OXIDATIVE EXTRACTION OF THIOPHENE FROM DODECANE IN CONTINUOUS PROCESS

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หัวข้อวิทยานิพนธ์	การใช้ปฏิกิริยาออกซิเดชันช่วยในการสกัดไธโอฟีนจากโดเดคเคนในกระบวนการแบบต่อเนื่อง
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บทคัดย่อ

งานวิจัยนี้เป็นการศึกษาปฏิกิริยาออกซิเดชันเพื่อช่วยในการสกัดไธโอฟีนจากโดเดคเคน โดยมีไทเทเนียม ซิลิกาไลต์ (TS-1) เป็นตัวเร่งปฏิกิริยาและไฮโดรเจนเปอร์ออกไซด์เป็นตัวออกซิไดซ์ ซึ่งผลิตภัณฑ์ที่ถูกออกซิไดซ์จะเคลื่อนที่ไปยังตัวทำละลายโดยกระบวนการสกัดโดยทำการทดลองที่อุณหภูมิห้องและที่ 60 องศาเซลเซียส ภายใต้ความดันบรรยากาศ ทั้งนี้สามารถสังเคราะห์ไทเทเนียม ซิลิกาไลต์ (TS-1) ได้จากไฮโดรเจลที่มีองค์ประกอบเป็น $94SiO_2 : 3.8TiO_2 : 15TPABr : 212NH_3 : 12.3H_2O_2 : 2168H_2O$ โดยตกผลึกที่อุณหภูมิ 185 องศาเซลเซียส เป็นเวลา 7 วัน จากนั้นเผาไล่สารอินทรีย์ของตัวเร่งปฏิกิริยาที่อุณหภูมิ 550 องศาเซลเซียส นำตัวเร่งปฏิกิริยาที่ได้วิเคราะห์ด้วยเทคนิคการเลี้ยวเบนของรังสีเอ็กซ์ เทคนิคเอ็กซ์เรย์ฟลูออเรสเซนต์ เทคนิคกล้องจุลทรรศน์แบบส่องกราด เครื่องวิเคราะห์การดูดซับก๊าซ และเทคนิคฟูเรียร์ทรานฟอร์มอินฟราเรดสเปกโตรสโคปี จากงานวิจัยพบว่าการใช้เมทานอลเป็นตัวทำละลายในกระบวนการแบบกะช่วยให้เกิดปฏิกิริยาได้ดีกว่าการใช้อะซิโตไนไตรล์ กรดอะซิติก และน้ำเป็นตัวทำละลาย นอกจากนั้นยังพบว่าอัตราส่วนของตัวทำละลายกับไฮโดรคาร์บอนที่เพิ่มขึ้น มีผลทำให้ปฏิกิริยาเกิดได้ดีขึ้น ปฏิกรณ์แบบปั่นกวนถูกนำมาใช้ในการทำปฏิกิริยาแบบต่อเนื่อง โดนทำการป้อนไธโอฟีนความเข้มข้น 1-3 % โดยน้ำหนักในโดเดคเคนและไฮโดรเจนเปอร์ออกไซด์ 4.5 มิลลิโมลในตัวทำละลายเมทานอล สู่ปฏิกรณ์แบบปั่นกวนซึ่งมี ไทเทเนียม ซิลิกาไลต์ 0.5-2.0 กรัม พบว่าเมื่อทำการเพิ่มปริมาณตัวเร่งปฏิกิริยาหรือลดอัตราการไหลของสารตั้งต้น มีผลทำให้เกิดปฏิกิริยาออกซิเดชันได้ดีขึ้นและ

ช่วยในการกำจัดไธโอฟีนได้มีประสิทธิภาพเพิ่มขึ้น จากการศึกษาการเสื่อมสภาพของตัวเร่งปฏิกิริยาพบว่ามีการละลายของไทเทเนียมจากตำแหน่งกัมมันต์เมื่อนำตัวเร่งปฏิกิริยากลับมาใช้ใหม่ และสามารถลดการสูญเสียตำแหน่งกัมมันต์ได้เมื่อใช้อุณหภูมิในการกำจัดสารอินทรีย์ของตัวเร่งปฏิกิริยาสูงขึ้น

Thesis Title Oxidative extraction of thiophene from dodecane in continuous process

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ABSTRACT

Liquid phase oxidation of thiophene in H_2O_2 and subsequently extraction of the oxidized product into the solvent were studied. Titanium silicalite (TS-1) and 30% of H_2O_2 were used as catalyst and oxidizing agent, respectively. The reactions were carried out at room temperature and 60 °C at atmospheric pressure. TS-1 was synthesized from a gel with molar composition $94SiO_2 : 3.8TiO_2 : 15TPABr : 212NH_3 : 12.3H_2O_2 : 2168H_2O$ at 185 °C for 7 days. The catalyst was calcined at 550 °C and characterized by XRD, XRF, SEM, BET and FT-IR. It was found that, in batch process the reaction using methanol as a solvent showed activity higher than that using acetonitrile, acetic acid and water respectively. The oxidation activity was increased when the solvent/oil ratio was increased. The continuous stirred tank reactor (CSTR) was used for the oxidative extraction in the continuous process. (1-3%) Thiophene in dodecane (10-25 ml/hrs) and (1.51%) H_2O_2 in methanol (10-25 ml/hrs) were fed by peristaltic pump into the CSTR (150 ml) containing (0.5-2.0 g.) TS-1. It was found that increasing amount of catalyst and decreasing feeding rate lead to an increase in oxidative extraction of thiophene. The deactivation of the catalyst due to titanium leaching was investigated by reusing catalyst after 8 hours on steam. It was found that the leaching of titanium active site can be reduced when the calcinations temperature was raised.

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Finally, the author dedicates her thesis to parents and her family for the constant love and encouragement.

Thasaneeya Napanang

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CHAPTER 1

INTRODUCTION

1.1 Motivation

Combustion of fuels containing sulfur compounds generates SO_x to atmosphere leads to air pollutions such as acid rain and smog generation [1]. It was hence legalized that the sulfur content in fuels should be reduced to an ultra-low level; below 10 ppm, by the year 2010 [2]. Hydrodesulfurization (HDS) is a typical process that used for removing sulfur containing compounds from hydrocarbon by transforming them to hydrogen sulfide. However, these processes are usually operated under severe conditions, i.e. high temperature and hydrogen pressure [3]. Furthermore, HDS is not effective for removing heterocyclic sulfur compounds. Oxidative desulfurization (ODS) is an alternative process for sulfur removal. It can be carried out under relatively milder condition, i.e. the reaction can be operated at room temperature and atmospheric pressure. In this process, sulfur compounds will be converted by chemical oxidation to slightly higher polar compounds, as compared with the hydrocarbons. Consequently, these oxidized products can be removed by extraction with high polar solvents, such as N-methyl pyrolidone (NMP), N,N-dimethylformamide (DMF), methanol (MeOH) [4] and dimethyl sulfoxide (DMSO) [4, 5]. The oxidation of sulfur compounds with H_2O_2 can be achieved over various catalysts, such as acetic acid [6-9], formic acid [10-12], polyoxomethalate [12-15], and Ti-containing molecular sieve [16, 17]. Among these, the Ti-containing molecular sieves act as effective catalysts for oxidation of several types of sulfur containing compounds in the presence of H_2O_2. In addition these catalysts are insoluble in hydrocarbon and solvent phase. Therefore, it can be easily separated from the reaction mixture. The oxidative extraction of sulfur compounds is usually tested in batch process [18] because a well mixing of solvent and hydrocarbon can be obtained. However, this can be an obstacle in development of the process to an industrial practice. Accordingly, the oxidative extraction for a continuous process was investigated in the thesis. The sufficient mixing of solvent, hydrocarbon and the catalyst were essentially required for an effective removal of sulfur containing compounds. Therefore, a well mixing reactor was designed for testing the catalytic activity in continuous process. *n*-Nonane and *n*-Dodecane containing thiophene will be used as a model feed for oxidative extraction using titanium silicalite as a catalyst. The effect of solvent will be primarily studied in a batch process and necessary factors for the continuous process, such as feeding rate, contact time and catalytic life-time will be investigated.

1.2 Objective

The overall objective of this thesis is to reduce sulfur compounds contained in fuel by oxidative extraction.

The specific objective of the study are as follow:

1.2.1 To accomplish the oxidative extraction of sulfur compounds in continuous process.

1.2.2 To obtain suitable condition for continuous process such as solvent, ratio of solvent, catalyst content, feed rate and catalytic life time for the high % removal of sulfur compounds.

1.3 Scope of study

1.3.1 Synthesis and characterization of Titanium silicalite-1 (TS-1).

1.3.2 Study on effect of solvent used for extracting oxidized products of sulfur compounds.

1.3.3 Study on effect of solvent/oil ratio.

1.3.4 Study on effect of catalyst content.

1.3.5 Design and construct a catalytic testing for continuous process.

1.3.6 Study on effect of feeding rate.

1.3.7 Study on effect of catalytic life time.

1.3.8 Study on leaching and stability of titanium framework.

1.4 Expected result

This research can provide alternative method for the reduction of sulfur compounds contained in fuel.

CHAPTER 2

LITERATURE REVIEWS AND THEORY

2.1 Zeolites

Zeolites are class of minerals that have a microporous structure. The name " Zeolite " come from the Greek words zeo (to boil) and lithos (stone). The term was originally coined in the 18th century by a Swedish mineralogist named Axel Fredrik Cronstedt who observed, upon rapidly heating natural mineral, that the stones began to dance about as the water evaporated. Using the Greek words which mean " stone that boils " he called this material zeolite [19].

The framework of zeolite is based on an extensive three-dimensional network in which the polyhedral sites, usually tetrahedral, are linked by oxygen atoms. The crystalline framework contains cages and channels of discrete size and 3-30 A° in diameter. The primary building unit of a zeolite is the individual tetrahedral unit. The topology of all known zeolite framework type can be described in terms of a finite number of specific combinations of tetrahedral called "secondary building units" (SBU's). In figure 2.1 the T atom belonging to a TO_4 tetrahedron is located at each corner, but the oxygen located near the mid-points of the lines joining each pair of T atom are not shown. A zeolite framework may well be made up of various type of SBU's.

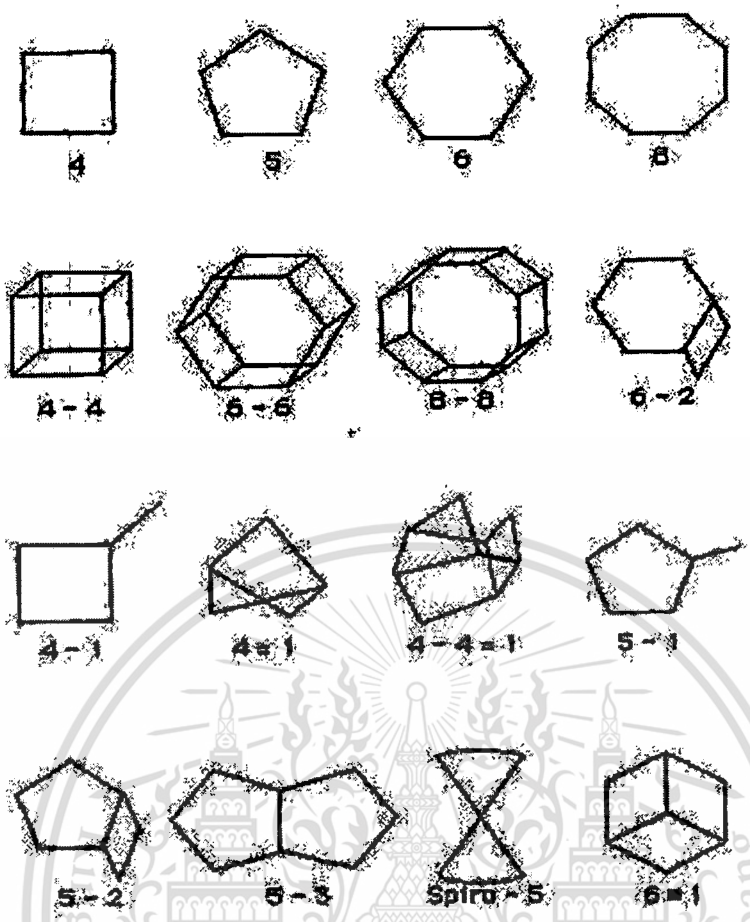


Figure 2.1 Secondary Building Units (SBU's) in zeolites. The corner of the polyhedral represent tetrahedral atoms

Description of the framework topology of a zeolite involves "tertiary" building units corresponding to different arrangements of the SBU's in space. Various alternative ways have been proposed. The framework may be considered in terms of large polyhedral building blocks forming characteristic cages. For example, sodalite, zeolite A and zeolite Y can all be generated by the truncated octahedron known as the [beta]-cage. An alternative method of describing extended structures uses the two-dimensional sheet building units.

