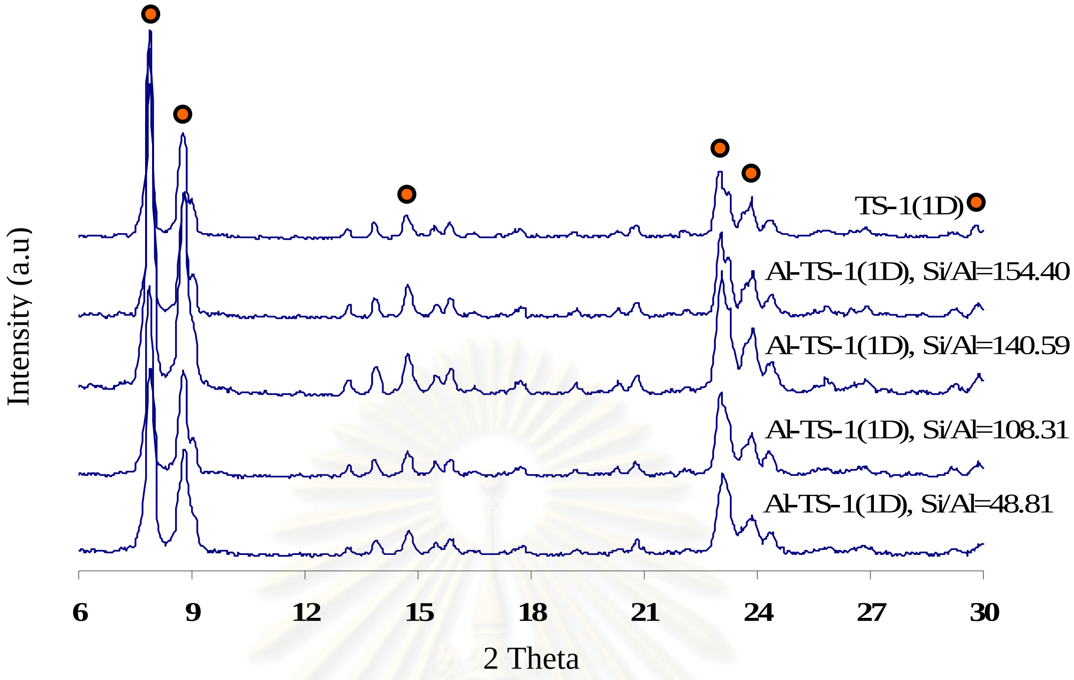


Figure 4.1 XRD patterns of the TS-1(1D) and Al-TS-1(1D) catalysts.

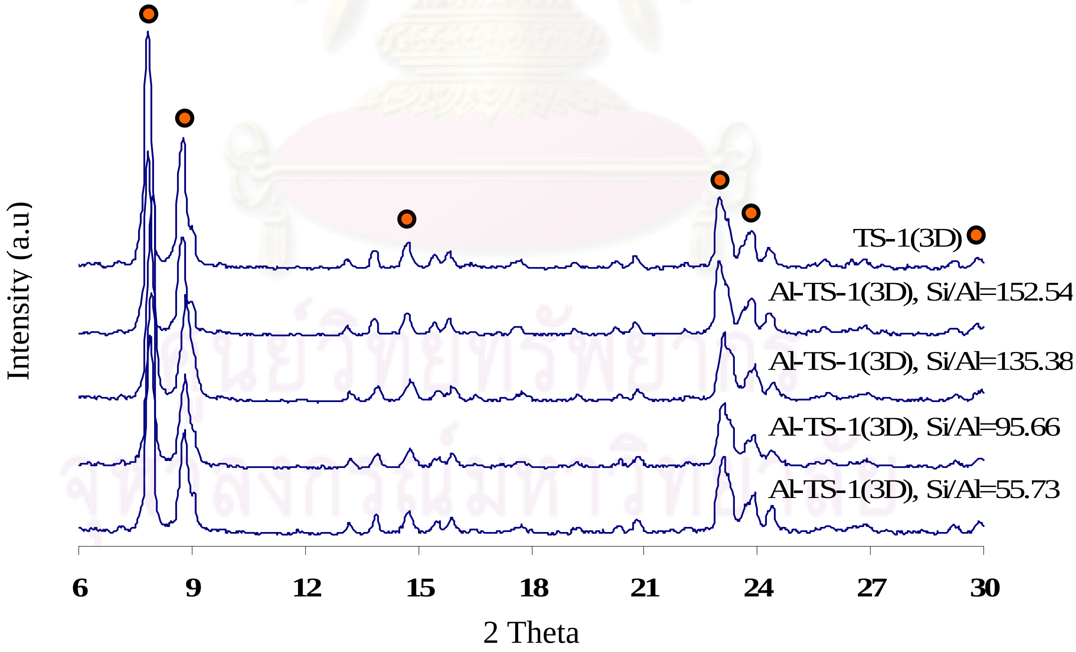


Figure 4.2 XRD patterns of the TS-1(3D) and Al-TS-1(3D) catalysts.

4.1.3 Fourier Transform Infrared (FT-IR)

FT-IR is used to indicate the existence of Ti^{4+} in the framework of the catalyst. The IR absorption spectra of all samples in $Ti(SiO)_4$ absorption region is showed in Figures 4.3 and 4.4. Figure 4.3 shows IR spectra of TS-1(1D) and Al-TS-1(1D). Figure 4.4 shows IR spectra of TS-1(3D) and Al-TS-1(3D). Each sample shows the absorption band around 960 cm^{-1} which indicates that Ti^{4+} has been incorporated into the silica framework (Halasz et al., 2003). This peak is also interpreted as the asymmetric Si-O-Ti stretching mode of Si- and Ti- containing in catalyst (Li et al., 2001).

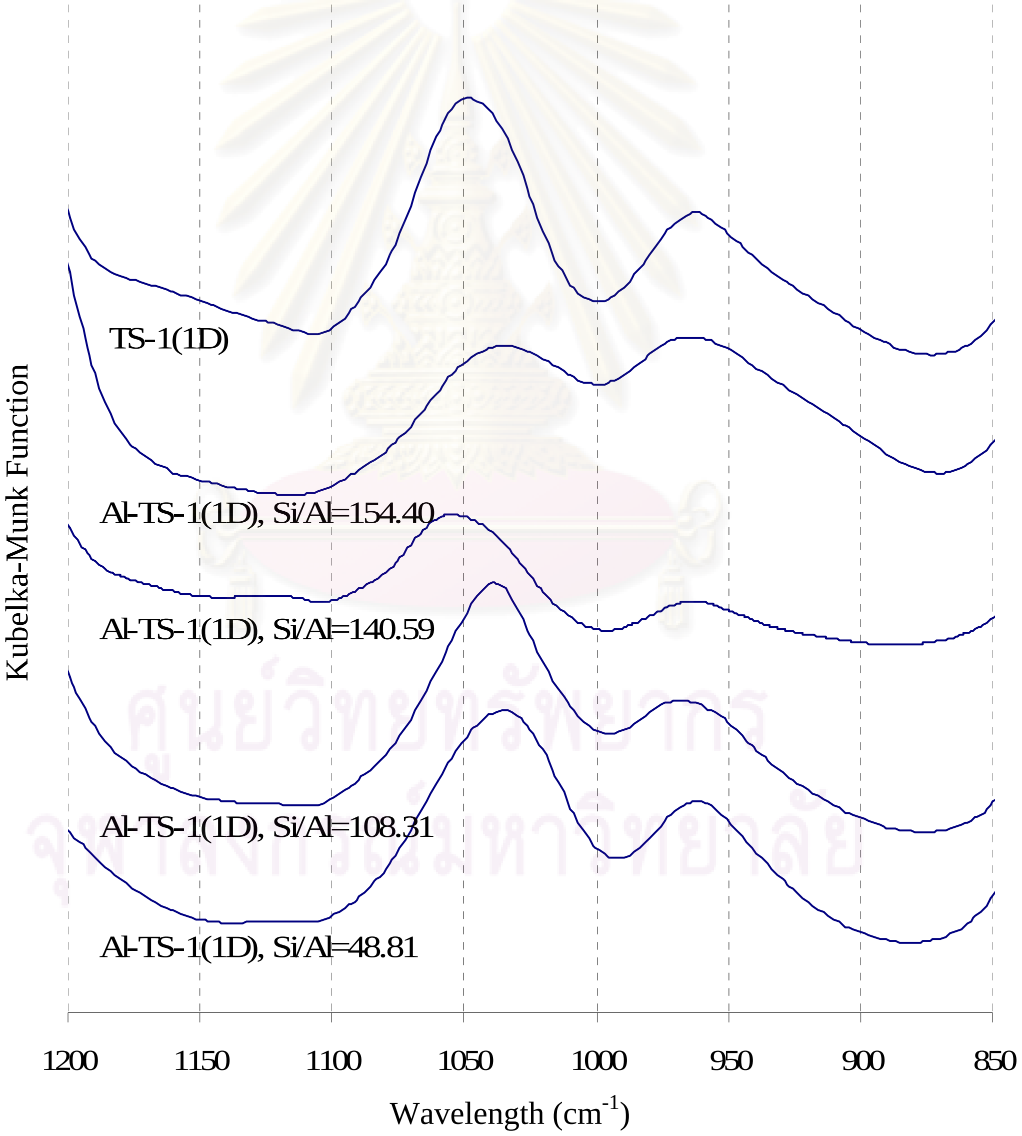


Figure 4.3 FT-IR spectra of TS-1(1D) and Al-TS-1(1D) catalysts.

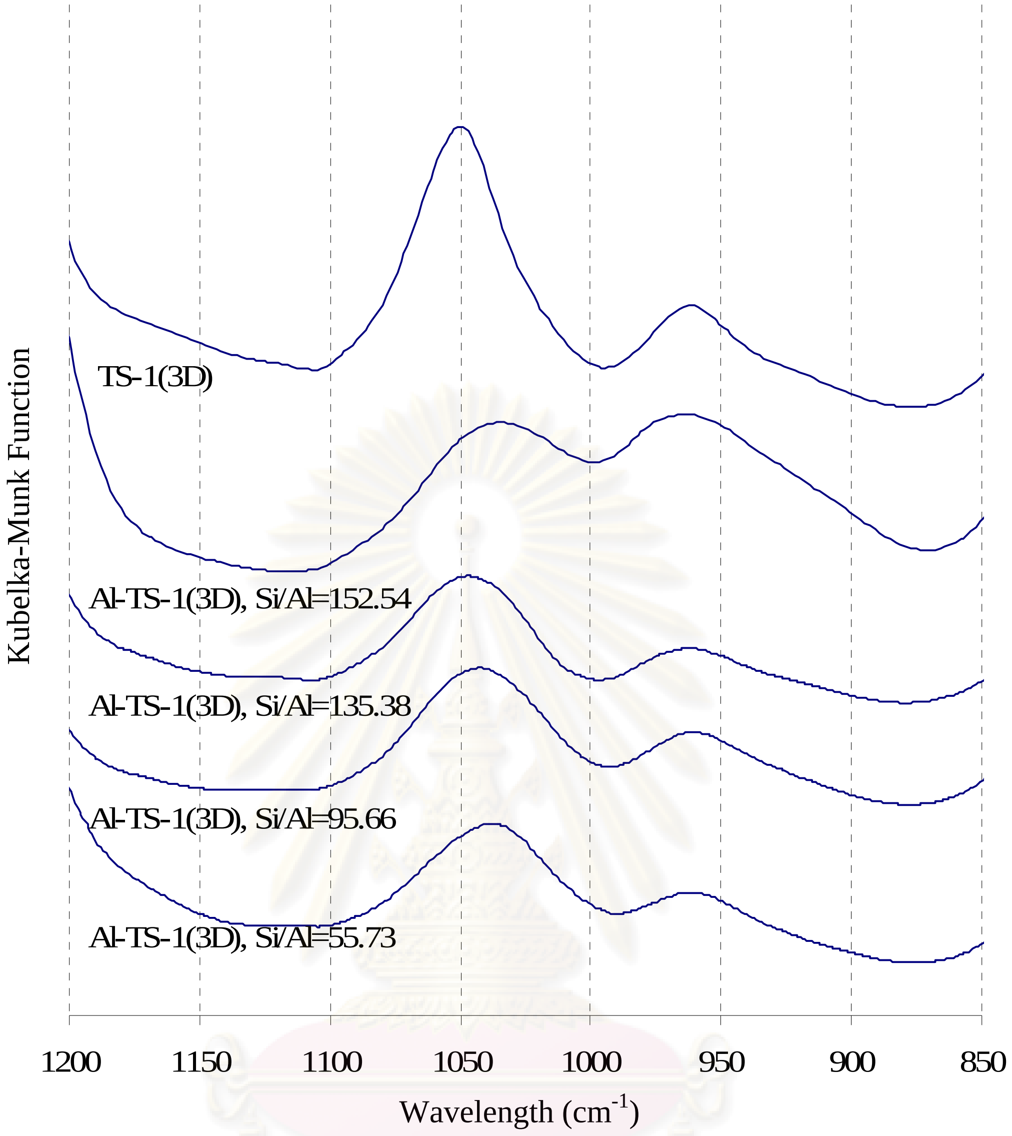


Figure 4.4 FT-IR spectra of TS-1(3D) and Al-TS-1(3D) catalysts.

4.1.4 Ultra Violet–Visible Spectroscopy (UV-vis)

The coordination of titanium is characterized by UV-Vis spectroscopy technique. Figures 4.5 and 4.6 show absorption band between 205 to 240 nm which is the absorption region of isolated tetrahedral titanium atoms (Ti^{4+}) in the framework (Halasz et al., 2003). It is found that none of all illustrated spectra shows any distinctive observable shoulder and/or peak.

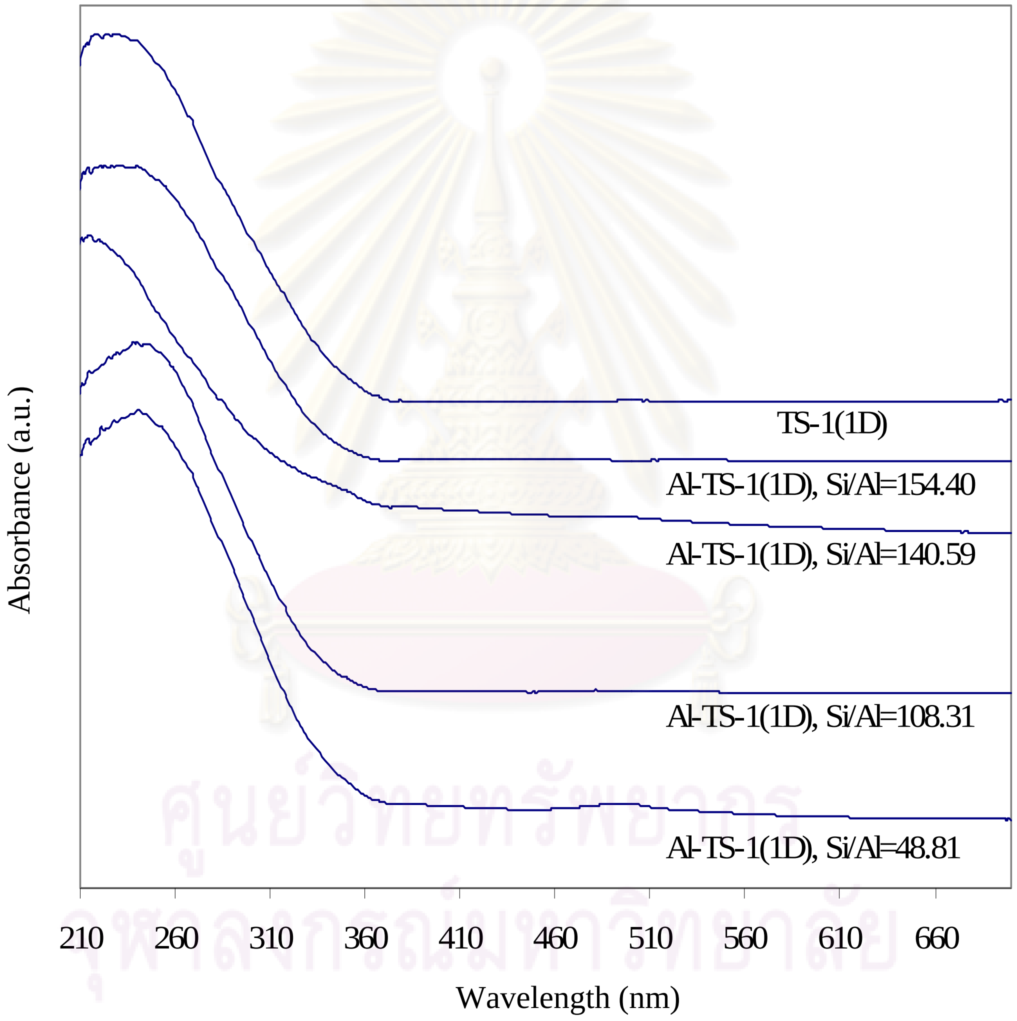


Figure 4.5 UV-vis of TS-1(1D) and Al-TS-1(1D) catalysts.

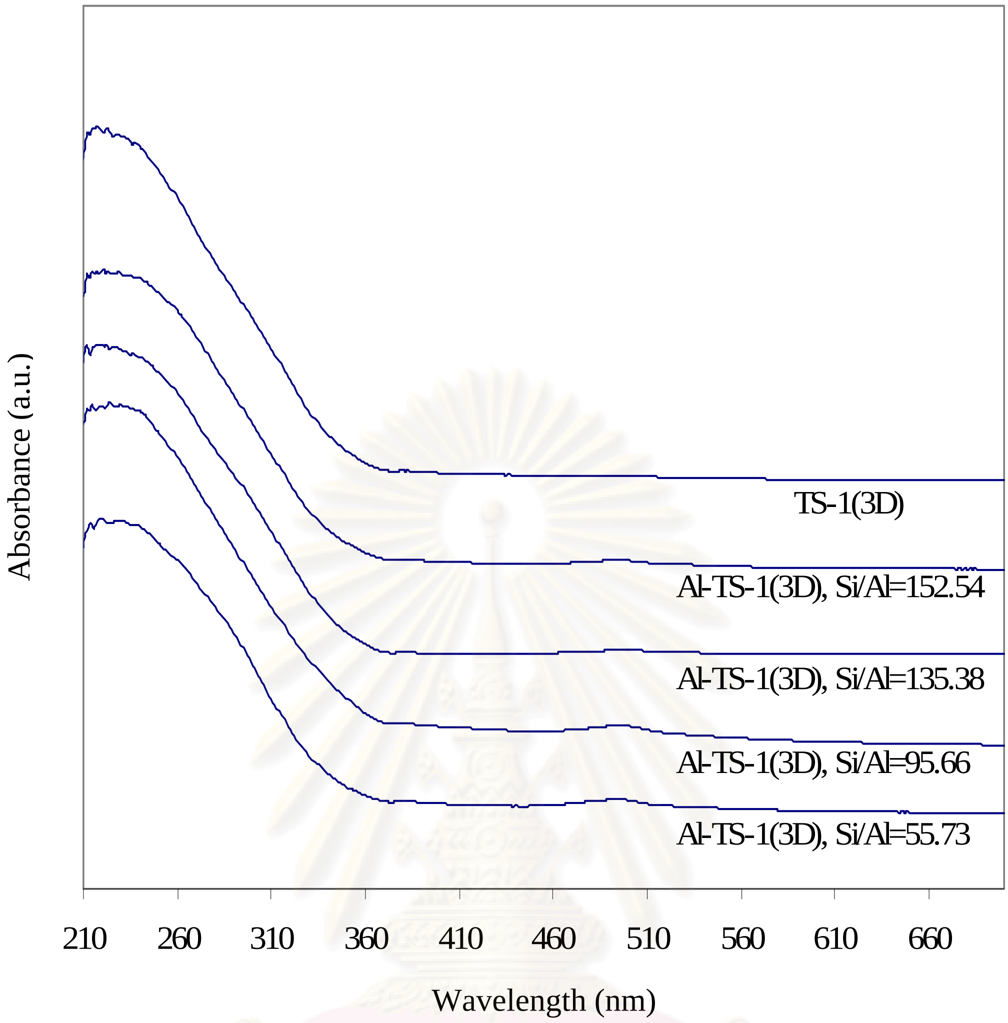


Figure 4.6 UV-vis of TS-1(3D) and Al-TS-1(3D) catalysts.

Up to this point, a conclusion can be drawn for XRD, FT-IR and UV-Vis analysis is that all synthesized catalysts have the MFI structure having Ti^{4+} in the framework.

4.1.5 Brunaur-Emmett (BET surface area)

The surface areas of all catalysts are determined by BET technique. The results are summarized in Table 4.2. It is found that all samples have surface area around 350 m^2/g which is not so different. Hence, any difference observed during catalytic testing should not be the result of the difference in catalyst surface area.

Table 4.2 BET surface areas of the TS-1 and Al-TS-1 catalysts.

Catalysts	**BET surface area (m^2/g)**	**Surface area of pores between 17A^o to 3000A$^{o\ (a)}$, (m^2/g)**	**Volume of pores between 17A^o to 3000A$^{o\ (b)}$, (cm^3/g)**
TS-1(1D)	340.08	137.17	0.1348
Al-TS-1(1D), Si/Al=200	356.87	139.47	0.1197
Al-TS-1(1D), Si/Al=150	371.73	195.26	0.1997
Al-TS-1(1D), Si/Al=100	321.79	112.28	0.0788
Al-TS-1(1D), Si/Al=50	331.91	130.46	0.0936
TS-1(3D)	351.69	148.31	0.1245
Al-TS-1(3D), Si/Al=200	354.35	161.85	0.1501
Al-TS-1(3D), Si/Al=150	354.33	145.54	0.1527
Al-TS-1(3D), Si/Al=100	349.76	142.91	0.1199
Al-TS-1(3D), Si/Al=50	347.63	112.84	0.1325

(a) BJH Desorption cumulative surface area of pores between 17A^o and 3000A^o width.

(b) BJH Desorption cumulative volume of pores between 17A^o and 3000A^o width.

Since, catalyst characteristics determined from XRD, FT-IR, UV-Vis, and BET surface area measurement are not so different, they should not affect catalytic properties of the catalyst. The major difference is the content of aluminium of each catalyst sample. The difference in catalytic activity which will be should in the next section. Therefore, should be the result of the difference in the content of aluminium of each sample.

4.1.6 Temperature Programmed Desorption of Ammonia (NH_3-TPD)

As demonstrated in sections 4.1.1-4.1.3 that the major difference is the amount of aluminium cation. Therefore, it is a topic of interest in this research to determine, if possible, why difference amount of aluminium causes difference catalytic behavior.

It is generally known that aluminium cation incorporated in the silicalite framework will act as an acidic site. The acidic strength of aluminium cation inversely proportion to the amount of aluminium content while the density of acidic site proportion to the amount of aluminium content. It is hypothesized that the acidic property of the catalysts may relate to the catalytic behavior of the catalyst. Therefore, all catalysts are subjected to NH_3-TPD measurement. The results are graphically showed in Figures 4.7-4.16. Figures 4.7-4.11 show NH_3-TPD profiles of TS-1(1D) and Al-TS-1(1D). Figures 4.12-4.16 show NH_3-TPD profiles of TS-1(3D) and Al-TS-1(3D). The peak disconsolation and fitting processes are carried out using a freeware “fityk” program. The amount of acidic site can be determined from percentage of each component peak and the total amount of ammonia desorbed.

Al-TS-1 catalysts synthesized in this research with difference various ratio of Si/Al is 200,150, 100 and 50 shows desorption signals in the temperature range 100-500 °C. The obtained NH_3-TPD desorption profiles can be separated into two main component peaks: weaker acid sites at a low temperature around 100-170 °C and stronger acid sites appear the peaks at a higher temperature around 190-400 °C. The NH_3-TPD desorption profiles reveal that when the aluminium content is increased, the amount of the stronger acid site also increases. In addition, the peak of the stronger acid site moves slightly to a higher temperature with the increased amount of aluminium.

The observed increase in the acid strength with the increase of aluminium content seems to contradict with what is mentioned in the above paragraph. It is hypothesized that when the amount of aluminium is increased, some aluminium ions, as well as some silicon, may not involve in the formation of the silicalite structure. They may form amorphous alumina-silica compound which also possesses strong acidic sites. This hypothesis comes from the analysis which shows the increase of acid strength with the increase of aluminium content and the absence of XRD peaks of other structure but MFI.

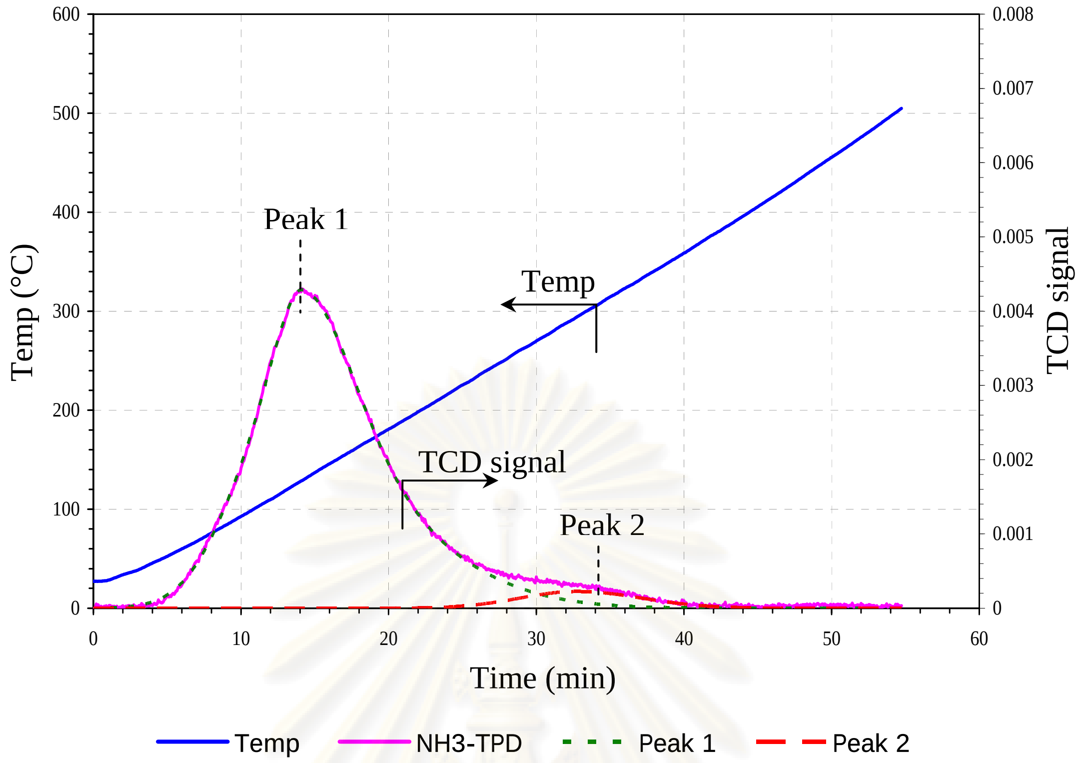


Figure 4.7 NH_3-TPD of TS-1(1D) catalyst.

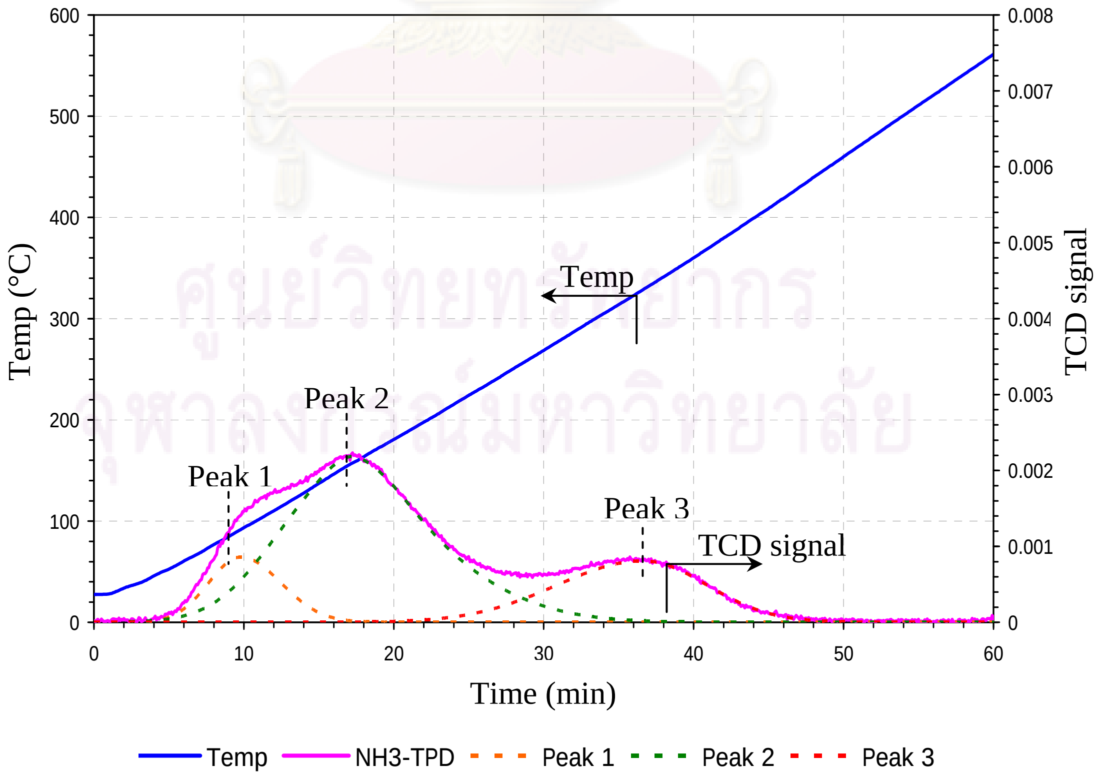


Figure 4.8 NH_3-TPD of Al-TS-1(1D) catalyst with various Si/Al is 154.40.