According to the so-called Loewenstein rule, Al-O-Al linkages in zeolitic frameworks are forbidden. As a result, all aluminate tetrahedra must be linked to four silicate tetrahedra, but a silicate tetrahedron may have five different possible environments: Si(0Al,4Si), Si(1Al,3Si), Si(2Al,2Si), Si(3Al,1Si) and Si(4Al,0Si).

A topological description and classification of zeolite framework types has been proposed by Meier and Moeck who considered "coordination sequences", representing the numbers of T atoms in the first, second, third, etc. tetrahedral coordination sphere of each topologically non-equivalent T-site. The topology of the framework is then expressed by the sequences of these numbers. The concept of a coordination sequence has proved to be vary useful in evaluating the degree of similarity among different zeolite structure types [20].

2.1.1 Application of zeolites [21,22]

There are three main uses for zeolites in industry, the most important begin catalysis, but others include gas separation and ion exchange:

2.1.1.1 Catalysis

Zeolites have the ability to act as catalysts for chemical reactions which take place within the internal cavities. An important class of reactions is that catalysted by hydrogen-exchanged zeolites, whose framework-bound protons give rise to very high acidity. This is exploited in many organic reactions, including crude oil cracking, isomerization and fuel synthesis. Zeolites can also serve as oxidation or reduction catalysts, often after metals have been introduced into the framework. Underpinning all these types of reaction is the unique microporous nature of zeolites, where the shape and size of particular pore system exerts a steric influence on the reaction, controlling the access of reactants and products. Thus zeolites are often said to act as shape-selective catalysts.

2.1.1.2 Adsorption and Separation

Zeolites are used to adsorb a variety of materials. This includes applications in drying, purification, and separation. They can remove water to vary low partial pressure and are vary effective desiccants, with a capacity of up to more than 25 % of their weight in water. They can remove volatile organic chemicals from air streams, separate isomer and mixture of gases. A wildly used property of zeolites is that of gas separation. The porous structure of zeolites can be used to "sieve" molecules having certain dimensions and allow them to enter the pores. This property can be fine tuned by variating the structure by changing the size and number of cations around the pores. Other application that can take place within the pore include polymerization of semiconducting materials and conducing polymers to produce materials having unusual physical and electrical attributes.

2.1.1.3 Ion Exchange

The loosely-bound nature of extra-framework metal ions (such as in zeolite NaA, right) means that they are often readily exchanged for other types of metal when in aqueous solution. This is exploited in a major way in water softening, where alkali metals such as sodium or potassium prefer to exchange out of the zeolite, being replaced by the "hard" calcium and magnesium ions from the water. Many commercial washing powders thus contain substantial amounts of zeolite. Commercial waste water containing heavy metals, and nuclear effluents containing radioactive isotopes can also be cleaned up using such zeolites.

2.1.2 Zeolite-like materials (zeotypes) containrning elements other than Si or Al in Tetrahedral framework sites [23].

The best known examples of such minerals are viseite and keoheite. Both claimed to have phosphorus-containing analcime-type framework.

Likely candidate elements for such isomorphous replacement are Ga (close to Al in Group 3 of the periodic table) and Ge (close to Si in Group 4). In addition many compounds based upon linkages of $(PO_4)^{3-}$ coordination polyhedral are well known (but not of open character except the layer phosphates such ac zirconium phosphates).

Two general approaches have been made to place elements other than Si and Al into zeolitic structure namely by (1) direct synthesis and (2) modification of existing zeolites.

So far as modification is concerned to improve zeolite catalyst performance. These treatments have resulted in, for instance, B being substituted into framework site (confirmed by MASNMR). In all these modifications the number of framework sites substituted is small although in the case of high silica ZSM-5 the replacement of Al by, say, B can be high, as a proportion of the original Al being replace.

Direct synthesis has expanded considerable in the last five years and has been shown to provide a route to many more structure. This can be seen from the literature which, since 1982, has described more than 50 new prospective zeotype, some of which have been well characterized.

2.1.3 Titanium Containing Zeolite

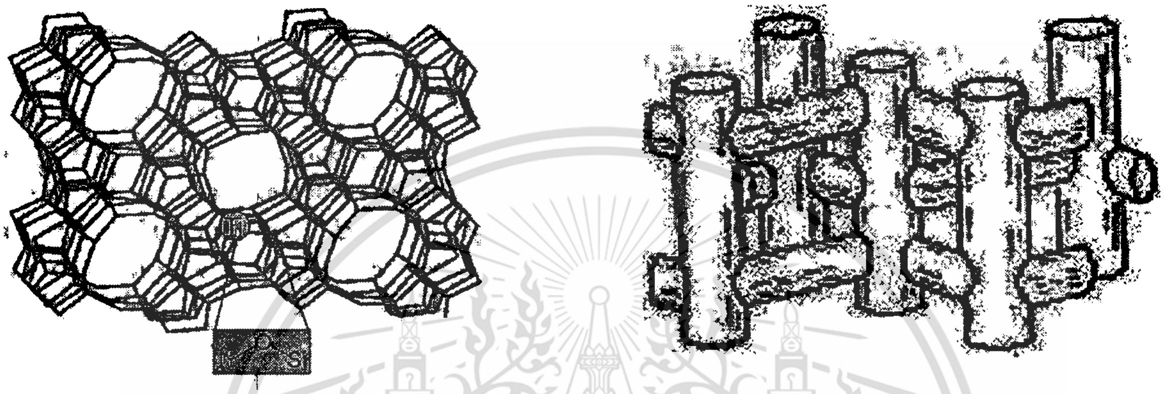
Titanium containing zeolites are the isomorphous substitution of Si by Ti into the zeolite framework provides useful catalysts for the oxidation of organic compounds under mild condition

2.1.3.1 Titanium silicalite-1 (TS-1)

Titanium silicalite (TS-1) catalyst, one of the most important innovation in heterogeneous catalysis over the last docades, is a high performances composit material specifically designed for industrial oxidation reaction with hydrogen peroxide [24].

Titanium silicalite is a zeotype crystalline material in which some of the silicon atom (within the silica framework) have been displaced by tetrahedrally coordinated titanium atom that behave as active site for catalysis [22,25]. It has a MFI structure. Titanium silicalite is shows a three-dimensional system of channels having molecular dimension of 5.1-5.6 A°. The structure of TS-1 is represented in Figure.2.2

(a). The 10-membered rings provide access to network of intersecting pores within the crystal. The pore structure enclosed by 10 oxygen windows but these do not link cavities as such in Figure 2.2 (b) there is a set of straight, parallel pores intersected by a set perpendicular zigzag pores. Numbers of molecules are small enough to penetrate into this intracrystalline pore structure where they may be catalytically converted [23,26].



(a) (b)

Figure 2.2 Representation of three-dimensional structure of TS-1 (MFI) (a) Structure formed by stracking of sequence (b) Schematic representation of the intracrystalline pore structure

The presence of Ti atom in TS-1 can be obtained from the IR band at 960 cm^{-1} which is considered as a framework Ti atom in tetrahedral as show in Figure2.3. The XRD pattern show in Figure 2.4 the characteristics of the MFI structure. The single peak at $2\theta = 24.4^{\circ}$ indicated a change from monoclinic symmetry (silicate) to orthorhombic symmetry (TS-1). The UV-Vis spectrum as show in Figure 2.5 it is possible to see the presence of two bands at 215 nm. and at about 250 nm. The crystalline nature of MFI is evident in the electron micrograph of Figure 2.6 with a high resolution electron microscope, it is even possible to see evident of the regularity in the pore structure of the material.

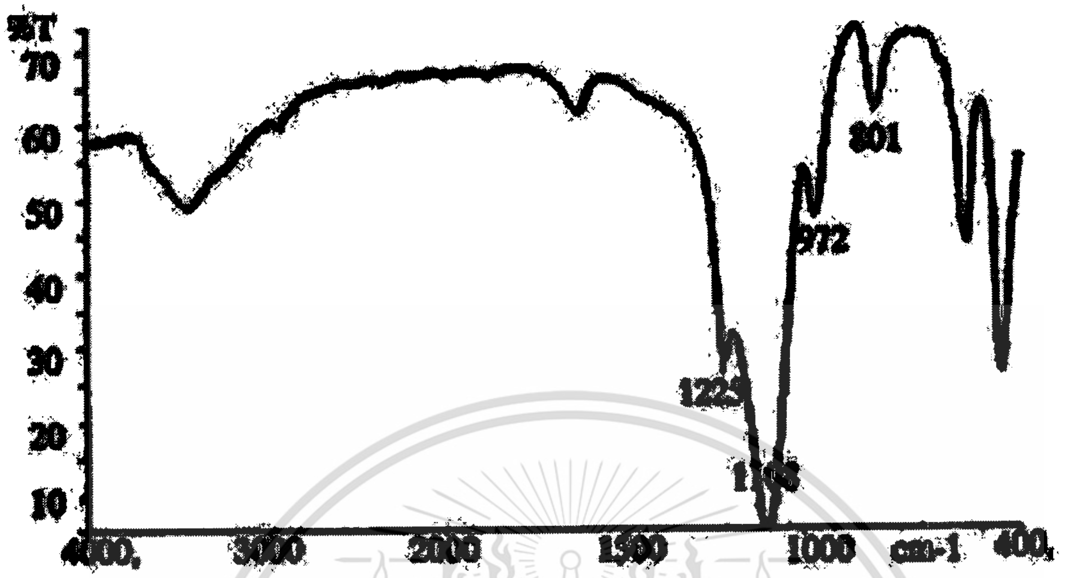


Figure 2.3 FT-IR spectrum of TS-1 sample [27]

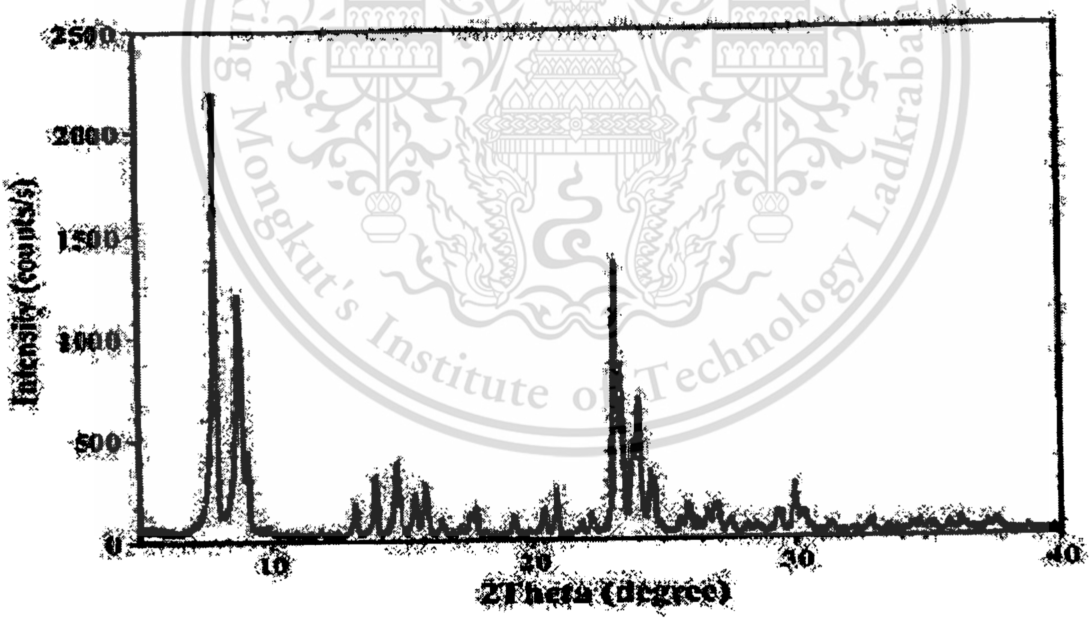


Figure 2.4 The XRD pattern of TS-1 [28]

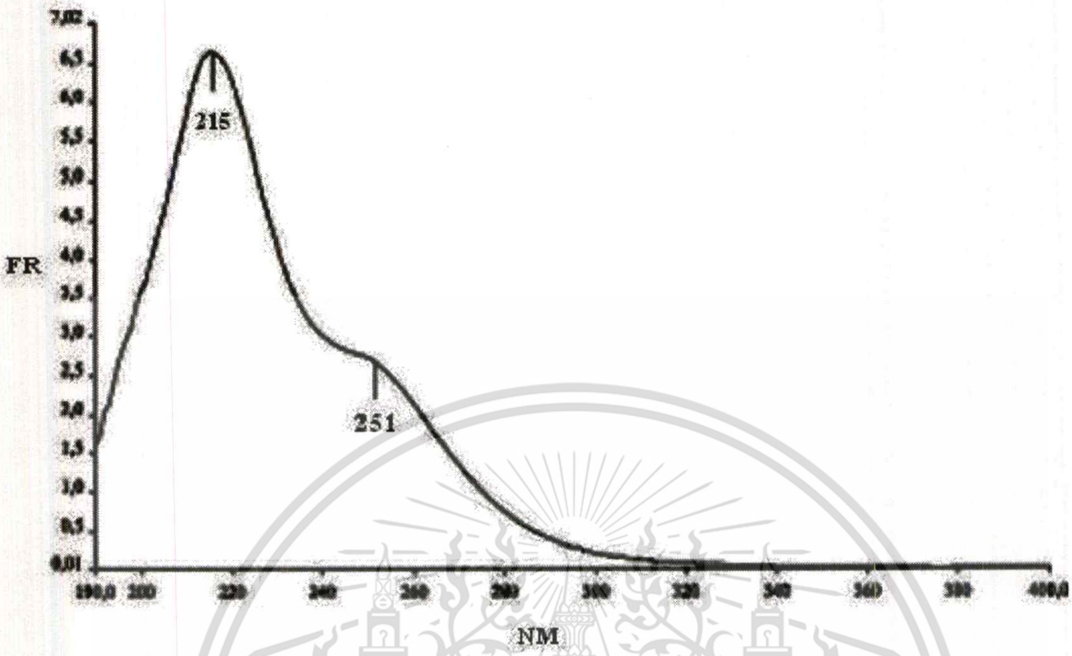


Figure 2.5 UV-Vis spectrum of the TS-1 [27]

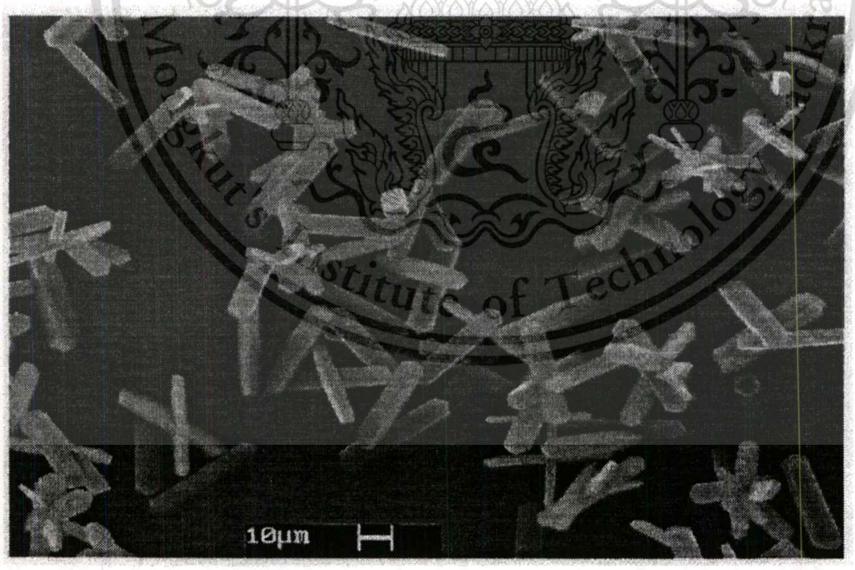


Figure 2.6 Scanning electron micrographs of TS-1 sample [29]

2.1.4 Oxidation by Ti-containing zeolite

Ti-containing zeolite are found to be efficient catalysts for the selective oxidation of large number of organic substrates, such as alkanes, alkene, alcohols, aromatic, phenol, amine, thioether and sulfoxide [10, 13, 16, 17, 27, 29-34] as shows in Figure 2.7. The reaction can be carried out under mild reaction condition using H_2O_2 as oxidant. Unlike the Group IV-VI metal oxide based catalysis. Ti-containing zeolite are active in the presence of diluted aqueous solution of hydrogen peroxide.

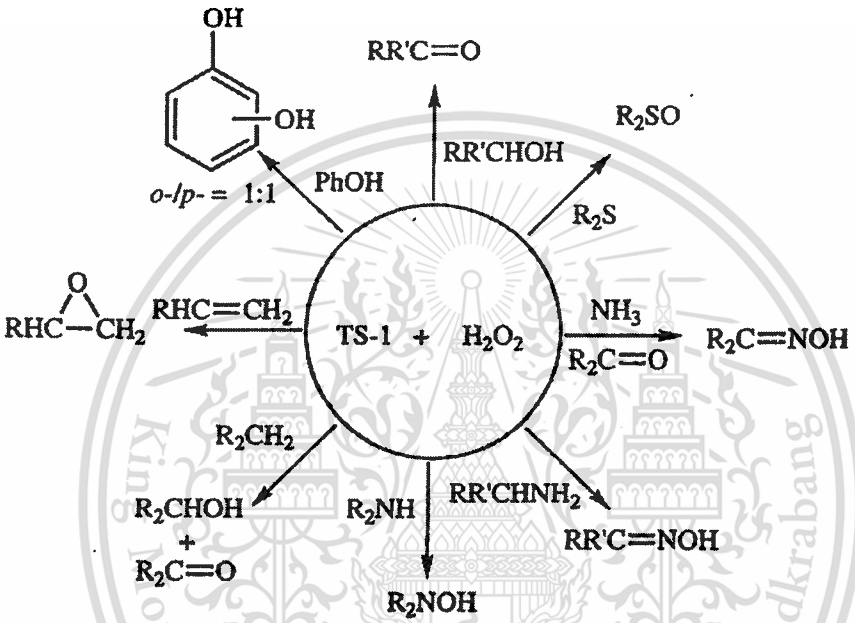


Figure 2.7 Catalytic oxidation by titanium-containing zeolites and aqueous hydrogen peroxide as oxidant agent

The active catalytic species in the oxidation reaction with hydrogen peroxide over Ti-containing zeolite is a complex containing a hydroperoxo ligand (Ti-OOH) as shown in Figure 2.8.

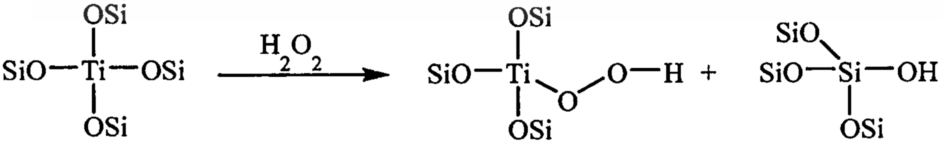


Figure 2.8 Postulated titanium active species

The catalytic activity of these zeolites is derived from the titanium tetrahedral in the framework. By addition of water, one Ti-O-Si bond can be hydrolyzed, but the tetracoordination is remains intact. Subsequently, the addition of another water molecules generates a pentacoordinate titanium species as shown in Figure 2.9.

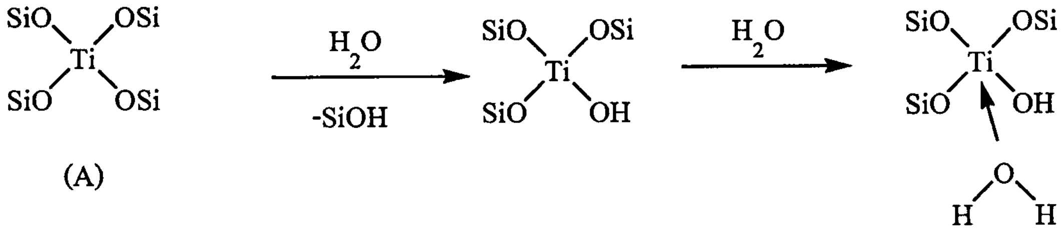


Figure 2.9 Postulated titanium species of the calcined from tetrahedral titanium species (A), its hydrolysis and hydration

The oxidation mechanism is summarized schematically in Figure 2.10. H_2O_2 first interacts with the tetrahedrally coordinated Ti sites in a regular to form (a) or in hydrated form (d) to form Ti-OOH species (b), which is probable present in a five-member cyclic structure through the interaction with a protic species [35, 36]. The alkane or another molecule, which is used as reducing agent, then penetrates into the pores to attack this active site to form a precursor for the formation of alcohol (c). The peroxyl group from the Ti-hydroperoxo complex is transferred to the adsorbed alkane to form alcohol. The alcohol is there released from the Ti site and reacts with (b) again to formed ketone and other products.

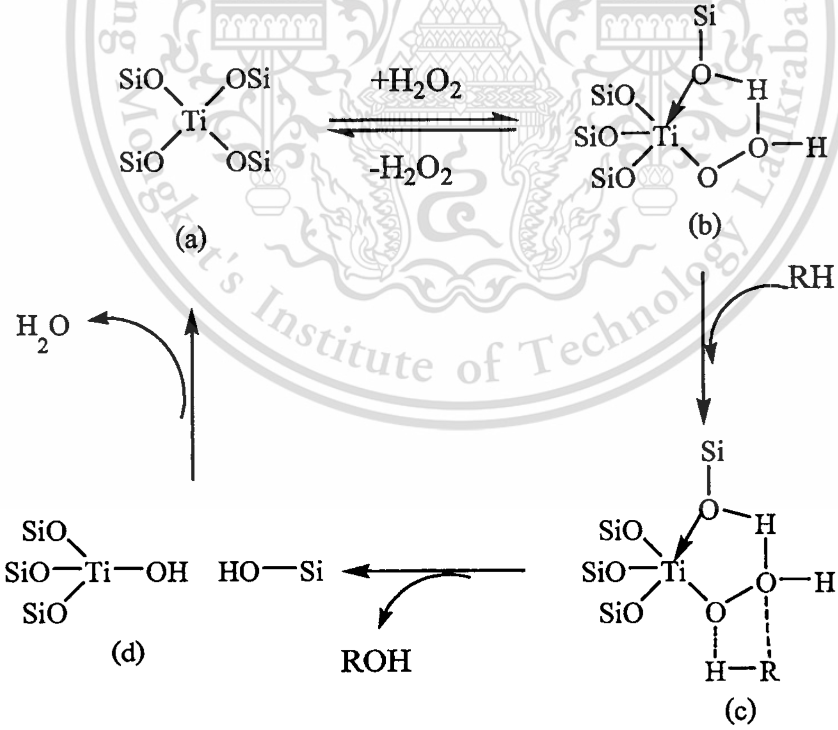


Figure 2.10 Postulated oxidation mechanism [31]

However, the use of TS-1 is restricted to reaction of relatively small molecules due to diffusion limitations which result from active sites being situated in a channel system of about 0.55 nm. average diameter [16,27,29,30,37,38].

2.1.5 Oxidative extraction of sulfur compounds over Ti-containing zeolites

To eliminate the undesirable sulfur compounds or to convert them into more innocuous forms, various process have been employed. Oxidative desulfurization is the method to produce oxidized compounds then can be removed by solvent extraction. Traditional oxidizing agent include hydrogen peroxide, peracid, hydroperoxide, chloride, nitrogen oxide, oxygen or ozone but the most common oxidant is hydrogen peroxide [39-41].

Organic sulfide are oxidized by hydrogen peroxide in heterolytic process involving the nucleophilic attack of the sulfur atom on the oxygen as shown in Figure 2.11.

Figure 2.11 Postulated the nucleophilic attack of the sulfur atom on the oxygen [32]

Due to the high nucleophilicity of the sulfur atom, organic sulfides are much more reactive than hydrocarbon compounds that sulfoxides are formed by partial oxidation of sulfides which upon further oxidation are converted to sulfones according to Figure 2.12 [32,42]. Hydrogen peroxide alone or associated with various solvents or catalysts is most wildly agent used for oxidized organic sulfide.

$$R_1SR_2 \xrightarrow{H_2O_2} R_1SOR_2 \xrightarrow{H_2O_2} R_1SO_2R_2$$

Figure 2.12 Postulated the formation of sulfoxide and sulfone by hydrogen peroxide

The catalytic activity of organic sulfide by Ti-containing zeolite which involves the coordination of solvent molecule to the active titanium site of hydroperoxo species as show in Figure 2.13.

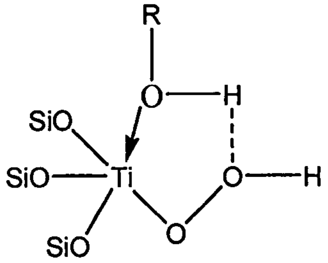


Figure 2.13 Proposed active species in oxidation catalyzed by Ti-containing zeolite

It is known that in such a complex the transition metal increase the electrophilicity of the peroxydic oxygen atom which makes the nucleophilic attack of organic substrate easies [34].

2.2 Liquid-Liquid Extraction

Liquid-Liquid extraction, often loosely referred to as solvent extraction, was carried out as Roman times when silver and gold were extracted from molten copper using lead as a solvent. The firth significant industrial application of solvent extraction was in the petrochemical industry. Since 1945 in the nuclear industry, in the refining of uranium, plutonium and other radioisotopes. Since 1960, solvent extraction has been applied on a large scale in the refining of other nonferrous metals.

The physical process of Liquid-Liquid extraction separates a dissolved component from its solvent by transfer to a second solvent, immiscible with the first but having a higher affinity for the transferred component. The latter is sometime called the consolute component. In the process of fraction extraction, two or more consolute component can be extracted and also separated if these have different distribution ratios between the two solvents.