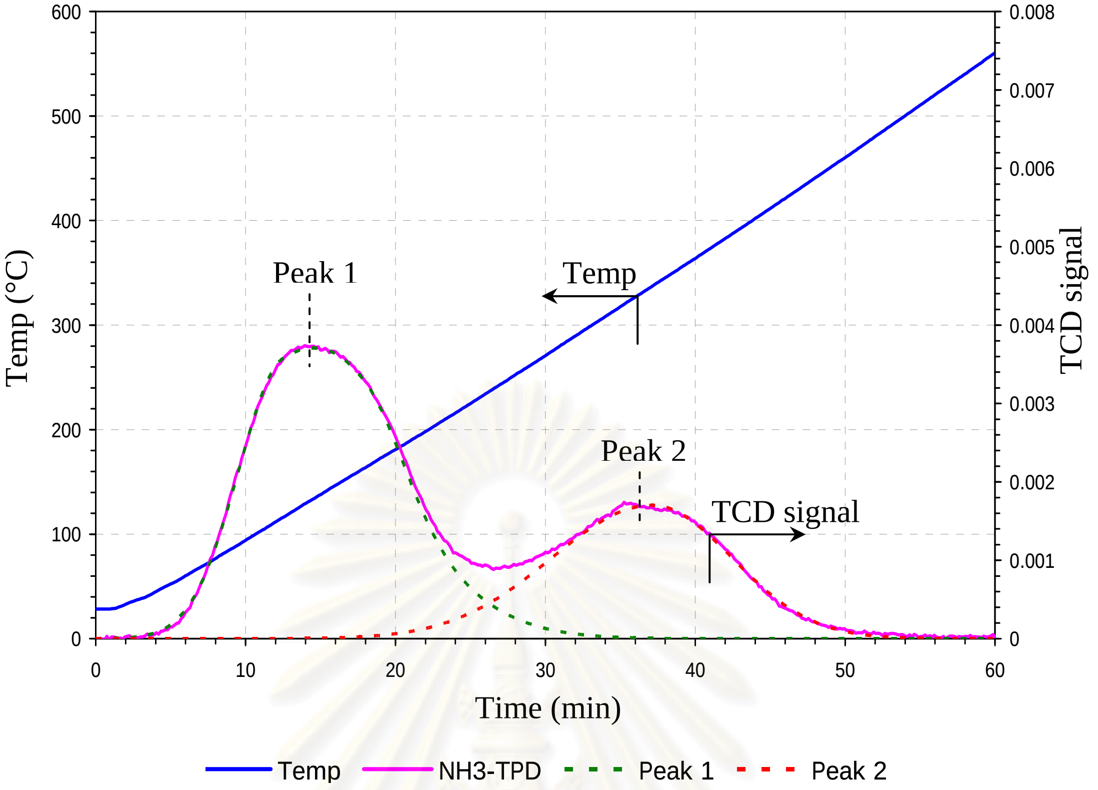


Figure 4.9 NH_3-TPD of Al-TS-1(1D) catalyst with various Si/Al is 140.59.

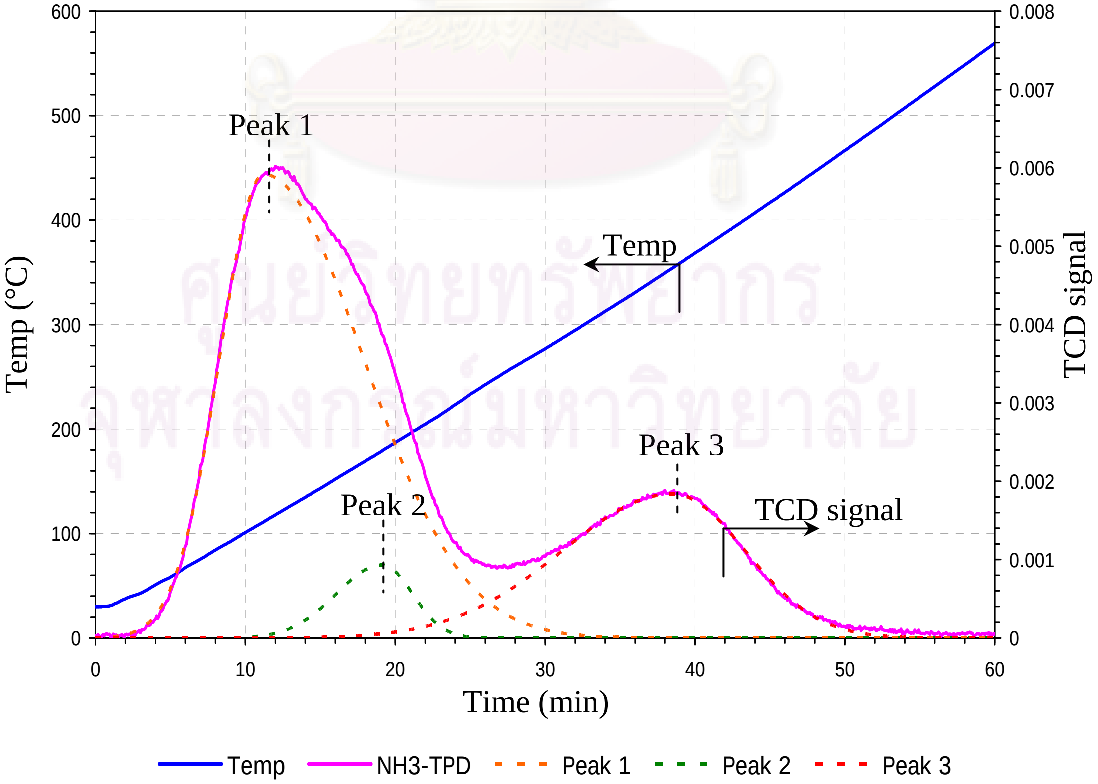


Figure 4.10 NH_3-TPD of Al-TS-1(1D) catalyst with various Si/Al is 108.31.

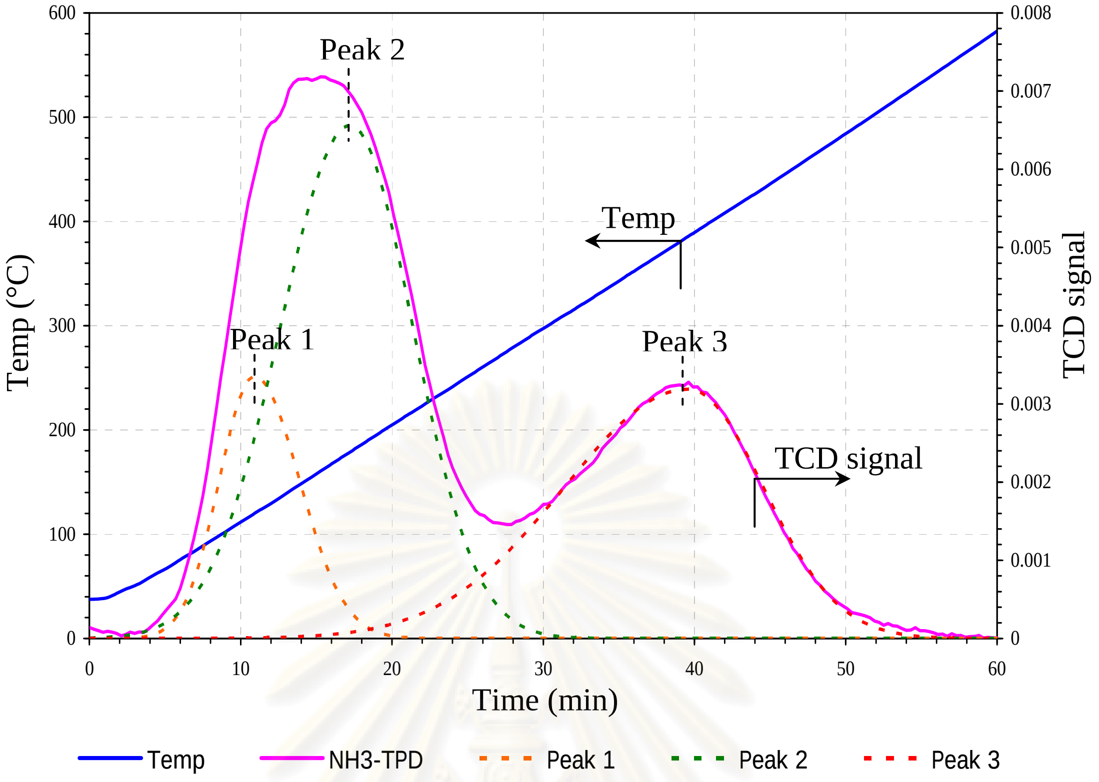


Figure 4.11 NH_3-TPD of Al-TS-1(1D) catalyst with various Si/Al is 48.81.

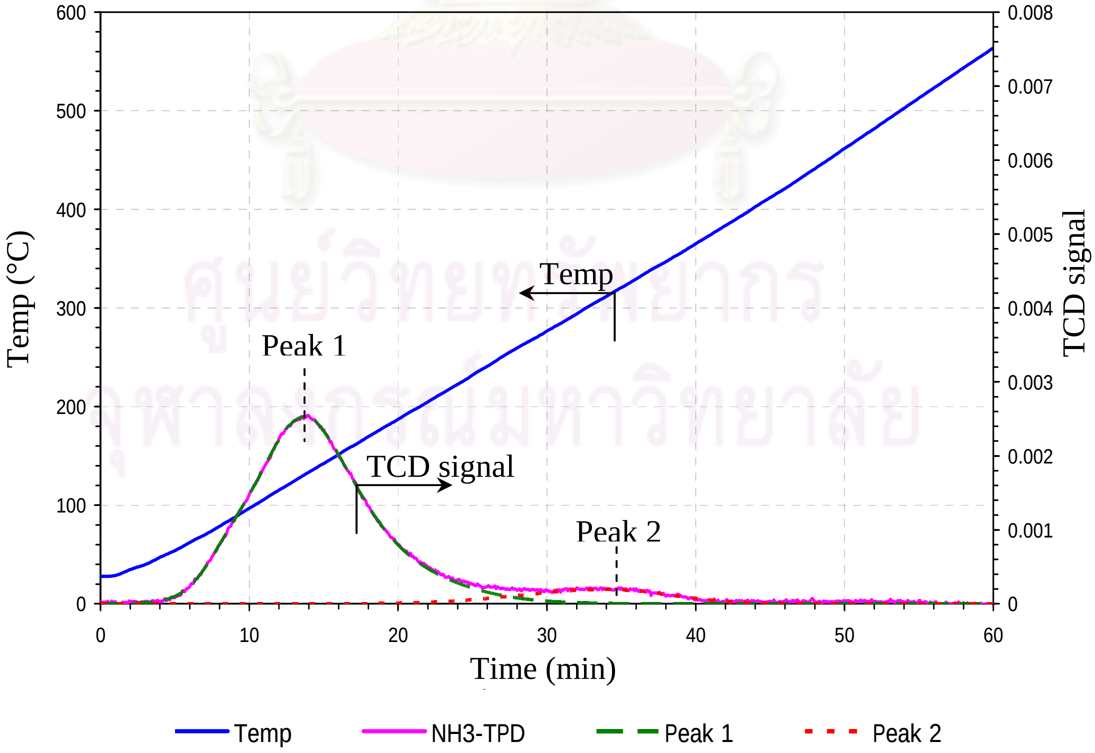


Figure 4.12 NH_3-TPD of TS-1(3D).

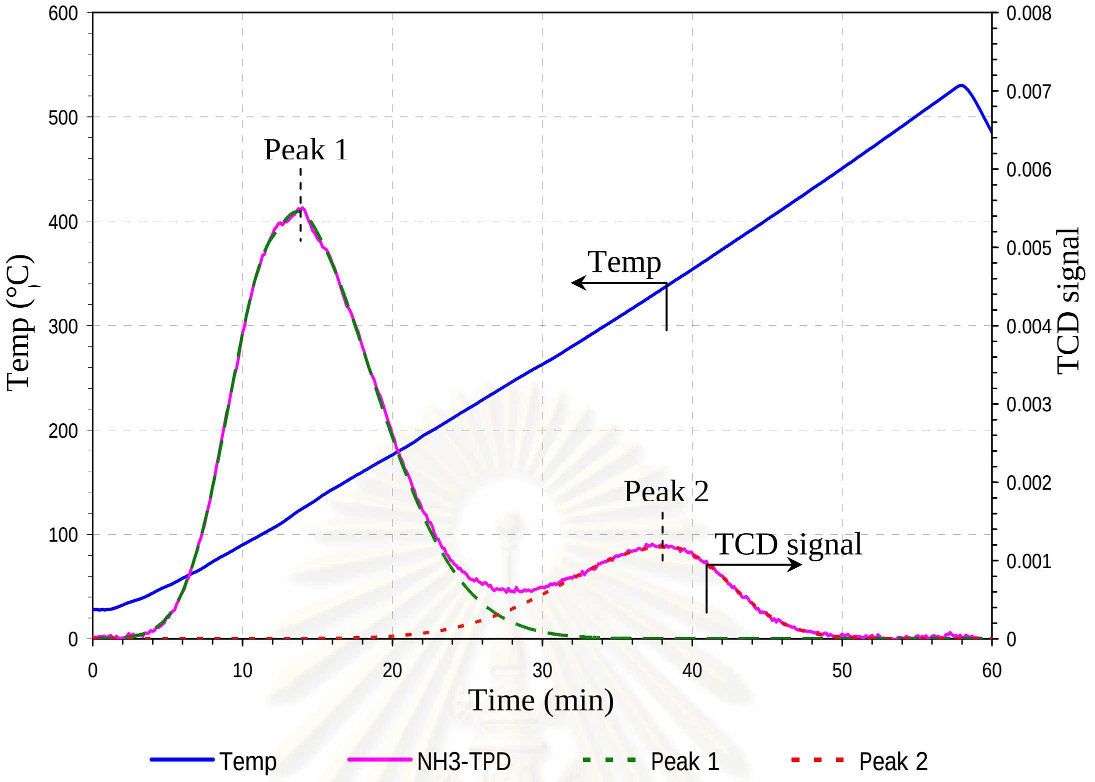


Figure 4.13 NH_3-TPD of Al-TS-1(3D) catalyst with various Si/Al is 152.54**.**

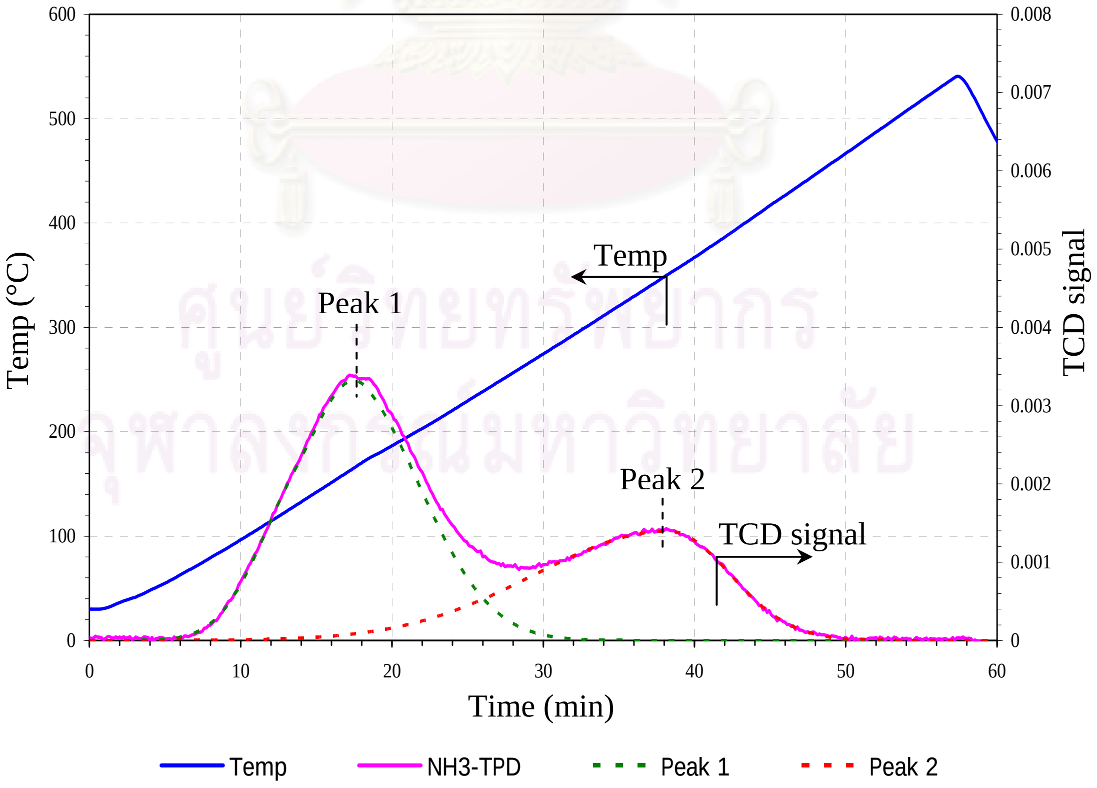


Figure 4.14 NH_3-TPD of Al-TS-1(3D) catalyst with various Si/Al is 135.38**.**

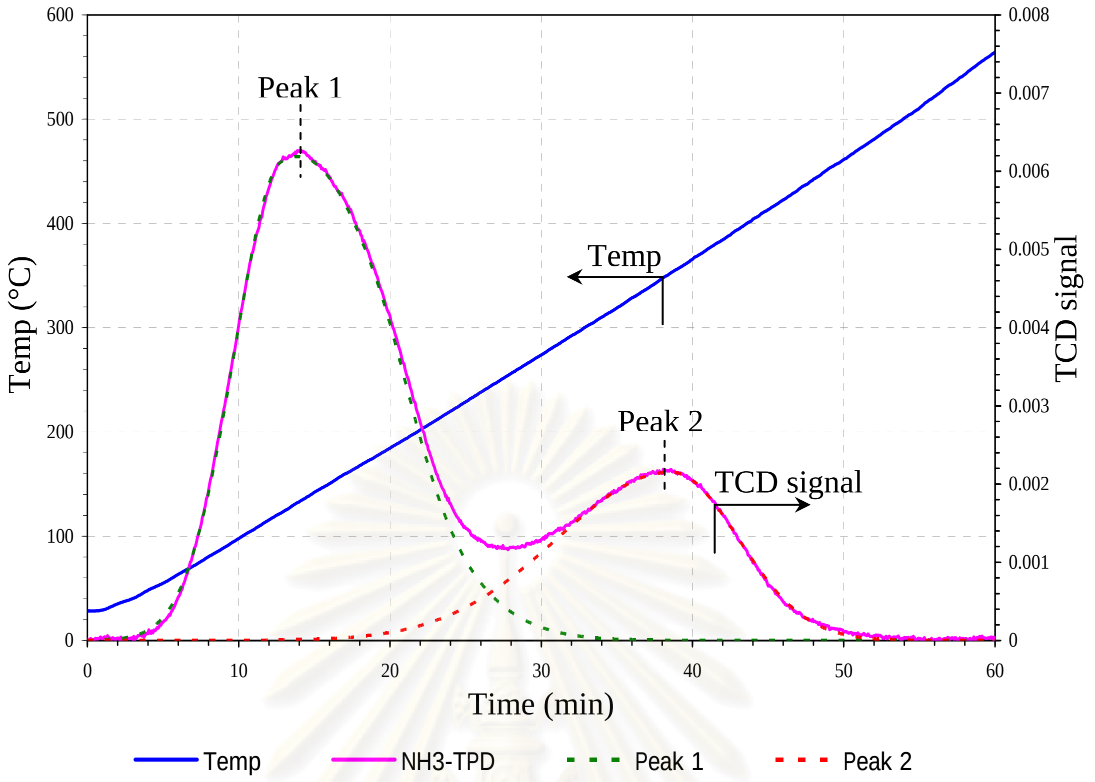


Figure 4.15 NH_3-TPD of Al-TS-1(3D) catalyst with various Si/Al is 95.66**.**

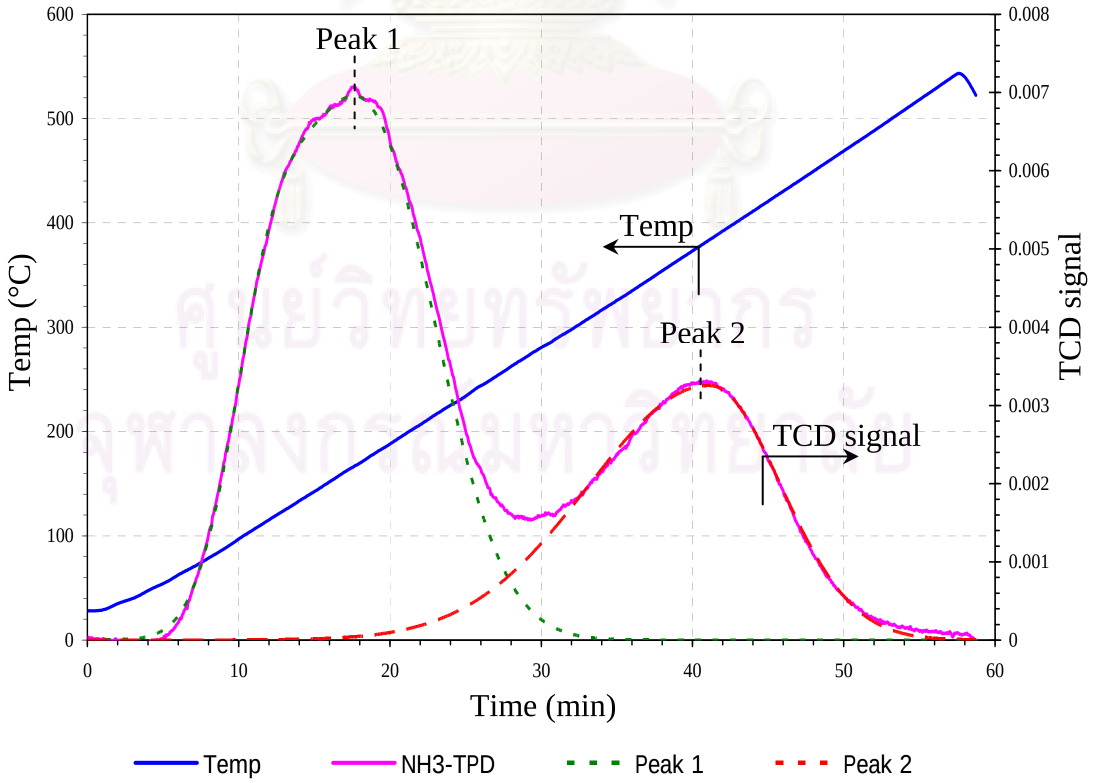


Figure 4.16 NH_3-TPD of Al-TS-1(3D) catalyst with various Si/Al is 55.73**.**

4.2 The catalytic reaction

This section collects catalytic activity testing of TS-1 and Al-TS-1 catalysts with various Al contents and Si/Al in the catalytic hydroxylation of toluene using H_2O_2 oxidant in a typical bubble reactor. This reaction produces three observable organic products: benzaldehyde, ortho-cresol and para-cresol. However, in this research the interested product is benzaldehyde. The experimental results are reported in the form of the total percent of converted hydrogen peroxide to product, selectivity of organic products, and mole of each product formed. In addition, this research also investigates the effect of H_2O_2 (30%wt., 7.5%wt.and 3%wt.) concentration, effect of aging time (1 day aging and 3 day aging), effect of various ratio of Si/Al (154.40, 140.59, 108.31 and 48.81 for 1 day catalysts) and various ratio of Si/Al (152.54, 135.38, 95.66, 55.73 for 3 day catalysts). The total volume of hydrogen peroxide solution used in each run is 40 ml and the total amount of liquid toluene used in each run is 1.5 ml.

Before discussing the reaction results, let have a look at mixing phenomena occurring in the reactor first. In the bubble reactor, a catalyst is put into the aqueous solution of hydrogen peroxide having determined concentration. Then the reactor is heated up to 90 ºC to remove gas from the pore of the catalyst and fill the pore with the hydrogen peroxide solution. Then the reactor is cooled down to the reaction temperature, 70 ºC.

It is well known that several cations can accelerate the decomposition reaction of H_2O_2. The rapid decomposition can lead to a dangerous situation. Because of this reason, an upper limit concentration of H_2O_2 that can run the reaction safely must be determined. To determine the upper limit concentration of H_2O_2, several H_2O_2 solutions having different concentrations were prepared. Then, the catalyst is put into the prepared H_2O_2 solutions at room temperature. The decomposition of H_2O_2 can be observed from the formation of gas bubbles which are the decomposition product. The severity of the decomposition reaction can be evaluated from the rate of bubble generation i.e. the faster the bubbles generate, the more severe the decomposition reaction. It should be also noted here that the rate of the decomposition reaction of hydrogen peroxide can increase with temperature and concentration of hydrogen peroxide solution. Thus, a catalyst that does not show any activity for the decomposition of hydrogen peroxide at room temperature may exhibit such activity at an elevated temperature. On the other hand, a catalyst that shows low activity for the decomposition of hydrogen peroxide at room temperature may exhibit high activity at an elevated temperature. The real concentration of the solution of hydrogen peroxide left in the reactor after the reactor is cooled down to the reaction temperature, therefore, is likely to be less than before it was boiled. It is observed during the boiling that each catalyst can cause the decomposition of H_2O_2 as can be seen from the amount of gas bubbles generated. The severity of the decomposition increases with the concentration of H_2O_2 (i.e. 3wt% < 7.5wt% << 30wt%) but the severity does not pose any harmful situation. Therefore, all catalysts are tested with H_2O_2 concentration up to 30wt%. In addition, the severity also increases with the content of aluminium in the catalyst (i.e. TS-1 < 154.40 < 140.59 < 108.31 < 48.81 for TS-1(1D) catalysts and TS-1 < 152.54 < 135.38 < 95.66 < 55.73 for TS-1(3D) catalysts). The role of this decomposition will be discussed later.

After the boiling process and before toluene vapor is fed to the reactor, the catalyst surface is covered with water and H_2O_2. When nitrogen carrier gas is bubbled through the H_2O_2 solution in the reactor, toluene vapor in the carrier gas would dissolve into the aqueous phase. Due to the solubility of toluene in water is rather low, this factor should play some roles in controlling the reaction rate by limiting the concentration of toluene in the aqueous phase. In addition the dissolved toluene must present on the catalyst surface before the hydroxylation reaction can occur. The concentration of toluene on the catalyst surface which depends on the concentration of dissolved toluene, therefore, should also plays some roles in controlling the reaction rate.

The interested product of this research is benzaldehyde. Since any H_2O_2 remained from the reaction can not be recovered, the maximum utilization of H_2O_2 is the most prefer. This work, therefore, reports the conversion in term of the conversion of H_2O_2 rather than toluene.

Figure 4.17 and 4.18 shows the conversion of hydrogen peroxide of each catalyst (1 day aging and 3 day aging) at different hydrogen peroxide concentration. These figures show that the conversion of H_2O_2 decreases with the increase of its concentration. The appearance decrease should not be interpreted that less H_2O_2 is converted with the increase of its concentration. In reality, the amount of H_2O_2 being converted increases with the increase of H_2O_2 concentration as shown in figures 4.17 and 4.18. The appearance decrease of H_2O_2 conversion with the increase of its concentration is due to the amount of H_2O_2 being converted is not increased linearly with its concentration.

The major organic product produced is benzaldehyde with trace amount of o-cresol and p-cresol. For the formation of benzaldehdye, two H_2O_2 molecules are needed per one molecule of toluene. For the formation of cresol (either o- or p-isomer), only one H_2O_2 is needed per one toluene molecule. Because of this reason, it is expected that the formation benzaldehyde will be much better than the formation of cresol on the catalyst surface riches in H_2O_2 molecule. The bubble reactor provides such situation by covering the catalyst surface firstly with H_2O_2 molecule and limiting the concentration of toluene on the catalyst surface via the low solubility of toluene in water. The combination of these factors results in 100% or nearly 100% selectivity towards benzaldehyde formation of each catalyst.

The data of the selectivities and productivities of each products formed of each catalyst are reported in tables 4.3 and 4.4, respectively. Figures 4.19 and 4.20 compare the productivity of benzaldehyde of each catalyst at different H_2O_2 concentration. The data in tables 4.5 and 4.6 clearly show that adding an appropriate amount of aluminium yields the maximum productivity of benzaldehyde. In our case, the appropriate amount is found to be around 0.6-0.7 wt% Al (catalysts Al-TS-1(1D), Si/Al=154.40, Al-TS-1(1D),Si/Al=140.59, Al-TS-1(3D),Si/Al=152.54, Al-TS-1(3D), Si/Al=135.38)

It is noticed that the activity of the catalysts relates to the presence of the stronger acidic site. TS-1(1D) and TS-1(3D) posses very small amount of the stronger acidic site while Al-TS-1(1D),Si/Al=108.31, Al-TS-1(1D),Si/Al=48.81, Al-TS-1(3D),Si/Al=95.66 and Al-TS-1(3D),Si/Al=55.73 posses higher amount with stronger strength of the acidic site. The acidic site, the metal cation, can induce both the formation of benzaldehye and the decomposition of H_2O_2 reactions. The proposed reaction scheme of benzaldehyde is provided in the next section (section 4.3). At a too high level of aluminium content, a significant amount of H_2O_2 may decompose during the boiling period which results in the productivity of benzaldehye does not increase linearly with the concentration of H_2O_2 used. In addition, the decomposition of H_2O_2 also generates gaseous oxygen (O_2) which may still be trapped inside the pore of the catalyst after the boiling. The amount of trapped gas increase with the concentration of H_2O_2 used. The catalyst having higher amount of trapped gas in the pore, therefore, has lower surface area/pore volume for the formation of benzaldehyde reaction. This may be the explanation why when the aluminium content is too high (such as Al-TS-1(1D),Si/Al=108.31, Al-TS-1(1D),Si/Al=48.81, Al-TS-1(3D),Si/Al=95.66 and Al-TS-1(3D),Si/Al=55.73), the productivity of benzaldehyde decreases.