In the simplest case, the feed solution consists of solvent A containing a consolute component C, which is brought into contact with a second solvent B. For efficient contact there must be a large interfacial area across which component C can transfer until equilibrium is reached or closely approached. Figure 2.14 as shown a single contacting single.

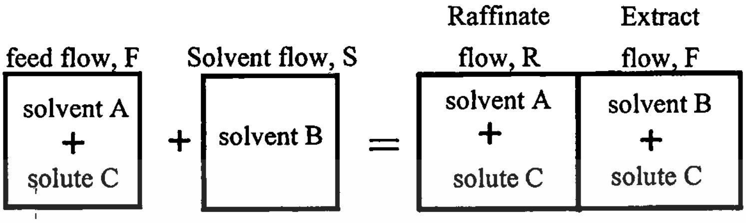


Figure 2.14 Single contacting stage

2.3 Literature Review

Sulfur compounds are slightly higher polar as compared to hydrocarbon molecule. Hence, the sulfur compounds may well be separated from H/C by the high polar solvent extraction. For example, hydrogen fluoride was used as the extraction solvent. An extremely high selectivity could be attained in the removal of sulfur compounds from middle distillate fractions [43]. For enhanced efficiency, Petrostar and UNIPURE announced a commercial oxidation process for desulfurization using peroxyacetic acid as catalyst [44,45]. More recently, Zannikos et al. remove 90 % of the sulfur in petroleum fraction under mild condition by performing a solvent extraction after the oxidation step [46]. The oxidation of sulfides to sulfoxides by hydrogen peroxide has proved to be one of the most attractive method. The oxidation of sulfides by hydrogen peroxide are shown in Figure 2.15.

$$R_1\text{-S-}R_2 \xrightarrow{H_2O_2} R_1\text{-}\overset{\overset{\large O}{\|}}{S}\text{-}R_2 + H_2O$$

Figure 2.15 Oxidation of organic sulfur compounds by hydrogen peroxide

The oxidation of sensitive sulfide by hydrogen peroxide usually proceeds under relatively mild condition [16,47]. The reaction can be carried out in non-acidic media, in the presence of transition-metal (Ti, Mo, Fe,V, W, Re, Ru) complexs. They are used as catalysts for the selective oxidation of thioether by H_2O_2 in homogeneous system [48-51]. Ti-containing zeolites are used as catalyst for the selective oxidation of sulfides into sulfoxides. These catalysts including TS-1 [16,17,32-34], TS-2 [17,47], Ti-β [16,32-34], Ti-MCM-41 [52,53], Ti-HMS [16,17], and Ti-MMM [54] show good catalytic properties for mild selective oxidation of sulfides by aqueous H_2O_2. Titanium silicate (TS-1) is used as a commercial oxidation catalyst in the reaction of relatively small molecules [16,17,32-34]. While Ti-β and Ti-mesoporous materials can be applied for the oxidation of bulkier sulfides [14].

Hulea *et al.*[32] compared the activity of Ti-β zeolite with TS-1. Both catalysts were tested in the hydrogen peroxide used as oxidizing agent. The result indicateds that TS-1 and Ti-β have the same activity towards the oxidation of small sized substates. It was also found that Ti-β was more active than TS-1 in the oxidation of hindered molecule. Application of TS-1 as the catalyst for the oxidation of various alkyl methyl sulfides was also studied by Robinson *et al* [55]. It was found that, the more hindered the sulfides, the less the sulfone were formed.

The nature of the solvent plays a vary important role in the catalytic reaction. It does not only modify the homogenity of the system, but also largely influence on side reaction which produce by-product and may even become promoter in some catalytic system. For example, the protic solvent; such as H_2O and methanol, give more epoxidation activity than aprotic solvent such as acetonitrile. However, a higher selectivity was obtained in aprotic solvent because the ring opening of epoxide is a major side reaction on epoxidation This side reaction can be largely promoted by the protic solvent forming the glycols or glycol ether [56]. In sulfoxidation reaction, the nature of the solvent can modify the rate ratio between the two step of sulfide to sulfoxide and sulfoxide to sulfone [34] as shown in Figure 2.16. For example, protic solvent such as ethanol give rate of formation of sulfoxide is higher than of formation of the sulfone as compared with aprotic solvent such as tetrahydrofuran and acetonitrile in two phase (solid-liquid) system.

$$R_1SR_2 \xrightarrow{H_2O_2} R_1SOR_2 \xrightarrow{H_2O_2} R_1SO_2R_2$$

Figure 2.16 Postulate two step of sulfoxidation reaction

CHAPTER 3

EXPERIMENTAL DETAILS

3.1 Reagents

1. Acetic acid (Carlo Erba Reagent)
2. Acetonitrile (Lab Scan)
3. Ammonia solution (30% w/w) (Carlo Erba Reagent)
4. Deionized water
5. Hydrogen peroxide (30 % w/w, Merck)
6. Ludox (suspension silica, 40%w/w SiO_2) (Aldrich)
7. Methanol (Fisher Scientiic)
8. nomal-Dodecane (Merck)
9. normal-Nonane (Fluka)
10. Sulfuric acid (Merck)
11. Tetrabutyl orthotitanate ($C_{16}H_{36}O_4Ti$) (Fluka)
12. Tetrapropylammonium bromide (TPABr) (Fluka)
13. Thiophene (Merck)

3.2 Apparatus

1. Autoclave reactor
2. Condenser
3. Cooling bath
4. Fourier transform infrared spectroscopy (FTIR Spectrum GX, Perkin Elmer)
5. Furnace (Vecstar Furnaces)
6. Gas Adsorption Analyser (Autosorb-1, Quantachrome)
7. Gas chromatography (3800 Gas Chromatograph, Varian)
8. Hot plate & stirrer
9. Laboratory glassware
10. Laboratory plasticware
11. Magnetic stirrer
12. Microkid reactor
13. Oven
14. Scanning electron microscope (LEO 1455VP, LEO Electron Microscopy,

Scientific Instruments Service Centre, KMIT'L)

15. Water aspirator and vacuum filtration
16. X-ray diffractometer (D8 Advance, Bruker AG, Scientific Instruments Service Centre, KMIT'L)
17. X-ray fluorescence spectrometer (SRS 3400, Bruker AG, Scientific Instruments Service Centre, KMIT'L)

3.3 Experiment

3.3.1 Preparation of catalyst

3.3.1.1 Titanium silicalite (TS-1)

Tetrabutyl orthotitanate was used as titanium source to prepare TS-1. 2.01 g. of tetrabutyl orthotitanate was mixed with 4.72 g. of deionized water at 5°C, followed by adding 8.58 g. of hydrogen peroxide solution (30%) under stirring for 30 minutes. Then, 16.68 g. of ammonia solution (30%, 5°C) was added and stirred. The solution was left overnight at room temperature. The solution will then be heated at 80-90°C for 45 minutes. Ammonia solution (30%) was then added to the last solution until it has just as much weight as solution before heating. After that this solution was mixed with mixture of 18.72 g. of deionized water, 6.16 g. of tetrapropylammonium bromine (TPABr) and 21.62 g. of Ludox. The mixture was stirred at 100 rpm for 8 hours. Finally, the yellow gel with a molar composition of 15 TPABr : 3.8 TiO_2 : 94 SiO_2 : 2168 H_2O : 212 NH_3 : 12.3 H_2O_2 were loaded in the autoclave and crystallized at 185°C. After 7 days, the synthetic zeolite was filtrated, washed by distillated water and dried at 80°C.

The synthetic zeolite was calcined under Air-zero at 550°C by a heating rate of 1°C/min. and hold at that temperature for 6 hours. After cool down, the catalyst is washed by 5 molar of sulfuric acid until pale-yellow of filtrate cannot be observed upon dropping hydrogen peroxide. The sample was then calcined using the same condition as previous.

3.3.2 Characterization of catalysts

3.3.2.1 Catalyst Structure

The structure of catalyst can be determined by X-ray diffractometer (D8 Advance, Bruker, Scientific Instruments Service Centre, KMITL). The sample was prepared by packing the catalyst in the sample holder. CuKα X-ray beam was used for analysis at 30 kV, 30 mA. The sample was scanned from 2θ angle 5° to 60° with 1 second/step time and 0.04 2θ/step increment. X-ray diffraction pattern of the sample can be compared with the X-ray diffraction pattern of standard catalyst for structure determination.

3.3.2.2 Crystal Morphology

The crystal morphology and crystal size of the catalysts can be determined by scanning electron microscope (LEO 1455VP, LEO Electron Microscopy, Scientific Instruments Service Centre, KMITL). The sample can be prepared by thoroughly placing catalyst onto the sample holder. It was then coated with gold by ion sputtering. The sample was placed in the sample chamber of scanning electron microscope and evacuated from ambient pressure to 10^{-1} mbar.

3.3.2.3 Silicon/titanium ratio

The silicon/titanium content can be determined by X-ray fluorescence spectrometer (SRS 3400, Bruker, Scientific Instruments Service, KMIT'L). The sample was prepared by mixing 0.5 gram of catalyst and 4.5 gram of boric acid as a binder and grind into powder by tungsten carbine (Rock Lab grinder). The mixture was packed onto aluminium cup and then compressed at 150 kN. The sample was then placed in the sample chamber. Lithium fluoride, pentaerythrite and W/Si multilayer were used as diffracting crystal and Rhodium was used as source for measurement at 50 kV, 60 mA.

3.3.2.4 Type of Titanium Species

Titanium species in the catalyst can be determined by Fourier transform infrared spectroscope (FTIR Spectrum GX, Perkin Elmer). The sample was analyzed using Attenuated Total Reflectance (ATR) technique. The characteristic vibration frequency at 960 cm^{-1} represents the vibration of Ti-O-Si bond in tetrahedral coordination.

3.3.2.5 Surface Area

Surface area of the catalysts can be determined by Gas Adsorption Analysis (Autosorb-1, Quantachrome). Approximating 0.02-0.04 gram of sample was loaded into the cleaned and dried sample cell. The sample was degassed at out-gas station at 350°C for 24 hours. Then, nitrogen was filled and the sample cell was moved to analysis station. The adsorption isotherm was measured in a pressure range of 0.05-0.30 P/P_0 at 70 K.

3.3.3 Catalytic testing

3.3.3.1 Batch process

The oxidative extraction of thiophene was carried out in a micro reactor (10 ml), equipped with a magnetic stirrer, a thermometer, and a condenser. In a typical run, water bath was heated up to the desired reaction temperature. TS-1 (0.02-0.10 g.) was used as catalyst. Then, thiophene (1% w/w) was dissolved in 2.50 ml *n*-nonane or *n*-dodecane and 2.50 ml of solvent. Finally, 4.10 mmol of hydrogen peroxide was added into the reaction mixture. The molar ratio of feed used in the oxidative extraction was: thiophene: (30 %w/w) H_2O_2 = 1:19. After a period of time (360 min.), the reaction can be stopped by removing heat. Subsequently, the resulting mixture was cooled to room temperature, and the catalyst was recovered by filtration. The mixture was left standing for separation. The oil phase was analyzed by gas chromatography Varian 3800 with capillary DB-5.625 column (30 m×0.25 μm.). Liquid sample 0.2 μL was injected to the injection port (200°C) using split ratio of 200. The separation temperature was started at 60°C for 1 minutes. Then, the temperature was raised to 120°C with a heating rate of 10°C/min and held at that temperature for 5 minutes. N_2 was used as carried gas at a flow rate of 1.0 ml/min.

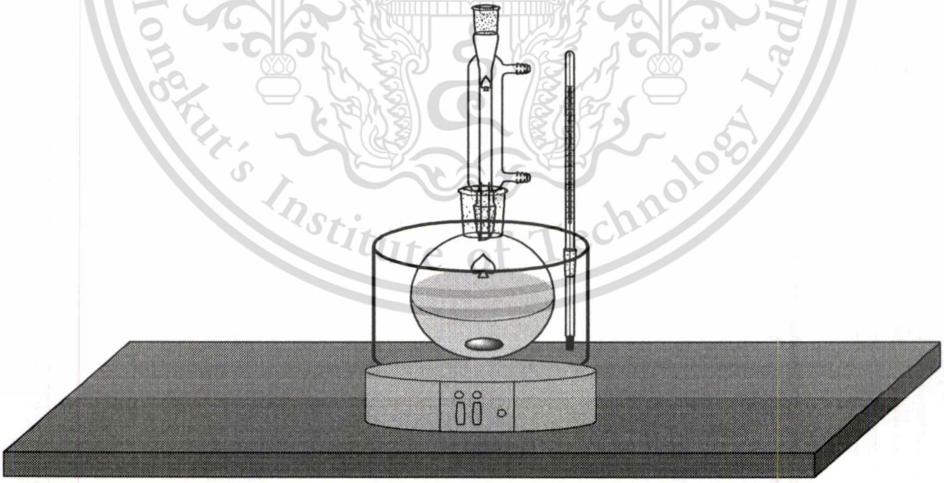


Figure 3.1 Schematic of catalytic testing in batch reactor

3.3.3.2 Continuous process

The oxidative extraction of thiophene in continuous process was performed in 150 ml continuous stirred tank reactor (CSTR) [57]. The reaction was carried out at 60°C using TS-1 (1.0-2.0 g.) as catalyst. The contact time was estimated from batch reactor. Typically, thiophene (1-3 % w/w) was mixed to *n*-dodecane (188.0 ml) in the first reservoir. While, hydrogen peroxide (10.0 ml) was mixed in methanol (179.0 ml) in the second reservoir. Both reservoirs were kept at 5°C for preventing H_2O_2 decomposition. Then, the two mixtures were fed into CSTR by peristaltic pump (GILSON miniplus3) at the same flow rate. The CSTR primarily contain all reactant and catalyst heated at 60°C. The two mixture were then fed into CSTR by peristaltic pump (GILSON miniplus3) at the flow rate 14.0 ml hrs^{-1} etc. The schematic diagram of continuous process was shown in Figure 3.2.