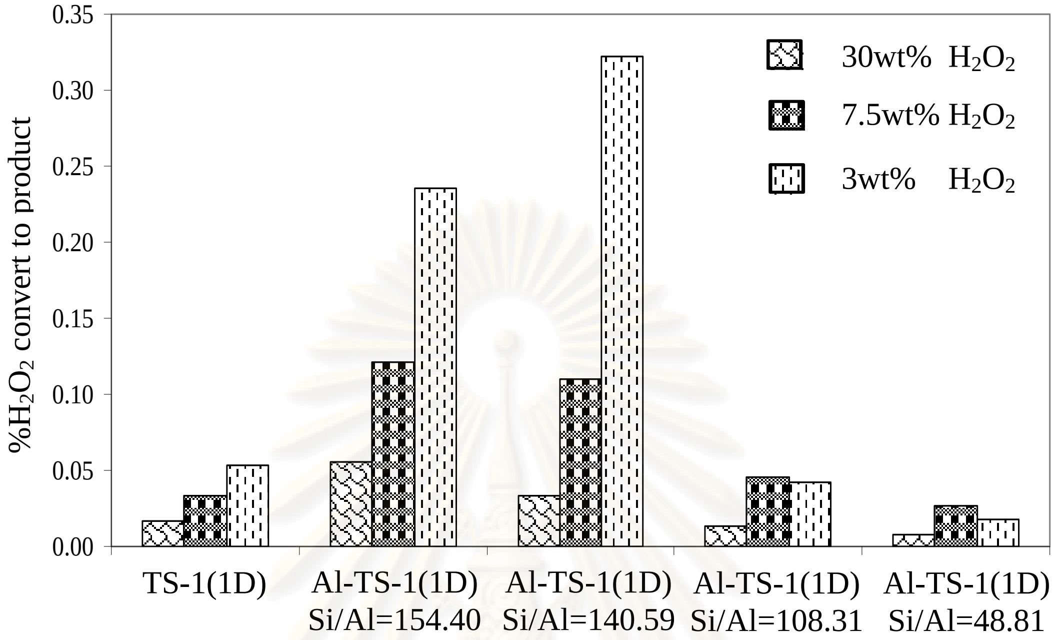


Figure 4.17 %H_2O_2 convert to product is TS-1(1D) and Al-TS-1(1D) catalyst with various Si/Al is 154.40, 140.59, 108.31 and 48.81.

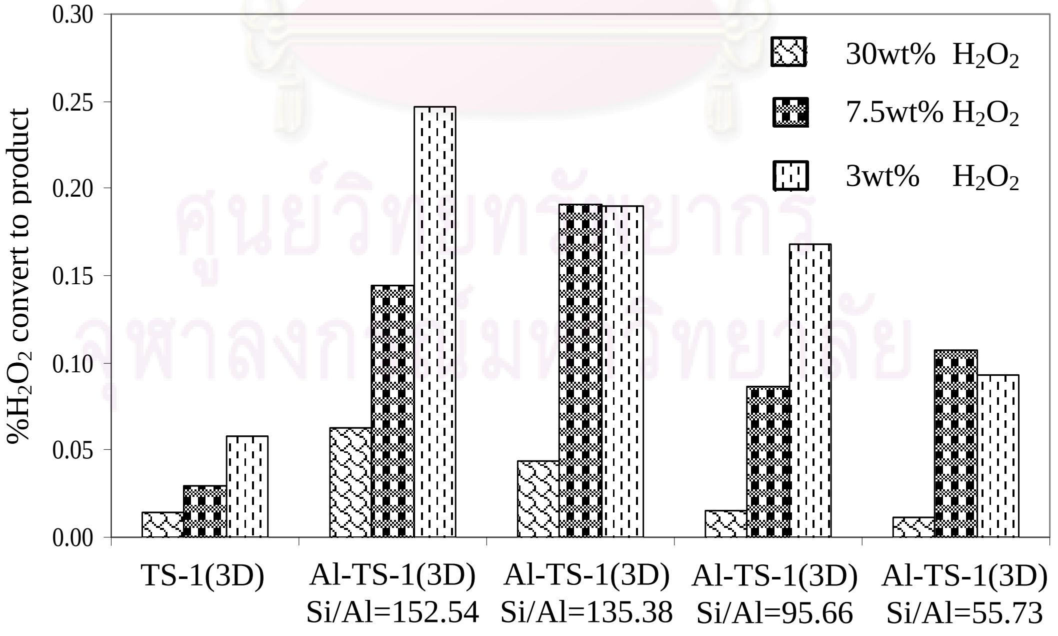


Figure 4.18 %H_2O_2 convert to product of TS-1(3D) and Al-TS-1(3D) catalyst with various Si/Al is 152.54, 135.38, 95.66 and 55.73.

Table 4.3 Selectivity of product (benzaldehyde, o-cresol, p-cresol) for TS-1(1D) and Al-TS-1(1D) catalysts.

Catalysts	**wt% H_2O_2**	**Selectivity**		
		benzaldehyde	**o-cresol**	**p-cresol**
TS-1 (1D)	3	80.7	19.3	0.0
	7.5	91.0	9.0	0.0
	30	97.4	2.6	0.0
Al-TS-1 (1D), Si/Al=154.40	3	96.0	4.0	0.0
	7.5	97.7	2.3	0.0
	30	98.7	1.3	0.0
Al-TS-1 (1D), Si/Al=140.59	3	97.3	2.7	0.0
	7.5	98.1	1.9	0.0
	30	97.9	2.1	0.0
Al-TS-1 (1D), Si/Al=108.31	3	100.0	0.0	0.0
	7.5	100.0	0.0	0.0
	30	100.0	0.0	0.0
Al-TS-1 (1D), Si/Al=48.81	3	100.0	0.0	0.0
	7.5	100.0	0.0	0.0
	30	100.0	0.0	0.0

Table 4.4 Selectivity of product (benzaldehyde, o-cresol, p-cresol) for TS-1(3D) and Al-TS-1(3D) catalysts.

Catalysts	**wt% H_2O_2**	**Selectivity**		
		benzaldehyde	**o-cresol**	**p-cresol**
TS-1 (3D)	3	94.5	5.5	0.0
	7.5	93.5	0.9	0.0
	30	96.2	3.8	0.0
Al-TS-1 (3D),Si/Al=152.54	3	99.0	1.0	0.0
	7.5	99.1	1.2	0.0
	30	99.4	0.6	0.0
Al-TS-1 (3D),Si/Al=135.38	3	98.0	3.1	0.0
	7.5	98.8	2.0	0.0
	30	98.6	1.3	0.0
Al-TS-1 (3D),Si/Al=95.66	3	95.4	2.0	2.6
	7.5	97.3	1.3	1.5
	30	96.9	3.1	0.0
Al-TS-1 (3D),Si/Al=55.73	3	100.0	0.0	0.0
	7.5	100.0	0.0	0.0
	30	100.0	0.0	0.0

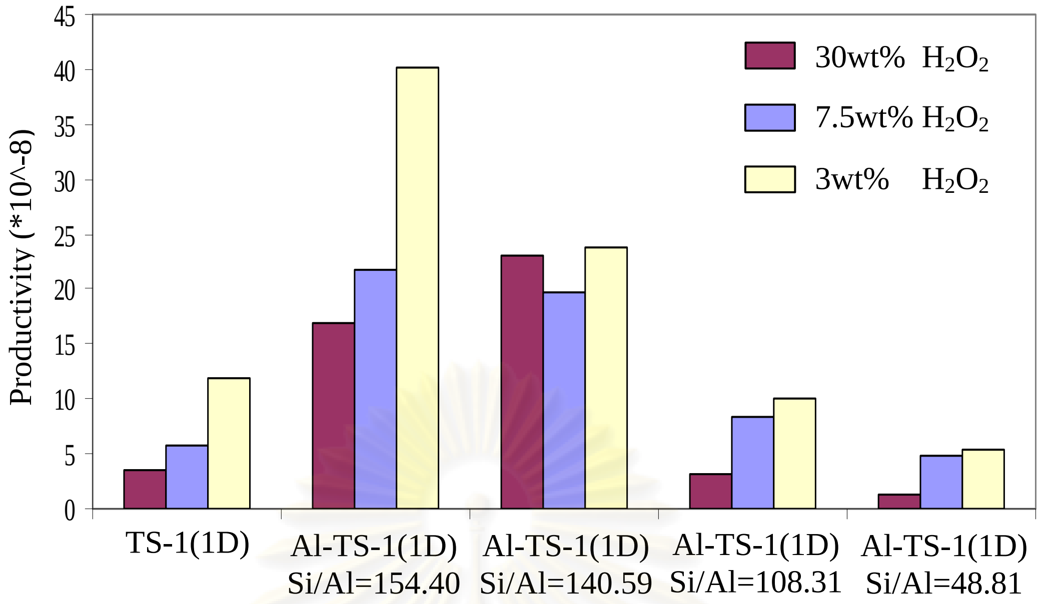


Figure 4.19 Productivity of TS-1(1D) and Al-TS-1(1D) catalyst with various Si/Al is 154.40, 140.59, 108.31 and 48.81.

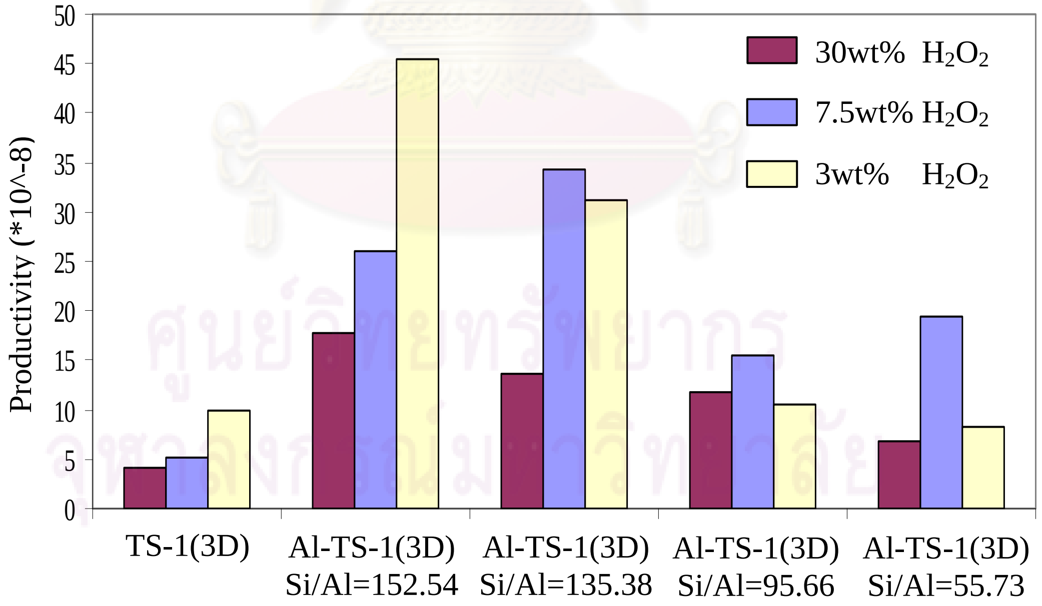


Figure 4.20 Productivity of TS-1(3D) and Al-TS-1(3D) catalyst with various Si/Al is 152.54, 135.38, 95.66 and 55.73.

Table 4.5 Productivity of product (benzaldehyde, o-cresol, p-cresol) for TS-1(1D) and Al-TS-1(1D) catalysts.

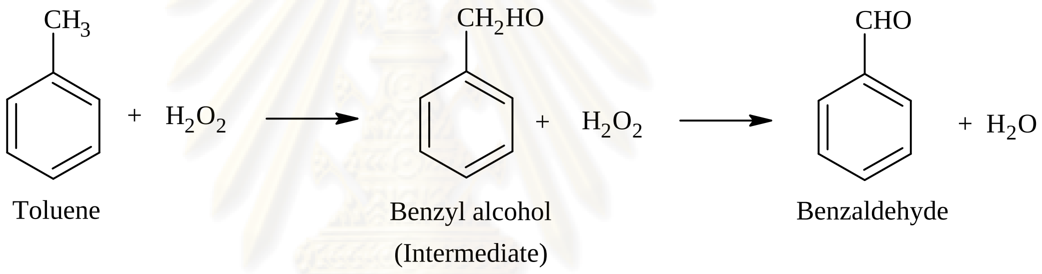
Catalysts	**wt% H_2O_2**	**productivity (*10^-8)**		
		benzaldehyde	**o-cresol**	**p-cresol**
TS-1 (1D)	3	3.618	0.433	0.000
	7.5	5.787	0.431	0.000
	30	11.810	0.238	0.000
Al-TS-1 (1D),Si/Al=154.40	3	16.867	0.353	0.000
	7.5	21.676	0.380	0.000
	30	40.237	0.408	0.000
Al-TS-1 (1D),Si/Al=140.59	3	23.820	0.392	0.000
	7.5	19.720	0.293	0.000
	30	23.116	0.327	0.000
Al-TS-1 (1D),Si/Al=108.31	3	9.957	0.000	0.000
	7.5	8.288	0.000	0.000
	30	3.083	0.000	0.000
Al-TS-1 (1D),Si/Al=48.81	3	5.405	0.000	0.000
	7.5	4.842	0.000	0.000
	30	1.304	0.000	0.000

Table 4.6 Productivity of product (benzaldehyde, o-cresol, p-cresol) for TS-1(3D) and Al-TS-1(3D) catalysts.

Catalysts	**wt% H_2O_2**	**productivity (*10^-8)**		
		benzaldehyde	**o-cresol**	**p-cresol**
TS-1 (3D)	3	4.058	0.119	0.000
	7.5	5.076	0.176	0.000
	30	9.999	0.199	0.000
Al-TS-1 (3D),Si/Al=152.54	3	17.830	0.093	0.000
	7.5	26.018	0.115	0.000
	30	45.550	0.148	0.000
Al-TS-1 (3D),Si/Al=135.38	3	13.657	0.141	0.000
	7.5	34.307	0.200	0.000
	30	31.224	0.214	0.000
Al-TS-1 (3D),Si/Al=95.66	3	11.870	0.128	0.160
	7.5	15.421	0.099	0.118
	30	10.596	0.168	0.000
Al-TS-1 (3D),Si/Al=55.73	3	6.757	0.000	0.000
	7.5	19.452	0.000	0.000
	30	8.255	0.000	0.000

4.3 Proposed reaction scheme for the formation of benzaldehyde

The reaction scheme of benzaldehyde formation is expected to be different from the reaction scheme of cresol formation. The hydrogen atoms of the alkyl group attached to the ring can be replaces by free radicals (such as H-O· and H-O-O·) more easily than hydrogen atom of the ring. Such free radicals may be generated from the decomposition of hydrogen peroxide by the presence of some cations. It is hypothesized that the formation of benzaldehyde will follow the reaction scheme similar to the halogenation of saturated hydrocarbon. The reaction scheme of the formation of benzaldehyde is showed in Figure 4.21. The active site in Figure 4.21 is possibly the cations of Al and Ti which act as acidic site having strength higher than any other catalysts.



Firure 4.21 The reaction scheme of benzaldehyde.

CHAPTER V

CONCLUSTION AND RECOMMENDATION

The present work investigates the hydroxylation of toluene in a bubble reactor over TS-1 and Al-TS-1 catalysts having different Si/Al ratios. The conclusions and recommendations for future study which can be drawn from the experimental results are summarized in sections 5.1 and 5.2, respectively.

5.1 Conclusion

From all of the experimental results and reasons explained above, it can be conclusion that Al-TS-1, having an appropriate amount of aluminium, has a potential to be used as a catalyst for the production of benzaldehyde via the reaction between toluene and hydrogen peroxide in a bubble reactor. The activity of the catalyst is believed to relate to the acidic strength of the catalyst. The stronger the acidic site, the more the benzaldehyde formed. Too strong acidic site, however, can cause sever decomposition of H_2O_2.

5.2 Recommendations

In order to improve the performance of the bubble reactor, the following recommendations are suggested for further study.

1. The height of the liquid level should be increased to increase the contact time between the bubble and hydrogen peroxide solution.

2. The toluene feed system should be modified to produce a continuous flow of toluene vapor to the reactor.

3. The catalyst preparation recipes should be studied to find a proper procedure that can better control the catalyst composition.

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APPENDICES

APPENDIX A

Titanium Silicalite-1

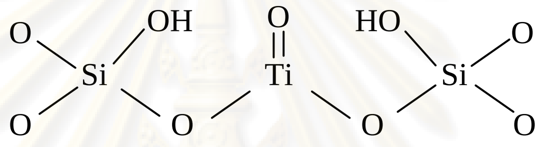
Titanium silicalite is the most interesting material obtained by isomorphic substitution of trivalent metals or tetravalent metals in the framework of crystalline aluminosilicates or silicates. Titanium silicalites with MFI (TS-1) and MFI/MEL (TS-2) structures have been used in several oxidation reactions with H_2O_2 as the oxidizing agent.

Titanium-silicalite, TS-1 is a microporous crystalline molecular-sieve having titanium and silicon in the framework. TS-1 has MFI structure, obtained by substitute titanium for partial silicon in the framework (tetrahedrally coordinated titanium atoms in a silicalite structure). Since it has MFI structure, the pore structure and pore sizes of TS-1 are also similar with ZSM-5 or silicalite type zeolite, with two channels containing 10 membered rings showed in Figure A1.

Titanium has a stable valence of 4 and in an oxidizing medium it is very likely that this valence is maintained. An examination of the chemistry of Ti^{4+} compounds immediately shows that Ti^{4+} has a strong tendency to assume a high coordination number: with oxygen, six groups in octahedral coordination form a stable and very frequently observed configuration, but to do this Ti^{4+} must have near neighbors capable of increasing their coordination number to satisfy at the same time titanium valence of four and coordination of six. When bulky groups are linked to Ti^{4+}, tetrahedral coordination is also observed. Coordination of seven in a pentagonal pyramidal arrangement like in peroxide compounds and of eight like in $Ti(NO_3)_4$ are also observed.

From the crystalline structure and the regular change in unit cell parameters which are consistent with isomorphous substitution of Si^{4+} with Ti^{4+} it seems justified to represent TS-l as a silicalite in which few Ti^{4+} have taken the place of Si^{4+}. The interpretation of the catalytic activity of TS-l must take into consideration the role played by these few Ti^{4+}: in fact pure silicalite is totally inactive, and other phases containing Ti have not been identified. Due to the fact that TS-l crystallizes from a homogeneous solution, it is reasonable to assume that the distribution of Ti^{4+} in the crystal lattice is at random; since the silicon/titanium ratio is in the range 40 - 90 in typical preparations, most Ti^{4+} must be isolated from each other by long sequences of -O-Si-O-Si-O-. If Ti^{4+} replaces a Si^{4+} it should be tetrahedrally coordinated by O$^{=}$ however, the presence of a band at 980 cm^{-1} closely corresponds to the band observed in other titanium compounds containing the $>$Ti = O group, whose stretching frequency is 975 cm^{-1} with bond distances of 1.66 – 1.79 Å; furthermore, hydroxyl groups are present at the surface as shown by the increase in selectivity which is obtained upon silylation.

Finally, near neighbour positions of Ti^{4+} are occupied by Si^{4+} which in a field of O$^{=}$ is stable only in tetrahedral coordination. A simple representation of the sites where substitution has occurred which takes into consideration the various pieces of experimental evidence could be



The amount of titanium positioned within the framework of the molecular sieve is believed to be important and beneficial in many reactions. However, it is also widely believed that non-framework Ti-species, on the exterior or interior surfaces of crystals may decrease the catalytic effectiveness of titanium-silicate molecular sieves. Similar deleterious effects may be caused by other contaminants such as aluminum and alkali elements. In particular, extra-framework massive Ti-oxides as well as other contaminants cause undesirable side reactions as a consequence losses of activity and selectivity of the catalyst.

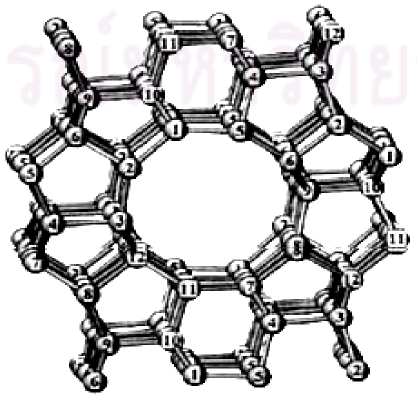


Figure A1 Structure of TS-1.

APPENDIX B

DATA OF EXPERIMENTS

Table B1 Data of experiments over TS-1(1D) and Al-TS-1(1D) catalysts.

Catalysts	wt% H_2O_2	% conversion Toluene	% Selectivity			Mole of products (*10^-8)		
			Benzaldehyde	*o*-cresol	*p*-cresol	Benzaldehyde	*o*-cresol	*p*-cresol
TS-1(1D)	3	0.05389	80.7	19.3	0.0	3.618	0.433	0.000
	7.5	0.03351	91.0	9.0	0.0	5.787	0.431	0.000
	30	0.01651	97.4	2.6	0.0	11.81	0.238	0.000
Al-TS-1(1D),	3	0.23589	96.0	4.0	0.0	16.867	0.353	0.000
Si/Al=200	7.5	0.12098	97.7	2.3	0.0	21.676	0.380	0.000
	30	0.05587	98.7	1.3	0.0	40.237	0.408	0.000
Al-TS-1(1D),	3	0.32185	97.3	2.7	0.0	23.116	0.327	0.000
Si/Al=150	7.5	0.10987	98.1	1.9	0.0	19.72	0.293	0.000
	30	0.03321	97.9	2.1	0.0	23.82	0.392	0.000
Al-TS-1(1D),	3	0.04252	100.0	0.0	0.0	3.083	0.000	0.000
Si/Al=100	7.5	0.04572	100.0	0.0	0.0	8.288	0.000	0.000
	30	0.01373	100.0	0.0	0.0	9.957	0.000	0.000
Al-TS-1(1D),	3	0.01798	100.0	0.0	0.0	1.304	0.000	0.000
Si/Al=50	7.5	0.02671	100.0	0.0	0.0	4.842	0.000	0.000
	30	0.00746	100.0	0.0	0.0	5.405	0.000	0.000

Table B2 Data of experiments over TS-1(3D) and Al-TS-1(3D) catalysts.

Catalysts	wt% H_2O_2	% conversion Toluene	% Selectivity			Mole of products (*10^-8)		
			Benzaldehyde	*o*-cresol	*p*-cresol	Benzaldehyde	*o*-cresol	*p*-cresol
TS-1(3D)	3	0.05762	94.5	5.5	0.0	4.058	0.119	0.000
	7.5	0.02900	93.5	0.9	0.0	5.076	0.176	0.000
	30	0.01407	96.2	3.8	0.0	9.999	0.199	0.000
Al-TS-1(3D),	3	0.24721	99.0	1.0	0.0	17.830	0.093	0.000
Si/Al=200	7.5	0.14429	99.1	1.2	0.0	26.018	0.115	0.000
	30	0.06303	99.4	0.6	0.0	45.550	0.148	0.000
Al-TS-1(3D),	3	0.19032	98.0	3.1	0.0	13.657	0.141	0.000
Si/Al=150	7.5	0.19053	98.8	2.0	0.0	34.307	0.200	0.000
	30	0.04336	98.6	1.3	0.0	31.224	0.214	0.000
Al-TS-1(3D),	3	0.16769	95.4	2.0	2.6	11.870	0.128	0.160
Si/Al=100	7.5	0.08635	97.3	1.3	1.5	15.421	0.099	0.118
	30	0.01485	96.9	3.1	0.0	10.596	0.168	0.000
Al-TS-1(3D),	3	0.09320	100.0	0.0	0.0	6.757	0.000	0.000
Si/Al=50	7.5	0.10741	100.0	0.0	0.0	19.452	0.000	0.000
	30	0.01139	100.0	0.0	0.0	8.255	0.000	0.000

APPENDIX C

CALIBRATION CURVES

This appendix shows the calibration curves for calculation of composition of products in hydroxylation of toluene reaction. The main product of hydroxylation of toluene is benzaldehyde and cresol.

The flame ionization detector, gas chromatography Shimadzu model 9A was used to analyze the concentration of benzaldehyde 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 curves of benzaldehyde, o-cresol, p-cresol are illustrated in Figure C1-C3, respectively.

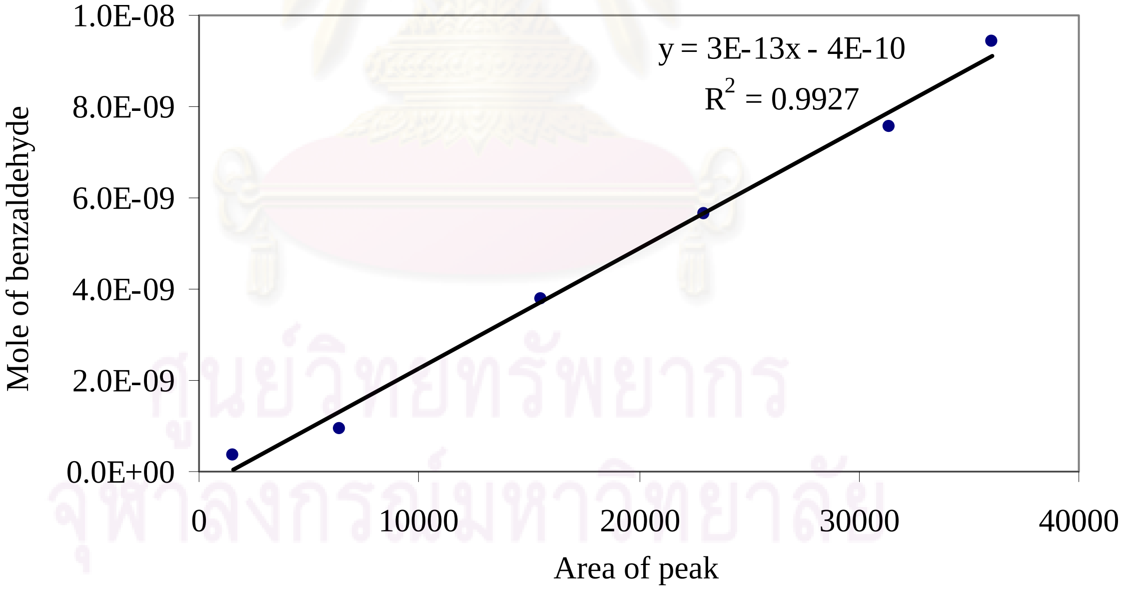


Figure C1 The calibration curve of benzaldehyde.

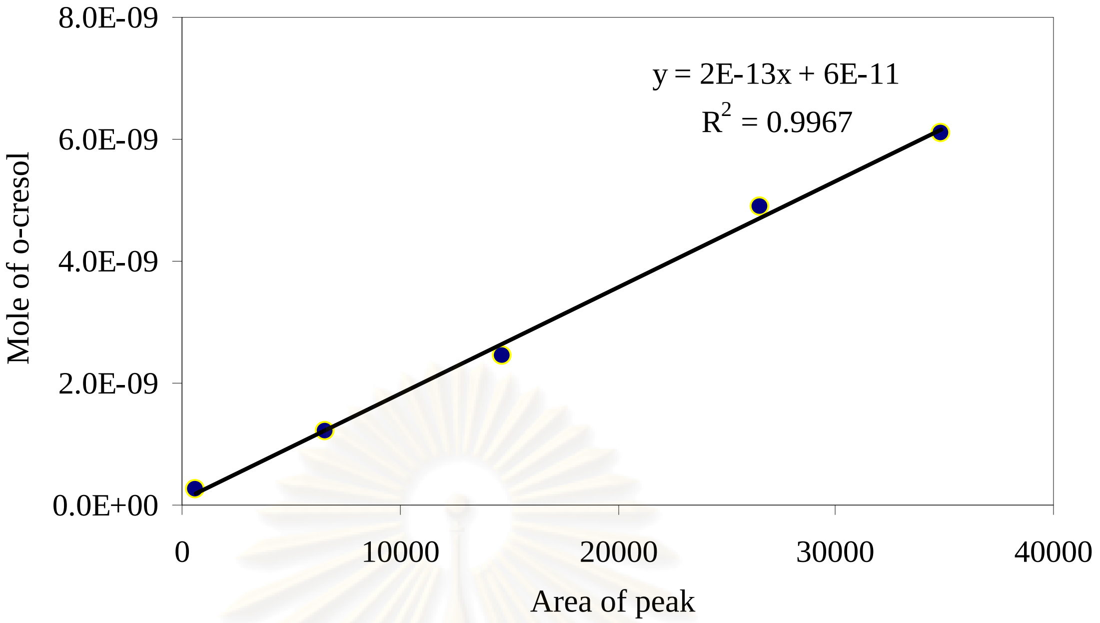


Figure C2 The calibration curve of o-cresol.