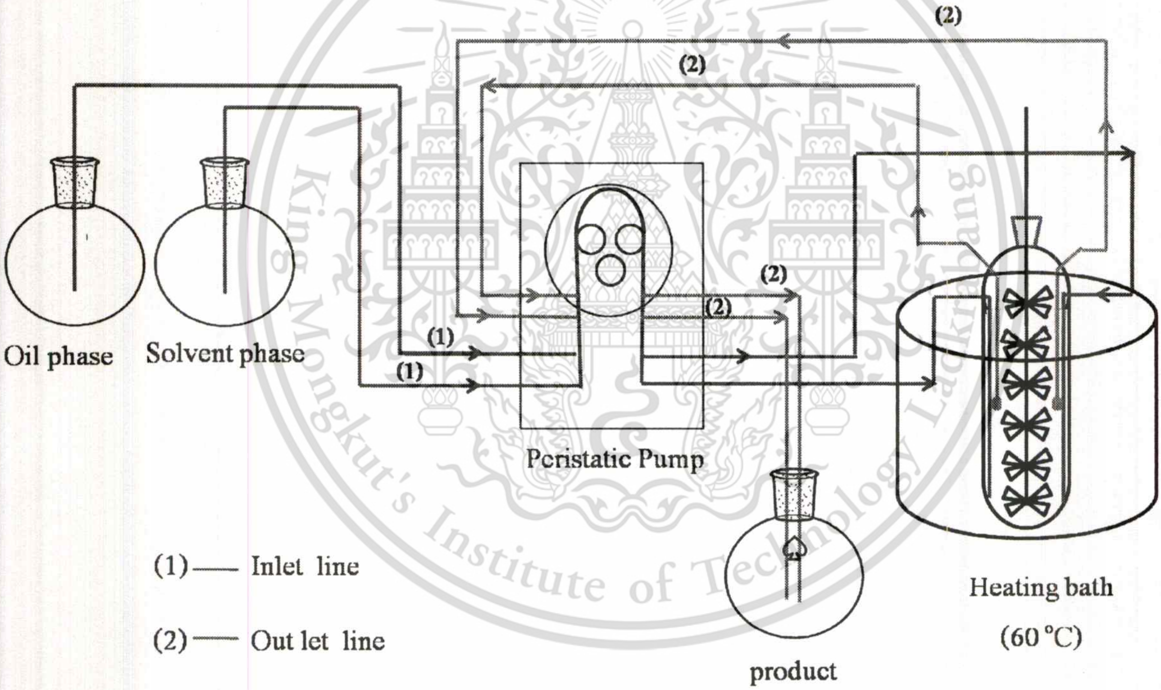


Figure 3.2 Diagram of catalytic testing of continuous process in stirred tank reactor

The effluent from the CSTR was collected every hour and left standing for separation. The oil phase was analyzed by Gas Chromatography using the same condition in the batch process.

3.3.3.3 Effect of Extraction Temperature

The effect of reaction temperature (room temperature and 60°C) was determined by using acetic acid as solvent in batch process.

3.3.3.4 Effect of Catalyst

The effect of catalyst was determined using acetic as solvent for 360 min.

3.3.3.5 Effect of Solvent

The effect of solvent was determined by the reaction using methanol, acetonitrile, acetic acid and water as solvent for 360 min.

3.3.3.6 Effect of Solvent/Oil Ratio

The effect of solvent to oil ratio (0.2, 0.4, 0.6, 0.8 and 1) was determined by using methanol as solvent.

3.3.3.7 Effect of Hydrocarbon Chain Length

The effect of hydrocarbon chain length was investigated using *n*-nonane and *n*-dodecane as feed models.

3.3.3.8 Effect of Catalyst Stability

The effect of catalyst stability was studied over 780 min of testing in reaction number.

3.3.3.9 Effect of Calcination Temperature

The effect of leaching of titanium framework was studied with different temperature of calcination (550°C and 575°C).

3.3.3.10 Effect of Catalyst Content

The effect of catalyst content was studied by continuous stirred tank reactor (CSRT) with different amount of catalyst (1.0 and 1.8 g).

3.3.3.11 Effect of Feeding Rate

The effect of feeding rate was determined with different total rate of feed (10, 14, 25 ml hrs^{-1}).

3.3.3.12 Effect of Feed Concentration

The effect of concentration the feed thiophene was determined with different concentration of feed thiophene (1%, 3% wt).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterization of catalyst

X-ray diffraction of TS-1 sample was shown in Figure 4.1. It can be seen that the TS-1 sample processes a well-define crystalline phase of MFI structure, showing characteristic peak at 2θ = 7.89, 8.84, 23.11, 23.34, 23.90, and 24.4. After the calcination and acid treatment, the intensity of peak at 2θ = 7.89 and 8.84 was increased. The additional characteristic peaks at 23.11, 23.34, 23.90 and 24.40 are decreased indicating the decomposition of organic template from the pore of TS-1 sample.

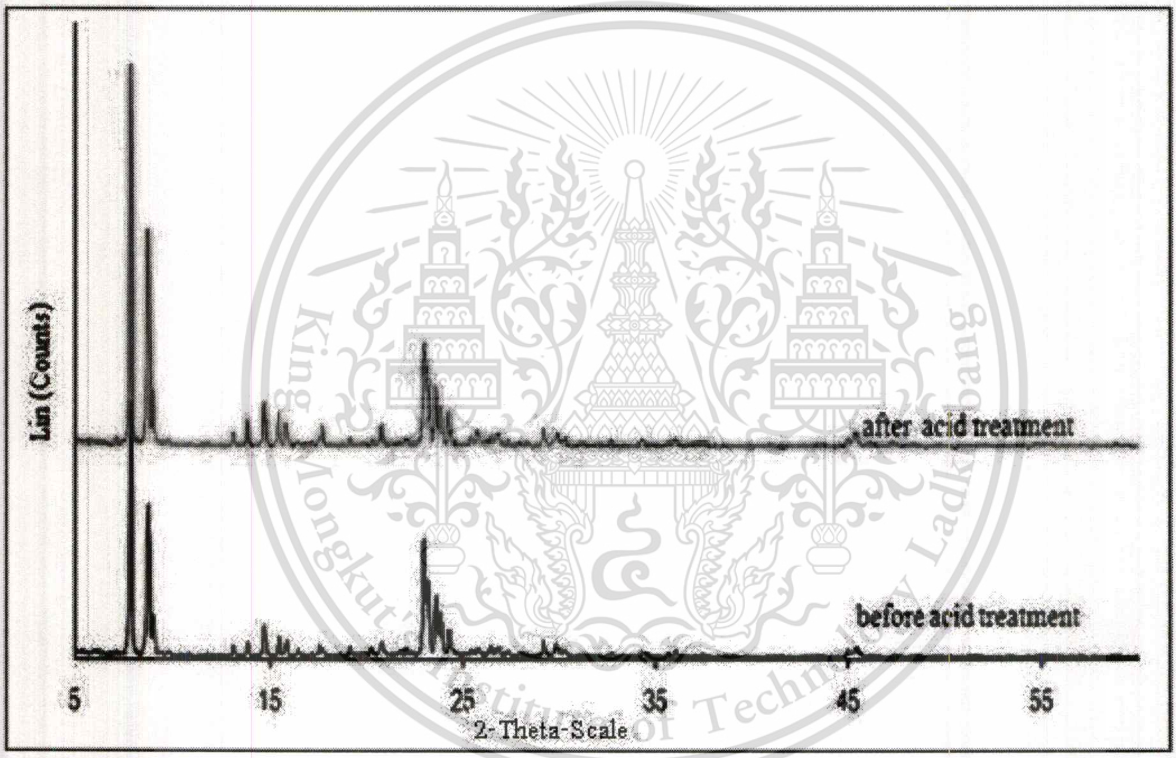
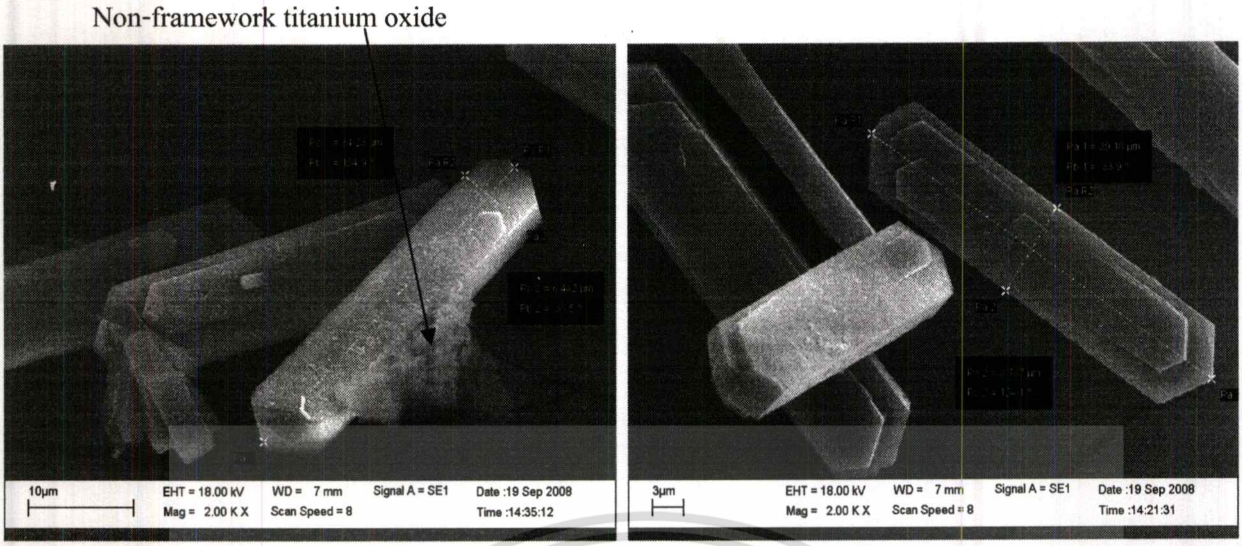


Figure 4.1 X-ray diffraction pattern of TS-1 before and after acid treatment

Scanning electron microscope was used to determine the morphology and crystallite size of the synthesized TS-1 sample. Figure 4.2, shows the SEM of TS-1 with a crystal size of 35-50 μm. The non-framework titanium oxide was observed in TS-1 sample as shown by irregular particles. However, these species can be removed by treating with strong acid solution. As seen in Figure 4.2 (b), the crystal of TS-1 sample after treating with sulfuric acid was relatively clean, as compared to that of TS-1 before treating with sulfuric acid (Figure 4.2 (a)).



(a) **(b)**

Figure 4.2 Scanning electron micrograph of TS-1 (a) before and (b) after acid treatment

The silicon to titanium ratio (Si/Ti) of the TS-1 synthesized was analyzed by the X-ray fluorescence spectrometer, as shown in Table 4.1.

Table 4.1 The silicon and titanium content and surface area of Titanium Silicalite (TS-1)

Zeolite	**Si/Ti**	**BET Surface area (m^2/g)**
TS-1 (before treating with sulfuric acid)	22	416
TS-1 (after treating with sulfuric acid)	32	473

It was shown that the titanium content in the TS-1 sample decreased after the sample was treated with 5 molar of sulfuric acid. This indicates that the non-framework titanium oxide was readily removed by acid treatment. While, the framework titanium species cannot be washed away. It was believed that after the treating with 5 molar sulfuric acid, only the framework titanium species remains in the TS-1 sample.

Also in Table 4.1, the increase in specific surface area of TS-1 sample is consistent with the observed increase in Si/Ti ratio discussed above. Before treating with sulfuric acid, it is likely that non-framework titanium oxide can be present in the pore of the TS-1 sample, in addition to the largely agglomeration observed by SEM. This can readily block the pore of TS-1 sample. The treatment with sulfuric acid can remove this non-framework titanium oxide from the pore of TS-1 sample, resulting in a higher surface area of TS-1.