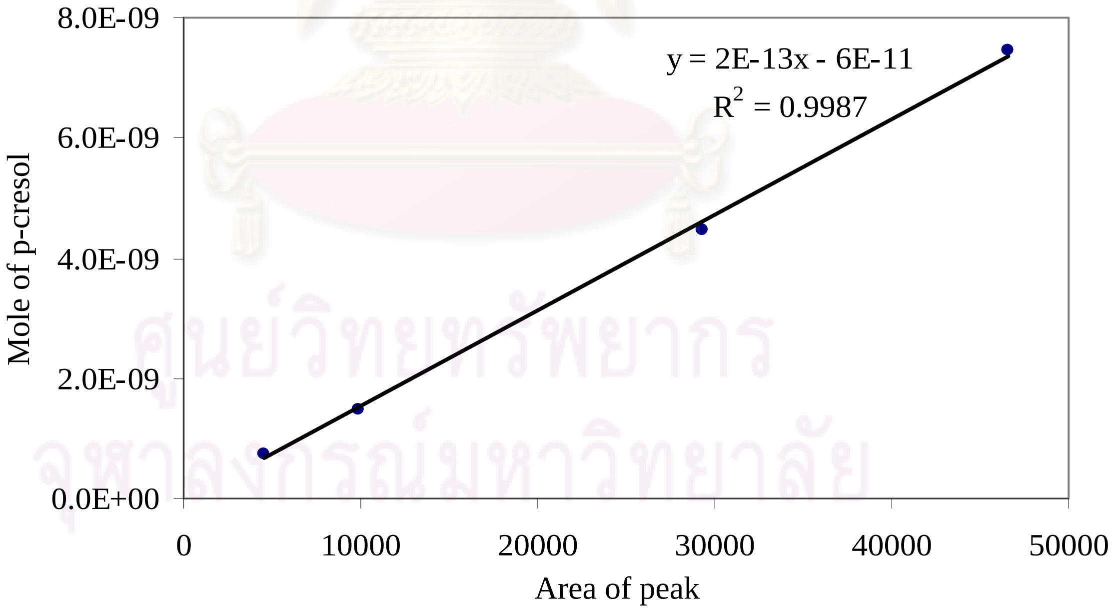


Figure C3 The calibration curve of p-cresol.

APPENDIX D

CALCULATION OF CONVERSION

The catalyst performance for the hydroxylation reaction was evaluated in conversion for terms of activity.

Activity of the catalyst performed in term conversion. The conversion is defined as overall mole of products with respect to overall mole of reactant feeding.

Example, in case of toluene hydroxylation

$$\%H_2O_2 \text{ convert to product} = 100 \times \frac{\text{Overall mole of benzaldehyde and cresol}}{\text{Overall mole of } H_2O_2} \qquad \text{(D1)}$$

Where overall mole of o-cresol can be measured as follows:

Overall mole of o-cresol

$$= \frac{\text{Mole of o-cresol} \times \text{Total volume of solution before injection into GC-9A}}{\text{Volume of injection into GC-9A}} \qquad \text{(D2)}$$

Where mole of o-cresol can be measured employing the calibration curve of o-cresol in Figure C2, Appendix C.

$$\text{Mole of o-cresol} = ((\text{area of o-cresol peak from integrator plot on GC-9A}) \times 2.0\times10^{-13}) \qquad \text{(D3)}$$

$$\text{Mole of all products} = (\text{mole of benzaldehyde} + \text{mole of o-cresol} + \text{mole of p-cresol}) \qquad \text{(D4)}$$

Where selectivity of o-cresol can be measured as follows:

$$\%\ \text{Selectivity of o-cresol} = \frac{\text{Mole of o-cresol}}{\text{Mole of all products}} \qquad \text{(D5)}$$

Where overall mole of H_2O_2 can be measured as follows:

$$\text{Overall mole of } H_2O_2 = \frac{\text{Volume of } H_2O_2 \text{ feeding} \times \text{Density of } H_2O_2}{\text{Molecular weight of } H_2O_2}$$

$$\text{Overall mole of } H_2O_2 = \frac{\text{Volume of } H_2O_2 \text{ feeding} \times 1.44}{34.02} \qquad \text{(D6)}$$

APPENDIX E

CALCULATION FOR CATALYST PREPARATION

The calculation is based on weight of Sodium Silicalite ($Na_2O\cdot SiO_2\cdot H_2O$) in B1 and B2 solutions.

Molecular Weight of Si = 28.0855

Molecular Weight of SiO_2 = 60.0843

Weight percent of SiO_2 in sodium Silicate = 28.5

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

$$\text{Mole of Si used} = \text{wt.}\times\frac{(\%)}{100}\times\frac{(\text{M.W. of Si})}{(\text{M.W. of SiO}_2)}\times\frac{(1\,\text{mole})}{(\text{M.W. of Si})}$$

$$= 69 \times (28.5/100) \times (1/60.0843)$$

$$= 0.3273$$

MFI catalyst

For example, to prepare Si/Ti atomic ratio of 50 by using $Ti[O(CH_2)_3CH_3]_4$ for titanium source.

Molecular weight of Ti = 47.88

Molecular weight of $Ti[O(CH_2)_3CH_3]_4$ = 340.36

Weight % purities of $Ti[O(CH_2)_3CH_3]_4$ = 97

Si/Ti atomic ratio = 50

Mole of $Ti[O(CH_2)_3CH_3]_4$ required = 0.3273/50

= 6.546×10^{-3} mole

Amount of $Ti[O(CH_2)_3CH_3]_4$ = $(6.546 \times 10^{-3}) \times (340.36) \times (100/97)$

= 2.2970 g

For example, to prepare Si/Al atomic ratio of 150 by using $Al(NO_3)_3.9H_2O$ for cobalt source.

Molecular weight of Al = 26.982
Molecular weight of $Al(NO_3)_3.9H_2O$ = 374.996

Si/Ti atomic ratio = 150

Mole of $Al(NO_3)_3.9H_2O$ required = 0.3273/150
= 2.18×10^{-3} mole
Amount of $Al(NO_3)_3.9H_2O$ = $(2.18 \times 10^{-3}) \times (374.996)$
= 0.82 g

which used in A1 and A2 solutions.

APPENDIX F

CALCULATION OF METAL QUANTITY

Example of the calculation of the metal quantity in Al-TS-1(3D), Si/Al=150 catalyst

The XRF results were reported in the amount of metal oxide as shown in Table G1

Table F1 Data from XRF technique.

Metal oxide	Concentration, wt%
Na_2O	0.0512
Al_2O_3	0.5959
SiO_2	95.1117
SO_3	0.2607
TiO_2	2.9609
Fe_2O_3	0.1858
CuO	0.0410

Molecular weights of the metal oxides are shown as follow:

Na_2O	61.979	SO_3	80.0622	Fe_2O_3	159.6922
Al_2O_3	101.963	TiO_2	79.9	CuO	79.5454
SiO_2	60.0843				

1. Mole of metal oxides

$$\text{Mole of } Fe_2O_3 = \frac{\text{weight of } Fe_2O_3}{\text{molecular weight of } Fe_2O_3}$$

$$\text{Mole of } Fe_2O_3 = \frac{0.1858}{159.6922} = 1.16\times10^{-3} \text{ mole}$$

2. Mole of cation (e.g. potassium: Fe)

$$\text{Mole of cation} = (\text{number of cation atom})\times(\text{mole of metal oxide})$$

$$\begin{aligned} \text{Mole of Fe} &= (2)\times(1.16\times10^{-3}) \\ &= 2.32\times10^{-3} \text{ mole} \end{aligned}$$

3. Mole percent of metal (e.g. potassium: Fe)

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

$$\text{Mole \% of Fe} = \frac{2.32\times10^{-3}}{1.647} = 0.0014 \text{ mole\%}$$

APPENDIX G

MATERIAL SAFETY DATA SHEET

Toluene

General

Synonyms: ethenylmethylbenzene, tolylethylene, NCI-C56406, vinyltoluene, 1-methyl-1-phenylethylene
Molecular formula: C_9H_{10}

Physical data

Appearance: colourless liquid with a strong and unpleasant odour
Melting point: -70 to -75 °C
Boiling point: 170 °C
Vapour density: 4.1 (air = 1)
Density (g cm-3): 0.903
Flash point: 54 °C
Explosion limits: 1.9 - 6.1 %
Water solubility: negligible

Stability

Stable. Flammable. Incompatible with oxidizing agents, peroxides, strong acids, aluminium chloride. May contain small amounts of t-butylcatechol to inhibit polymerization.

Toxicology

Harmful if swallowed or inhaled. Chronic exposure may lead to liver or kidney damage. Experimental teratogen.

Personal protection

Safety glasses, good ventilation.

Hydrogen peroxide

General

Synonyms: Peroxide, 100 volume peroxide, Hydrogen dioxide solution, Hydrogen peroxde, 30%, unstabilized, Hydrogen Peroxide, 30%

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.

Molecular formula: H_2O_2

Physical data

Appearance: colourless liquid
Melting point: -28 °C
Boiling point: 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 causes serious burns. Eye contact can cause serious injury, possibly blindness. Harmful by inhalation, ingestion and skin contact. Typical OEL 1 ppm.

Hazards Identification

Danger! Strong oxidizer. Contact with other material may cause a fire. Harmful if inhaled. Corrosive. Causes eye and skin burns. May cause severe respiratory tract irritation with possible burns. May cause severe digestive tract irritation with possible burns.

Potential Health Effects

Inhalation: Vapors are corrosive and irritating to the respiratory tract. Inhalation of mist may burn the mucous membrane of the nose and throat. In severe cases, exposures may result in pulmonary edema and death.

Ingestion: Corrosive and irritating to the mouth, throat, and abdomen. Large doses may cause symptoms of abdominal pain, vomiting, and diarrhea as well as blistering or tissue destruction. Stomach distention (due to rapid liberation of oxygen), and risk of stomach perforation, convulsions, pulmonary edema, coma, possible cerebral edema (fluid on the brain), and death are possible.

Skin Contact: Corrosive. Symptoms of redness, pain, and severe burn can occur.

Eye Contact: Vapors are very corrosive and irritating to the eyes. Symptoms include pain, redness and blurred vision. Splashes can cause permanent tissue destruction.

Personal protection

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

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: C_7H_8O

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
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

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: $CH_3C_6H_4OH$

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)
Water solubility: moderate

Stability

Stable. Combustible. Incompatible with strong oxidizing agents. Air and light-sensitive. Hygroscopic.

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. May cause serious eye damage. Severe skin and eye irritant.

Personal protection

Safety glasses, gloves, adequate ventilation.

Benzaldehyde

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.

Personal protection

Safety glasses, adequate ventilation.

Titanium (IV) n-butoxide

General

Synonyms: Tetra-n-butyl titanate, TNBT, Titanium(IV) n-butoxide (TYZOR TNBT), Tetra-n-butyl orthotitanate for synthesis, titanium tetrabutanolate, Titanium(IV)n-butoxide (TYZOR TBT), Butyl Titanate, Titaniumbutoxide colorlessliq, Titanium n-butoxide, Titanium(IV)n-butoxide, 99+%Tetra-n-utoxytitanium(IV)~Tetra-n-butylorthotitanate, Titanium tetrabutoxide, Triethoxy Methane, Titanium tetrabutylate, Orthotitanic acid tetrabutyl ester
Molecular formula: $C_{16}H_{36}O_4Ti$
Chemical formula: $Ti[O(CH_2)_3CH_3]_4$

Physical data

Boiling point: 310-314 °C
Flash point: 78 °C
Density : 1.486 g/cm^3

Toxicology

Irritating to eyes, respiratory system and skin.

Personal protection

Avoid contact with skin and eyes.

Tetrapropylammonium bromide

General

Synonyms: 1-Propanaminium, N, N, N-tripropyl, bromide or Tetra-n-propylammonium bromide or TPBr or TPABr
Molecular formula: $C_{12}H_{28}N.Br$
Chemical formula : $(C_3H_7)_4NBr$

Physical data

Solubility in Water: 60% (20 °C)
pH : 5 - 10 for solution
Melting Point : 275-278 °C (decomposes)

Stability and reactivity

Stable at ambient temperatures. Do not expose to high temperatures. Oxidizers should be tested for compatibility before use.

Hazardous decomposition

In fire conditions: Carbon monoxide, Hydrobromic acid and Nitrogen oxides. If heated to decomposition, tripropylamine may be released.

Potential health effect

Inhalation: May cause irritation.
Eye Contact : May cause irritation.
Skin Contact : May cause irritation.
Ingestion: No toxicity or other health effects information available.
Chronic: May cause irritation. No additional information available.

First aid measure

Inhalation: Remove to fresh air. If breathing has stopped, give artificial respiration. Consult a physician.

Eye Contact: Immediately flush with water until no evidence of chemical remains (at least 15-20 minutes) and consult a physician.

Skin Contact: Immediately flush with water with sufficient volume until there is no evidence of the chemical on the affected area.

Ingestion: If person is conscious and able to swallow, have them drink a large volume of water and milk and induce vomiting. Contact a physician.

Fire fighting measures

Wear S.C.B.A. May use water spray, carbon dioxide, dry chemical or chemical foam to fight fire.

Hazardous product combustion

May emit Nitrogen oxides, Hydrobromic acid and Carbon monoxide.

Sodium chloride

General

Synonyms: extra fine 200 salt, extra fine 325 salt, H.G. blending, salt, sea salt, table salt, common salt, dendritis, rock salt, top flake, white crystal, saline, halite, purex, USP sodium chloride
Molecular formula: NaCl

Physical data

Appearance : colorless crystals or white powder
Melting point: 804 °C
Boiling point : 1413 °C
Vapor pressure : 1 mm Hg at 865°C
Specific gravity : 2.16 g cm^{-3}
Solubility in water : 35.7 g/100g at °C

Stability

Stable. Incompatible with strong oxidizing agents.

Toxicology

May cause skin, eye or respiratory irritation.

Personal protection

Not believed to present a significant hazard to health.

Sodium hydroxide

General

Synonyms: caustic soda, soda lye, lye, white caustic, aetznatron, ascarite, Collo-Grillrein, Collo-Tapetta, sodium hydrate, fotofoil etchant, NAOH, STCC 4935235, sodium hydroxide pellets, Lewis red devil lye
Molecular formula: NaOH

Physical data

Appearance : colorless white solid (often sold as pellets)
Melting point : 318 °C
Boiling point : 1390 °C
Vapor pressure : 1 mm Hg at 739 °C
Specific gravity : 2.12 g cm^{-3}
Water solubility : high (Note: dissolution in water is highly exothermic)

Stability

Stable. Incompatible with a wide variety of materials including many metals, ammonium compounds, cyanides, acids, nitro compounds, phenols, combustible organics. Hygroscopic. Heat of solution is very high and may lead to a dangerously hot solution if small amounts of water are used. Absorbs carbon dioxide from the air.

Toxicology

Very corrosive. Causes severe burns. May cause serious permanent eye damage. Very harmful by ingestion. Harmful by skin contact or by inhalation of dust.

Personal protection

Safety glasses, adequate ventilation, Neoprene or PVC gloves.

Sodium silicate

General

Synonyms: silicic acid sodium salt, water glass, sodium water glass, soluble glass, silicate of soda, silicon sodium oxide, sodium orthosilicate, sodium sesquisilicate, sodium silicate glass, agrosil S, barasil S, britesil, carsil 2000, chemfin 60, chemsilicate, crystal 79, crystal 96, ineos 140, inosil Na 4237, portil A, pyramid 8, vitrosol N40, ZhS 3, very large number of further trade names

Molecular formula: Na_4O_4Si

Physical data

Appearance : colourless liquid as usually supplied (solution)

Boiling point : ca. 102 °C for a 40% aqueous solution

Specific gravity: approximately 1.3 for a ca. 40% solution

Stability

Stable. Incompatible with acids, most metals, many organic materials.

Toxicology

Harmful by ingestion. Corrosive - may cause burns through skin or eye contact. Very destructive of mucous membranes.

Personal protection

Safety glasses, gloves.

Aluminium(III)nitrate nonahydrate

General

Synonyms: aluminum nitrate 9-hydrate, aluminium nitrate nonahydrate, aluminum nitrate nonahydrate, nitric acid aluminium salt

Molecular formula: $Al(NO_3)_3\ 9H_2O$

Physical data

Appearance: white crystalline powder

Melting point: 73 °C

Water solubility: appreciable

Stability

Strong oxidizer - contact with combustible material may lead to fire. Incompatible with water, most common metals, organics. Moisture-sensitive.

Toxicology

May be harmful if swallowed. Skin, eye and respiratory irritant. May cause serious eye irritation.

Personal protection

Safety glasses, adequate ventilation.

Ethanol

General

Synonyms: ethanol, grain alcohol, fermentation alcohol, alcohol, methylcarbinol, absolute alcohol, absolute ethanol, anhydrous alcohol, alcohol dehydrated, algrain, anhydrol, cologne spirit, ethyl hydrate, ethyl hydroxide, jaysol, jaysol s, molasses alcohol, potato alcohol, sekundasprit, spirits of wine.

Molecular C_2H_5OH

Physical data

Appearance: colourless liquid
Melting point: -144 °C
Boiling point: 78 °C
Specific gravity: 0.789
Vapour pressure: 1.59
Flash point: 14 °C (closed cup)
Explosion limits: 3.3% - 24.5%
Autoignition temperature: 363 °C
Water solubility: miscible in all proportions

Stability

Stable. Substances to be avoided include strong oxidizing agents, peroxides, acids, acid chlorides, acid anhydrides, alkali metals, ammonia, moisture. Forms explosive mixtures with air. Hygroscopic.

Toxicology

Causes skin and eye irritation. Ingestion can cause nausea, vomitting and inebriation; chronic use can cause serious liver damage. Note that "absolute" alcohol, which is close to 100% ethanol, may nevertheless contain traces of 2-propanol, together with methanol or benzene. The latter two are very toxic, while "denatured" alcohol has substances added to it which make it unpleasant and possibly hazardous to consume.

Personal protection

Safety glasses. Suitable ventilation.

APPENDIX H

LIST OF PUBLICATION

Phawana Wongbunrod and Tharathon Mongkhonsi “Benzaldehyde synthesis by the hydroxylation of toluene in bubble rector, 18th Thailand Chemical Engineering and Applied Chemistry Conference, Chonburi, Thailand, October, 2008, R036-KC-006-02.

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Clean Energy Techology(cont.)

Book of Abstracts of the 18th Thailland Chemical Engineering and Applied Chemistry Conference
October 20-21, 2008, Pattaya, Thailand

Benzaldehyde synthesis by the hydroxylation of toluene in a bubble reactor

Phawana Wongbunrod, Suchitraporn Sakullimcharoen and Tharathon Mongkhonsi
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Currently, benzaldehyde, an important intermediate is several fine chemical industry such aroma, dyes, and pharmaceutical is produced by several processes consist of several reaction steps and significant amount of unwanted by-products formed. Some examples of such processes are (i) the chlorination of toluene follows by hydrolysis of benzalchloride, and (ii) the oxidation of toluene. This present research has studied a new route to produce benzaldehyde directly from the hydroxylation of toluene using hydrogen peroxide as the oxidant and titanium silicalite-1 (TS-1) as the catalyst. TS-1 was prepared by using the conventional hydrothermal technique with different aging time (0, 1 and 3 days). The investigation has been covering factors affecting product formation such as the catalyst preparation method, the effect of a promoter (Al) and the concentration of H_2O_2. Al-modified TS-1 is synthesized by adding an aluminium precursor to the TS-1 recipe. The reaction is performed in a glass bubble reactor filled with 40 ml H_2O_2 solution (3, 7.5 and 30 wt%) at 70°C and atmospheric pressure. 1.0 g of catalyst is used in each experiment. Toluene (total volume 1.5 ml) is fed to the bottom of the reactor by vaporizing and mixed with N_2 carrier gas. The total reaction time is 0.5 hours. Catalyst characterizations by XRD and FT-IR confirm that the prepared catalysts (TS-1 and Al-TS-1) have the MFI structure with Ti^{4+} present in the MFI structure. The catalytic study shows that the catalysts with the aging time 0 and 1 day give the highest benzaldehyde selectivity. The catalyst with the aging time 3 days has the higher activity but lower selectivity towards benzaldehyde with cresols (ortho and para) appear as co-products. In addition, adding Al to the catalyst (Al-TS-1) and using high concentration of H_2O_2 improve the formation of benzaldehyde.

Keywords: Titanium Silicalite-1(TS-1), Al-TS-1, hydroxylation, bubble reactor, benzaldehyde

The 18^h Thailand Chemical Engineering and Applied Chemistry Conference October 20-21,2008,Pattaya Thailand

Benzaldehyde synthesis by the hydroxylation of toluene in a bubble reactor

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Abstract

This research studies the benzaldehyde synthesis by the hydroxylation of toluene in a bubble reactor using titanium silicalite-1(TS-1) and titanium silicalite-1 modified with Al(Al-TS-1). The catalysts are synthesized using hydrothermal technique and characterized using XRD, UV-vis, FT-IR, XRF BET, and NH_3-TPD. The results show that the addition of Al can increase the activity and selectivity toward benzaldehyde of TS-1.

1. Introduction

Benzaldehyde is widely used in dyestuff, perfumery, and pharmaceutical industries. In the latter industry it is used for the manufacture of intermediates for chloramphenicol, analgin, ephedrine, and ampicillin. For the production of benzaldehyde, particularly for the grade conforming to pharmaceutical and perfumery standards which is required to be free from compounds containing chlorine in the nucleus, the vapor phase **[1]** oxidation of toluene is well established.

The invention of titanium silicalite-1 (TS-1), a MFI-type zeolite firstly reported by Taramasso et al. in 1983 **[3]**, Opens a new route for chemical synthesis using hydrogen peroxide as the oxidant. The lattice titanium (Ti^{4+}) in TS-1 isomorphously replaces silicon (Si^{4+}) in the tetrahedral site of the MFI silicalite lattice. The MFI structure leads to various types of shape selectivity. In the partial oxidation of many organic compounds with H_2O_2, TS-1 exhibits as a very efficient catalyst for the such reaction such as alkane oxyfunctionalization , hydroxylation of aromatic, ammoximation of cyclohexanone, olefin epoxidation, alcohol oxidation **[2]**.

The MFI type catalyst is frequetly loaded with another metal(s), especially transition metals to modify some properties of the synthesized catalyst. The method commonly employed is the impregnation technique, a two step method which begins by firstly synthesize TS-1 followed by impregnate the obtained TS-1 with a desired metal.

This present research has studied a new route to produce benzaldehyde directly from the hydroxylation of toluene using hydrogen peroxide as the oxidant and titanium silicalite-1 (TS-1) as the catalyst. The process should have advantage can be produced in only one step. In addition, the modified TS-1 is synthesized in a single step by adding the second metal during the formation of TS-1 structure. The investigation also covers factors effecting product formation such as the catalyst preparation method, the concentration of H_2O_2, and the content of aluminium in the catalyst.

2. Experimental

2.1 The preparation of the TS-1 catalyst

The TS-1 catalyst is prepared by hydrothermal method using titanium(IV)butoxide 97% as Ti source, sodium silicate solution as Si source and aluminium(III)nitrate nanohydrate as promoter. The crystallization is carried out in a stainless steel autoclave from room temperature to 180°C and with a heating rate of 2 °C/min under nitrogen gas atmosphere. The content in the reactor is kept at 180°C for 3 days before allowing to cool down to room temperature. The product crystals are then washed with de-ionized water to remove chloride out of the crystals. Then the crystals are dried overnight at 110 °C. and calcined in an air stream at 550°C for 7 hrs.

2.2 Characterization methods of TS-1

The crystal structure of the synthesized catalysts is determine using an x-ray diffractometer SIEMENS D5000 connected with a computer with Diffract AT version 3.3 program for fully control of XRD analyzer. The experiments are carried out by using Cu Kα radiation with Ni filter. Scans were preformed over the 2 theta ranges from 6 to 40. The x-ray diffraction (XRD) patterns show that all of the synthesized catalysts show the six main characteristic peaks of MFI structure at 8, 8.8, 14.8, 23.1, 24 and 26.7.

UV-vis spectroscopy technique is also used and found that all the catalyst samples show an absorption band at around 220 nm, resulting from the charge transfer from O^{2-} to Ti^{4+} species tetrahedrally coordinated in the zeolite framework **[3]**. The IR measurement, carried out using Nicolet Impact 400 also reveals the absorption band at 960 cm^{-1}, due to Si-O-Ti stretching vibration.

The chemical composition of the catalysts is determined by x-ray fluorescence spectroscopy (XRF), Philips PW2400 spectrometer. The surface area of the catalyst is characterized using BET technique (BET Micromeritrics ASAP 2020). 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.

2.3 The catalytic reaction

The hydroxylation of toluene is performed in a glass bubble reactor at atmospheric pressure filled with 1.0 gram of catalyst, 40 ml (hydrogen peroxide + water) and a magnetic bar. The reactor is firstly heated up by raising the oil bath temperature to 90°C for 1 hr to remove gas from the pore of the catalyst. After that the reactor is cooled down to 70°C and toluene is added into reactor by mixing with nitrogen gas bubbling from the bottom of the reactor. The reaction is carried out using the concentration of H_2O_2 of 30%, 7.5% and 3%. The products are analyzed by a gas chromatograph equipped with a FID detector (SHIMADZU GC9A).

3. Result and Discussion

The results obtained from the hydroxylation of toluene in a bubble reactor are reported in Figures 1-4.

Figures 1 and 2 are the conversion and selectivity comparisons between TS-1 and Al-TS-1. Figure 1 clearly demonstrates that Al-TS-1 has much higher catalytic activity than TS-1 (21 times higher) and figure 2 shows that the selectivity toward benzaldehyde of Al-TS-1 is also better than TS-1. Al-TS-1 produces nearly 100% benzaldehyde selectivity with a very small amount of cresol while TS-1 produces cresols, undesired products in this study, up to 25%. Figures 3 and 4 show the catalytic activity and product selectivities of Al-TS-1 at different H_2O_2 concentration. It is found that the concentration of H_2O_2 significantly affects the conversion but the selectivity. The selectivity of aldehyde is still up to 100% regardless of H_2O_2 concentration. The observed conversion follows the following order Al-TS-1(30%) > Al-TS-1(7.5%) >> Al-TS-1(3%). It should be noted here that the conversion of toluene slightly decreases (only 16% decrease) when the concentration of H_2O_2 is decreased from 30% to 7.5% but greatly reduces (64% decrease) when the concentration of H_2O_2 is decreased from 7.5% to 3%. This phenomenon is likely due to the nature of the catalyst surface which prefers the adsorption of a non-polar molecule. At a too low H_2O_2 concentration, H_2O_2 molecule is less likely to be adsorbed on the catalyst surface thus leading to much lower conversion.

The reaction pathway of the hydroxylation is presented schematically in Figure 5. Theoretically, the oxidation at the side chain methyl group can yield benzyl alcohol and/or benzaldehyde and the hydroxylation at the ring can yield o-cresol and/or p-cresol. What is found from the experiment is Al-TS-1 produces mainly benzaldehyde with trace amount cresols (both ortho and para isomers). Such finding demonstrates that the addition of Al to TS-1 can improve the catalytic activity of TS-1 and alters the product selectivity.

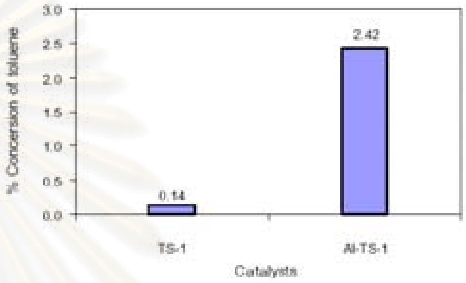

Figure 1 %conversion of toluene with 30wt.% of H_2O_2

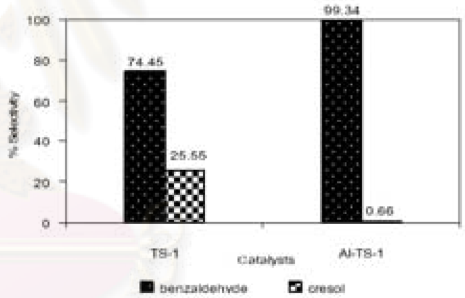

Figure 2 %Selectivity of product with 30wt.% of H_2O_2

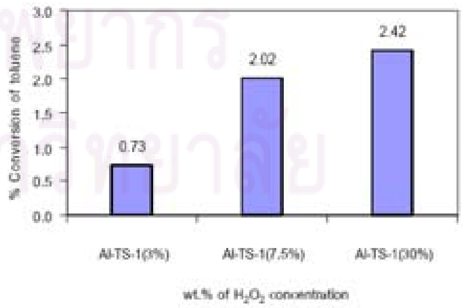

Figure 3 %conversion of toluene with various wt.% of H_2O_2

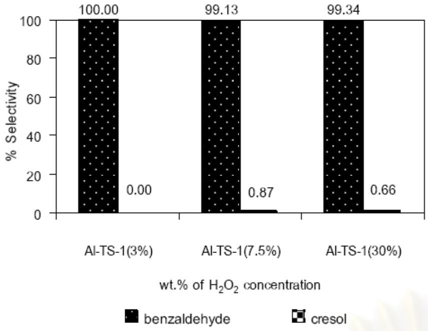

Figure 4 %Selectivity of product with various wt.% of H_2O_2

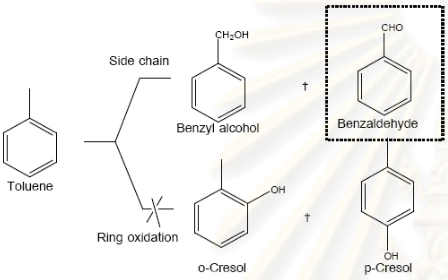

Figure 5 The hydroxylation of toluene

4. Conclusion

The present work demonstrates that benzaldehyde can be synthesized in a one step reaction via the hydroxylation of toluene in a bubble reactor over Al-TS-1. The addition of Al can increase both catalytic activity and product selectivity of TS-1.

5. References

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