FT-IR spectra of the TS-1 samples before and after acid treatment were shown in Figure 4.3. It is clear that, both TS-1 sample presented an absorption band at about 960 cm^{-1} indicating that titanium was incorporated into the framework of the zeolite (Ti-O-Si). There is no significant difference in the intensity of this band (960 cm^{-1}) for both samples. Hence, it is suggested that the framework of titanium species were not leached when treated with acid.

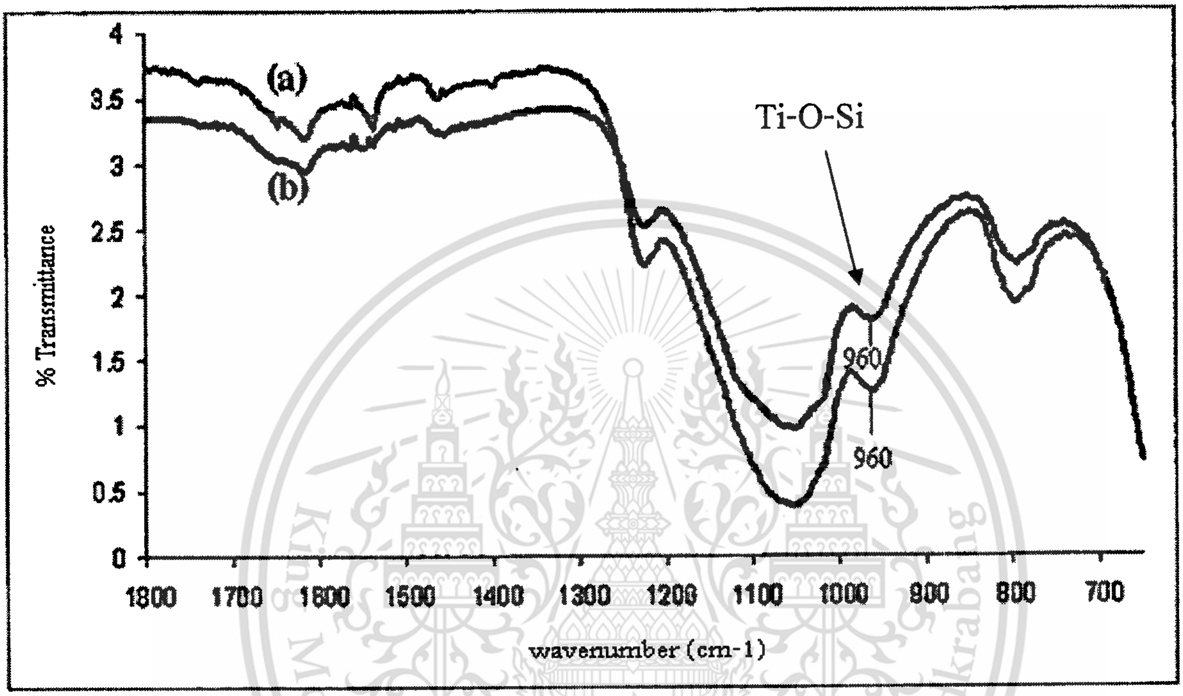


Figure 4.3 Fourier transformed IR spectra of TS-1 (a) before and (b) after acid treatment

4.2 Catalytic Testing in Batch Process

In the oxidative extraction, it is known that the organosulfur compounds can be oxidized to the higher polar compounds with Ti-containing zeolite using hydrogen peroxide as oxidizing agent [17] and the oxidized product can be extracted by polar solvent [16]. In this reaction, the oxidative extraction of thiophene was preliminarily tested in a batch reactor (10 ml) using hydrogen peroxide and TS-1 as oxidizing agent and catalyst, respectively. The catalytic activity was determined by % removal of thiophene which was expressed as

$$\%\ \text{removal} = \frac{C_o - C_t}{C_o} \times 100$$

Where

C_o is initial concentration of thiophene in feed and C_t is concentration of thiophene in oil phase after t min

4.2.1 Effect of Extraction Temperature

The effect of the extraction temperature of thiophene was shown in Figure 4.4.

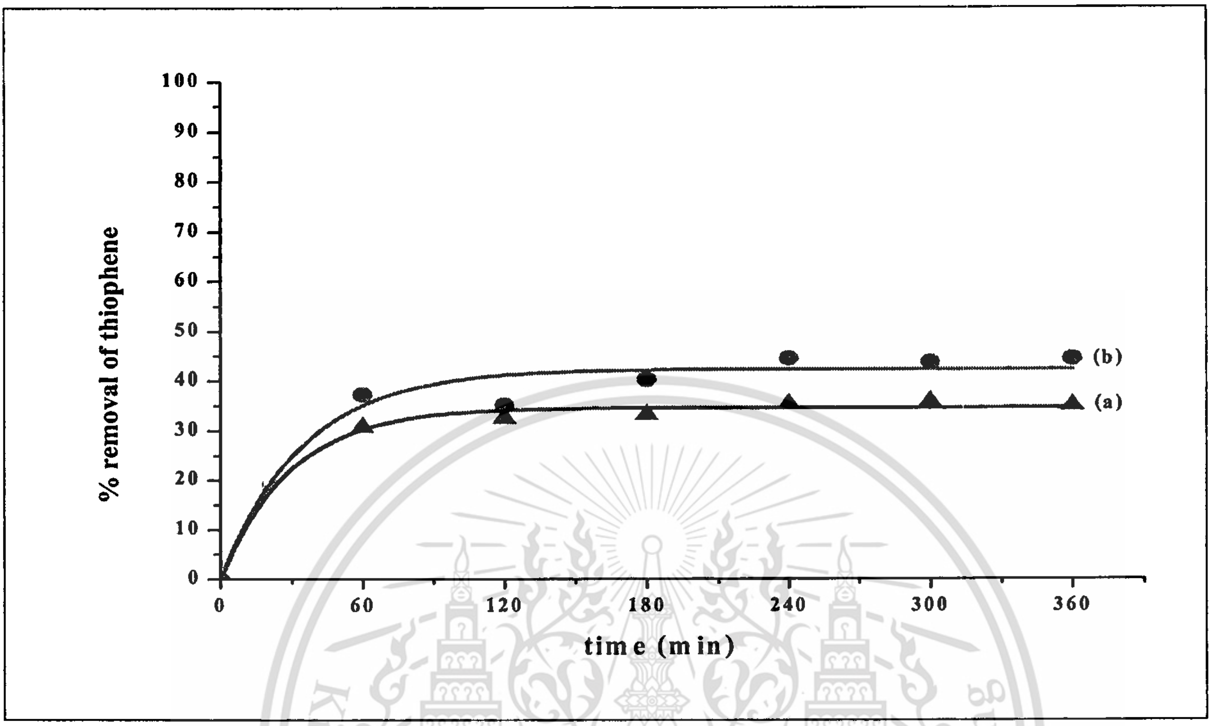


Figure 4.4 The effect of temperature on the % removal of thiophene using (a) room-temperature (30°C), (b) 60°C. Reaction condition : (1%TH) n-nonane; 2.5 ml, acetic acid; 2.5 ml., reaction time; 360 min.

In the reaction using acetic acid as a solvent, an increase in % removal of thiophene was obtained when the extraction temperature increase from room-temperature to 60°C. This is because the increases in extraction temperature would increase the partition coefficient in acetic acid/*n*-nonane ratio. The thiophene partitioning between acetic acid and *n*-nonane was increase from 0.55 at room-temperature to 0.74 at 60°C. Therefore, the oxidative extraction will be tested at temperature of 60°C since the oxidation activity would also prefer high temperature.

4.2.2 Effect of Catalyst

The % removal of thiophene from the reaction using acetic acid as solvent was shown in Figure 4.5.

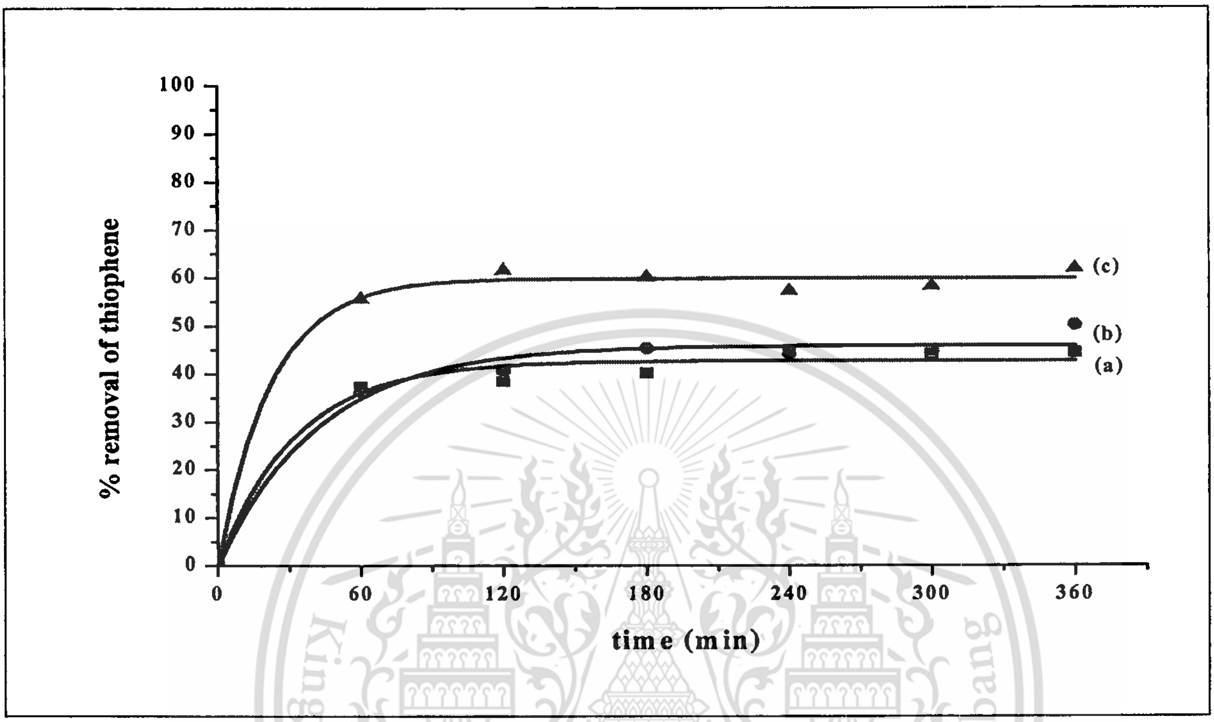
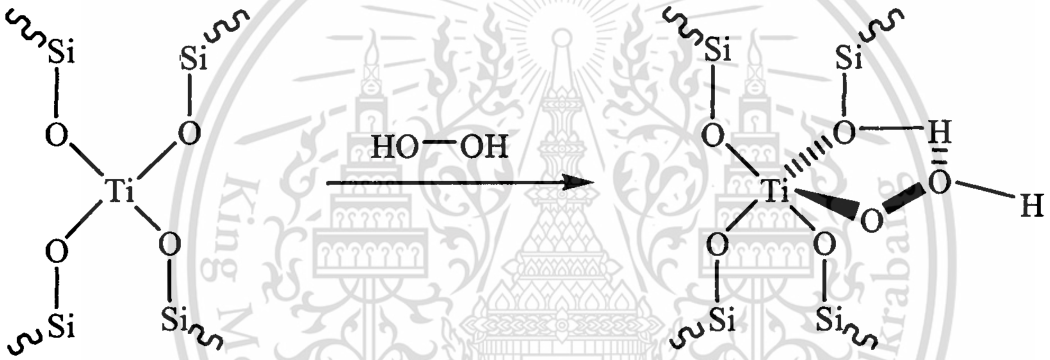


Figure 4.5 The effect of catalyst on the % removal of thiophene, (a) extraction, (b) H_2O_2 without TS-1, (c) H_2O_2 , TS-1. Reaction condition : temperature; 60°C, (1% TH) n-nonane; 2.5 ml, acetic acid; 2.5 ml, hydrogen peroxide solution (30% w/w); 4.1 mmol, TS-1; 0.06 g, reaction time; 360 min

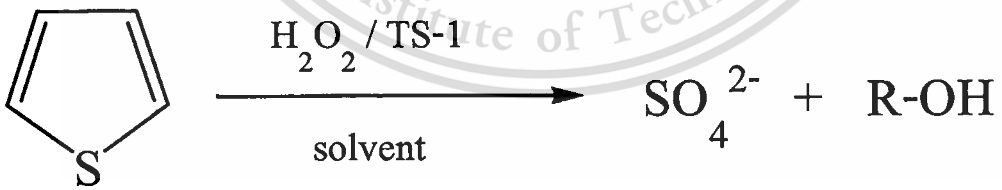
The extractability of the solvent was tested in the absence of TS-1 and hydrogen peroxide. From the Figure 4.5, it was found that, thiophene can be transferred from the oil phase by the solvent extraction (acetic acid). This is because acetic acid is polar solvent and thiophene is slightly polar compound. This permits the removal of thiophene from oil phase by solvent extraction.

When hydrogen peroxide was added into the reaction mixture without TS-1 catalyst, a slight increase in % thiophene removal was observed, as compared to the reaction with the absence of TS-1 and hydrogen peroxide. This is due to the fact that the thiophene can be partially oxidized by hydrogen peroxide without TS-1. However, as thiophene is a highly stable heterocyclic compound, it cannot be efficiently oxidized by hydrogen peroxide alone. This is consistent with the previous study [58] suggesting that the hydrogen peroxide cannot oxidize sulfur atom in the thiophene that possesses the suggesting that the hydrogen peroxide cannot oxidize sulfur atom in the thiophene that possesses the electron density of 5.696. It was suggested that the oxidizing ability of hydrogen peroxide is limited for the sulfur compounds with an electron density between 5.716 and 5.739. Hence, no significant increase in % removal of thiophene can be noticeably achieved when only hydrogen peroxide was added.

However, it can be seen that when TS-1 was used as catalyst, % removal of thiophene was increased as compared to the reaction using hydrogen peroxide alone. This is because the tetrahedral titanium in TS-1 can form a hydroperoxo complex with hydrogen peroxide (Scheme 1). This species can readily promote the oxidative cleavage of thiophene to form sulfate (SO_4^{2-}) and other sulfur-free compounds. These oxidized products are relatively high polar and can be readily transferred to the polar solvent phase as extractants.



Scheme 4 1 Propose reaction pathway for the formation of titanium hydroperoxo complex



Scheme 4 2 Propose reaction pathway for the oxidative extraction of thiophene using hydrogen peroxide and TS-1 as oxidizing agent and catalyst, respectively.

4.2.3 Effect of Solvent

Effect of solvent on the oxidative extraction of thiophene were studied using methanol, acetonitrile, acetic acid and water. The % removal of thiophene obtained under this condition was shown in Figure. 4.6.

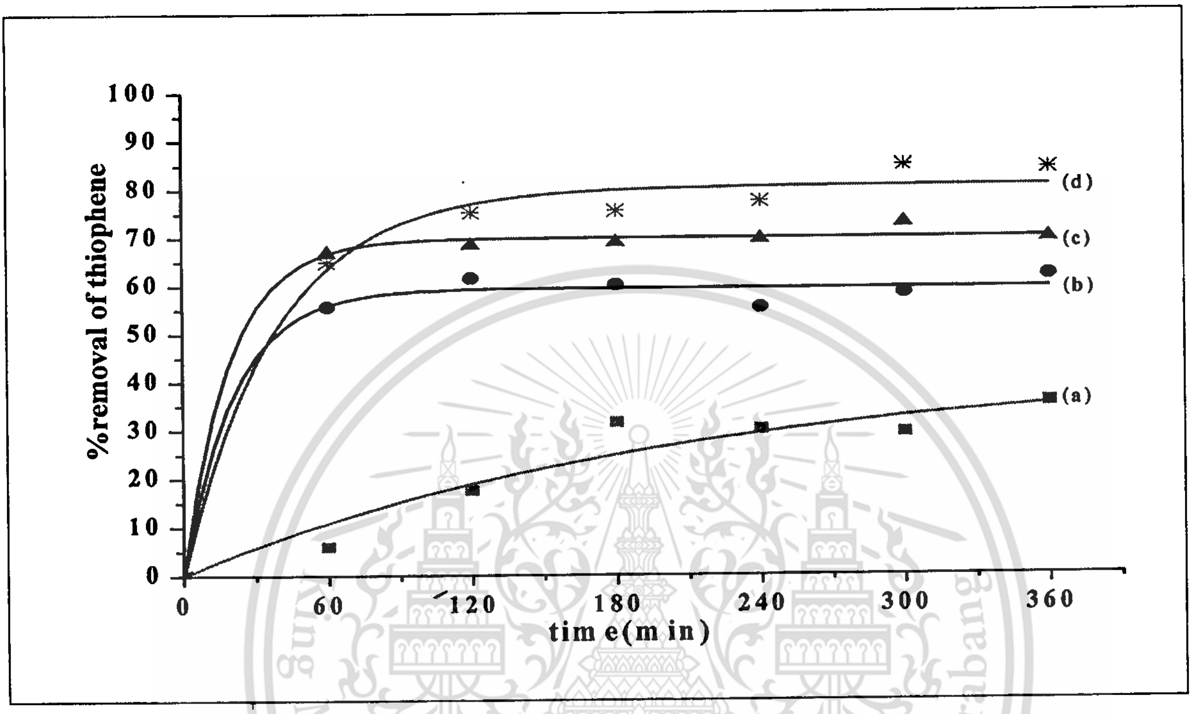
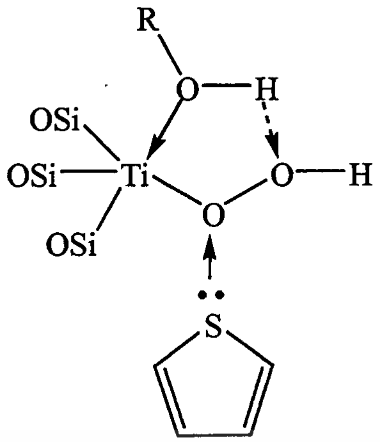


Figure 4.6 The effect of solvent on the % removal of thiophene using (a) water, (b) acetic acid, (c) acetonitrile, (d) methanol as solvents. Reaction condition : temperature; $60^{\circ}C$, (1% TH) n-nonane; 2.5 ml, solvent; 2.5 ml, hydrogen peroxide solution (30% w/w); 4.1 mmol, TS-1; 0.06 g, reaction time; 360 min.

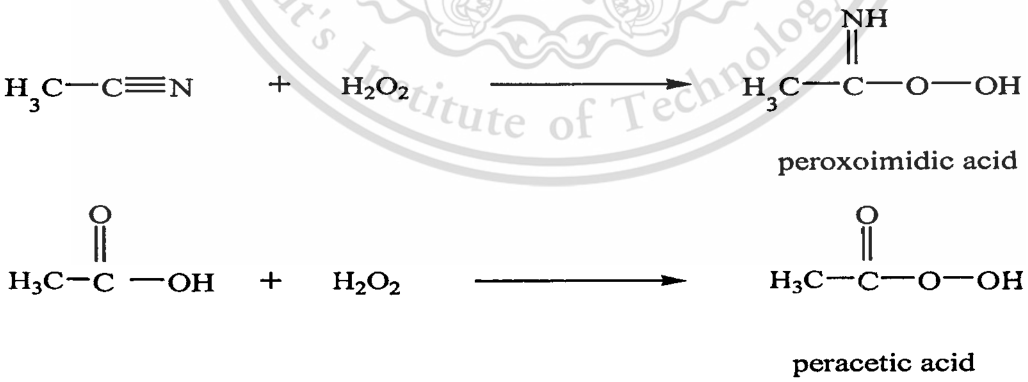
From Figure 4.6, it was found that the % removal of thiophene was decreased in the order of methanol > acetonitrile > acetic acid > water. The fact that methanol shows the best result may well be attributed to a high solubility of the oxidized product in this solution. Since sulfate (SO_4^{2-}) is a highly polar anionic species, the sulfate can be easily dissolved in protic solvent such as methanol and efficiently transferred from the oil phase.

In addition, methanol can facilitate the formation of the active titanium species. Hence, there are more available active sites for thiophene oxidation. It was proposed that [32,34] methanol can coordinate with the partially dislodged titianium site as shown in Scheme 3. The electrophilicity of the peroxydic oxygen atom would be increased which facilitates the nucleophilic attack of the thiophene substrate. This would lead to the higher activity for the oxidation of thiophene.



Scheme 4 3 Proposed active species in oxidation catalyzed by Ti-containing zeolite [33]

In the reaction using acetonitrile and acetic acid as solvents, the % removal of thiophene were relatively moderate. This is presumably explained that the addition of acetonitrile or acetic acid into the reaction of hydrogen peroxide, leads to the formation of peroxoimidic acid (R-C(=NH)-O-O-H) and peracetic acid (CH_3-(CO)-O-O-H) [59], respectively. These species can react with titanium tetrahedral producing peroxo complex in a manner similar to that generated from the hydrogen peroxide (Scheme 1). These species were known to be an active oxidizing agent toward various organic substances [34]. However, the solubility of the oxidized product (SO_4^{2-}) obtained from thiophene in acetonitrile and acetic acid were lower than that in methanol. This is due to the fact that the oxidized product and the methanol are highly polar. Therefore, the % removal of thiophene from the reactions using acetonitrile and acetic acid as solvents were lower than that obtained from the methanol.



Scheme 4 4 Propose reaction pathway for the formation of peroxoimidic acid and peracetic acid using hydrogen peroxide as oxidizing agent

Although the oxidized product (SO_4^{2-}) is fully soluble in water, water is a poor solvent for the oxidation of thiophene. This is because TS-1 catalyst is hydrophobic in character. The TS-1 framework does not interact well with water, resulting in a decrease in the formation of titanium hydroperoxo complex. Accordingly the observed activity in water was relatively low.

4.2.4 Effect of Solvent/Oil Ratio

From the above results, it was found that methanol was the best solvent for the oxidative extraction of thiophene. Hence, it was chosen for the study on the effect of solvent to oil ratio.

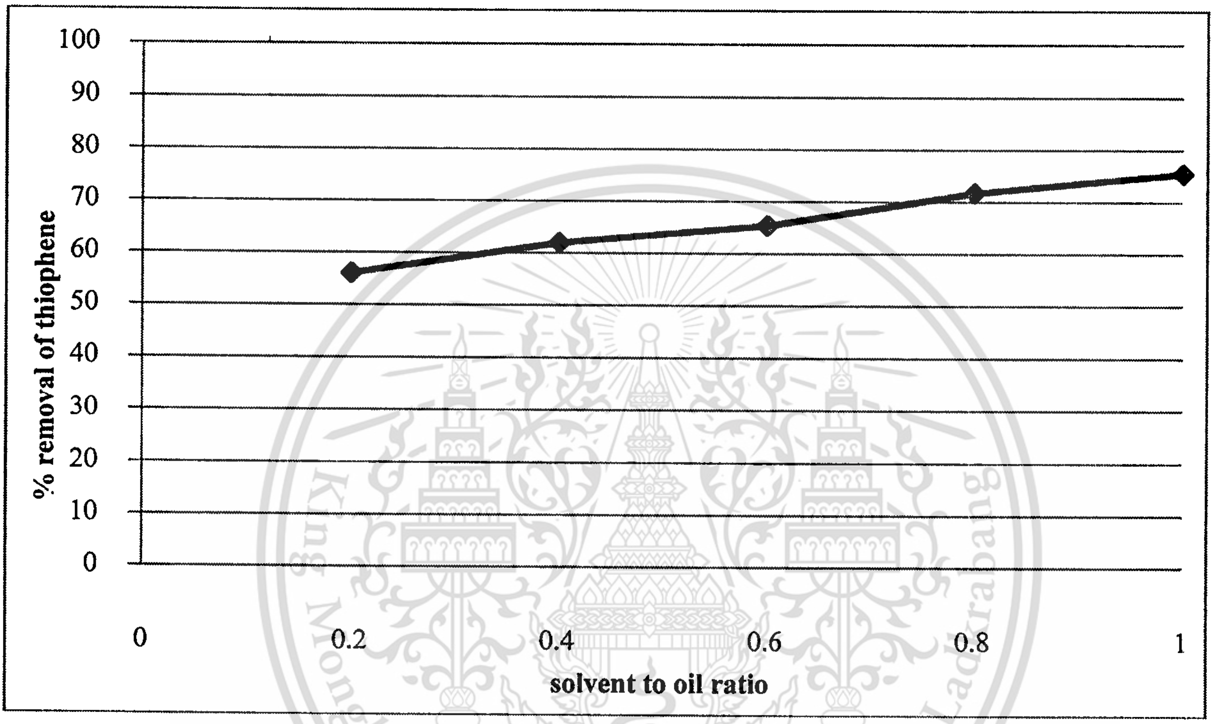


Figure 4.7 The effect of solvent to oil ratio on the % removal of thiophene : Reaction condition temperature; 60°C, hydrogen peroxide solution (30% w/w); 4.1 mmol, TS-1; 0.06 g, reaction time; 180 min.

From Figure 4.7, it can be seen that the % removal of the thiophene was increased with the methanol to oil ratio. This is clearly explained that the higher amount of methanol would increase the homogeneity of the system by reducing size of the oil drop that suspended in the solvent phase (oil-in-methanol). This gives a better dispersion of oil drop in methanol and more sulfate species can be extracted from the oil phase. Hence, a higher % removal of thiophene was observed when methanol to oil ratio is increased. However, the smaller the ratio of methanol to *n*-nonane, the longer the time required for a good separation. A greater volume of solvent means a higher cost of the extraction and recovery process. In addition, the oil phase may be extensively lost with the increased volume of solvent.

According to such drawbacks, the ratio of methanol to nonane = 1 was used for oxidative extraction of thiophene in this study.

4.2.5 Effect of Hydrocarbon Chain length

Diesel is generally consist of hydrocarbon ranging from C_{10}-C_{25}[60]. Therefore, the effect of hydrocarbon chain length on the % removal of thiophene were investigated using *n*-nonane and *n*-dodecane as feed models.

Table 4.2 The effect of hydrocarbon chain length on the % removal of thiophene using *n*-nonane and *n*-dodecane

Feed	**% removal of thiophene**			
	Water	**Acetic acid**	**Acetonitrile**	**Methanol**
extraction (C_9)	5.34	40.20	40.67	44.48
H_2O_2, TS-1 (C_9)	31.5	60.16	68.85	75.48
H_2O_2, TS-1 (C_{12})	36.74	63.61	73.77	76.13

Reaction condition: temperature; 60°C, hydrogen peroxide solution (30% w/w); 4.1 mmol, TS-1; 0.06 g, reaction time; 180 min.

When *n*-dodecane was used as oil feed model (Table 4.2), the % removal of thiophene was slightly higher than that using *n*-nonane as oil feed. This may be because the difference in the polarity between oxidized product and *n*-dodecane was slightly higher than that between the oxidized product and *n*-nonane. Accordingly, it can be presumed that the chain length of hydrocarbon shows only slightly effect on the removal of thiophene. In continuous process, *n*-dodecane was used instead of *n*-nonane, in order of preventing an error due to loss of hydrocarbon phase by evaporation during the continuous feeding.

4.3 Catalytic Testing in Continuous Process

The oxidative extraction of organosulfur compounds in hydrocarbon using hydrogen peroxide as an oxidizing agent is prefered in a batch type reactor. This is because a well mixing of solvent and hydrocarbon can be obtained. However, the mixing of the reaction with three phase system (solid-liquid-liquid) cannot be readily accomplished in a fixed bed continuous process. As the reacting fluid flow through the catalyst bed, the hydrophilic phase (H_2O_2 and methanol) and the hydrophobic phase (thiophene and *n*-dodecane) may not contact with the catalyst at the same active site. This can inhibit the reaction rate since both hydrogen peroxide (hydrophilic phase) and thiophene (hydrophobic phase) must interact with the tetrahedral titanium in the catalyst (solid phase). Hence, a well mixing is essentially required for the continuous process. Although the fluidized bed reactor may be applicable, it consists of complicated system involving multiple reactors and the loss of catalyst may be encountered. Therefore, in this work, the continuous stirred tank reactor (CSTR) with specially designed agitator and feeding flow path was chosen to study the oxidative extraction of thiophene in the continuous process. The schematic diagram of the agitator and feeding flow path for the designed reactor is shown in Figure 4.8.

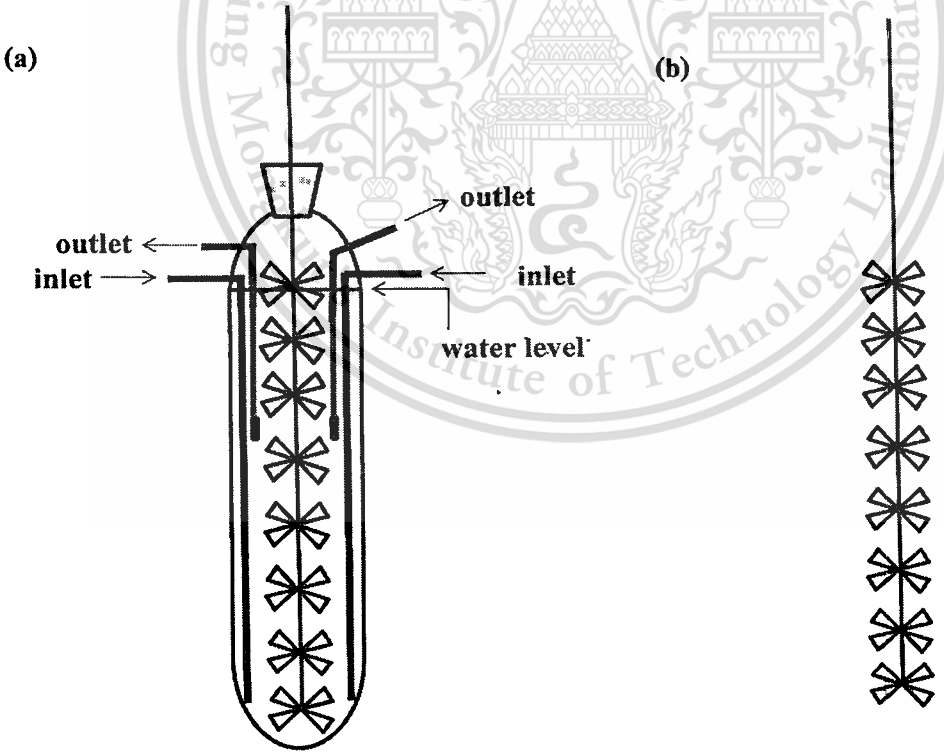


Figure 4.8 Schematic diagram of (a) reactor; (b) agitator

4.3.1 Effect of Catalyst Stability

A long catalytic life time is prefered for the continuous process as it is an essential factor for the industrial application. The % removal of thiophene in continuous process over 780 min on stream is shown in Figure 4.9.

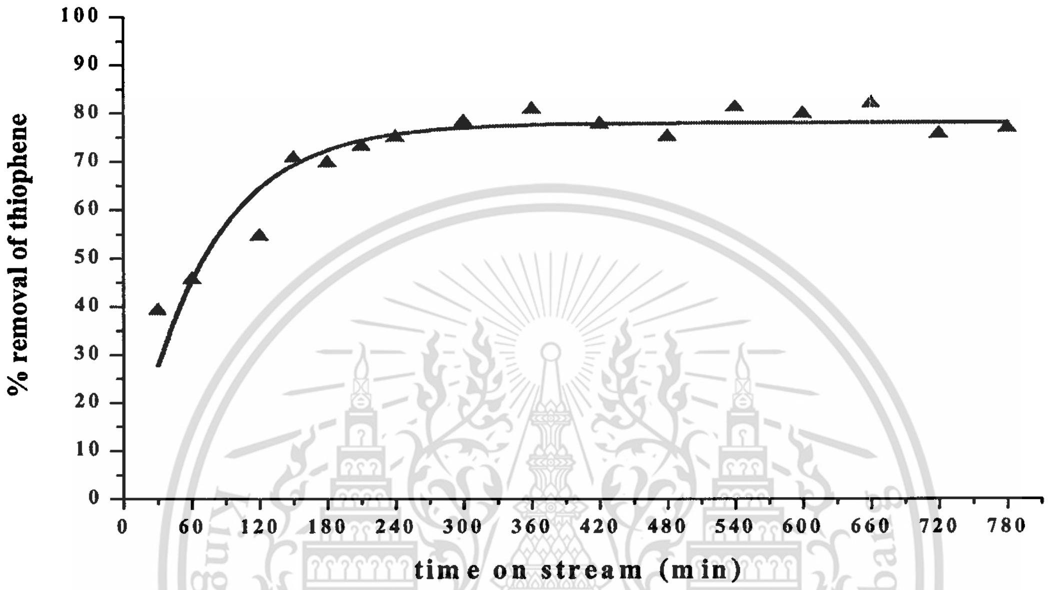


Figure 4.9 The effect of catalytic life time on the % removal of thiophene. Reaction condition: temperature; 60°C, solvent; methanol, H_2O_2; 4.1 mmol, W/F; 775 $g_{catalyst}$ hr mol^{-1}, time on steam 780 min.

Figure 4.9 shows catalytic activity of TS-1 for the oxidative extraction of thiophene. With a stability higher than 780 min on stream, 75% removal of thiophene can be obtained in the reaction of 1% (wt) thiophene in *n*-dodecane. A steady-state was reached within 4 hours on stream. It appears that the catalyst would be active over a long period of time which is preferred for the continuous process. However, it would be much better if the catalyst can be reused without regeneration. Accordingly the catalyst used for 780 min was washed and reused.

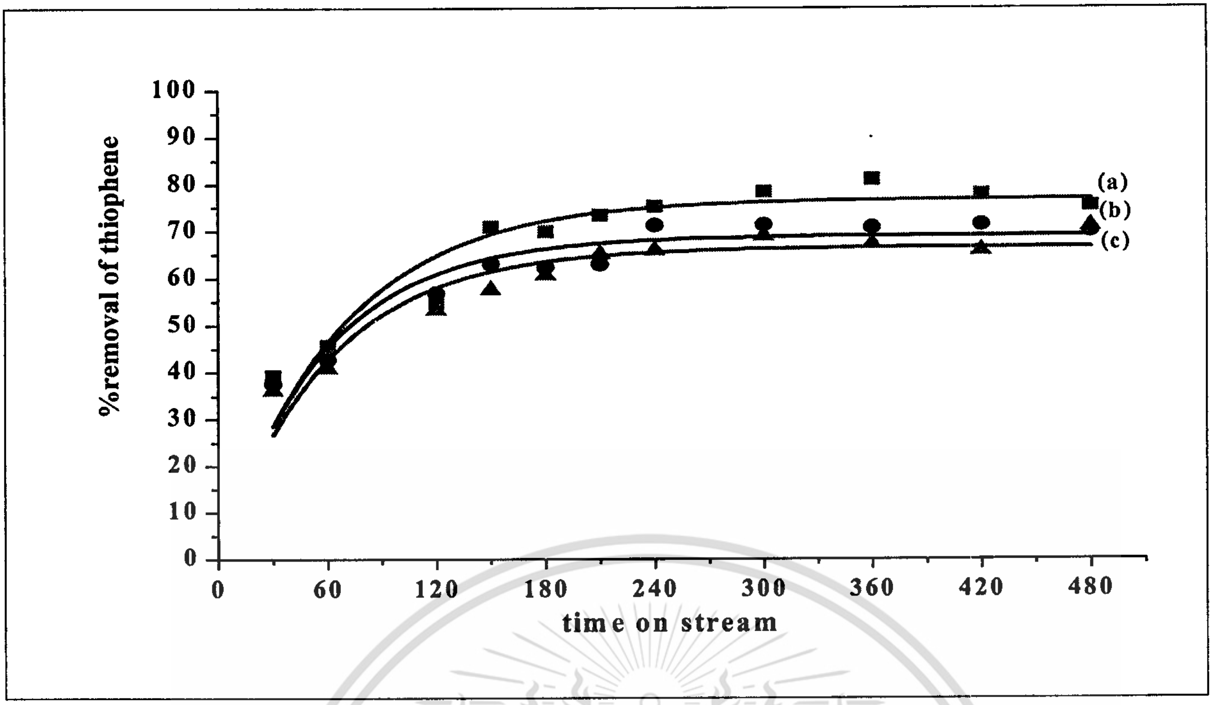


Figure 4.10 % Removal of thiophene from the study of leaching of catalyst using (a) fresh catalyst, (b) reused catalyst, (c) regenerate catalyst. Reaction condition: temperature; 60°C, solvent; methanol, H_2O_2 ;4.1 mmol, W/F; 775 $g_{catalyst}$ hr mol^{-1},time on stream; 480 min.

It can be seen that (Figure 4.10(b)) the reused catalyst is still active and relatively stable. However, the % removal of thiophene was slightly decreased over the reused TS-1 as compared to the fresh TS-1 (Figure 4.10(a)). Although, no deactivation of the catalyst can be observed over the first 780 min on stream, the observed activity over the TS-1 (Figure 4.9) may be derived from the catalyst that partially leached titanium. This is because the catalyst was contacted with high concentration of H_2O_2 and some of the active titanium may be already leached from the catalyst before the catalytic activity can be observed. The previous study [61] suggests that the framework titanium can be leached from the catalyst into solution after contact with H_2O_2. However, the catalyst deactivation may be also caused by the deposits retained on the catalyst after used for a long period of time (780 min). In order to verify the cause of the decreased activity, the reused TS-1 was regenerated by calcining at 550°C for 6 hours. It was found from Figure. 4.10 (c) that, there was no significant change in the % removal of thiophene when using regenerated TS-1 as compared to the reused catalyst. Therefore, the decrease in % removal of thiophene due to the deposition on the catalyst was excluded. On the other hand, the reduction of % removal of thiophene would be influenced mainly by the leaching of titanium framework into the liquid mixture after using for a long period of time. In support with this view, the titanium content of the regenerated catalyst was decreased (Si/Ti = 47), as compared to that of the fresh one (Si/Ti = 32). It should be noted that the titanium content in the regenerated and the reused catalysts were presumably similar.

4.3.2 Effect of Calcination Temperature

From the previous section, it can be seen that small amounts of titanium were leached from the catalyst framework. This depends on the stability of titanium active site which may well be improved by increasing the calcination temperature. The TS-1 catalyst calcined at 575°C was then tested for oxidative extraction.

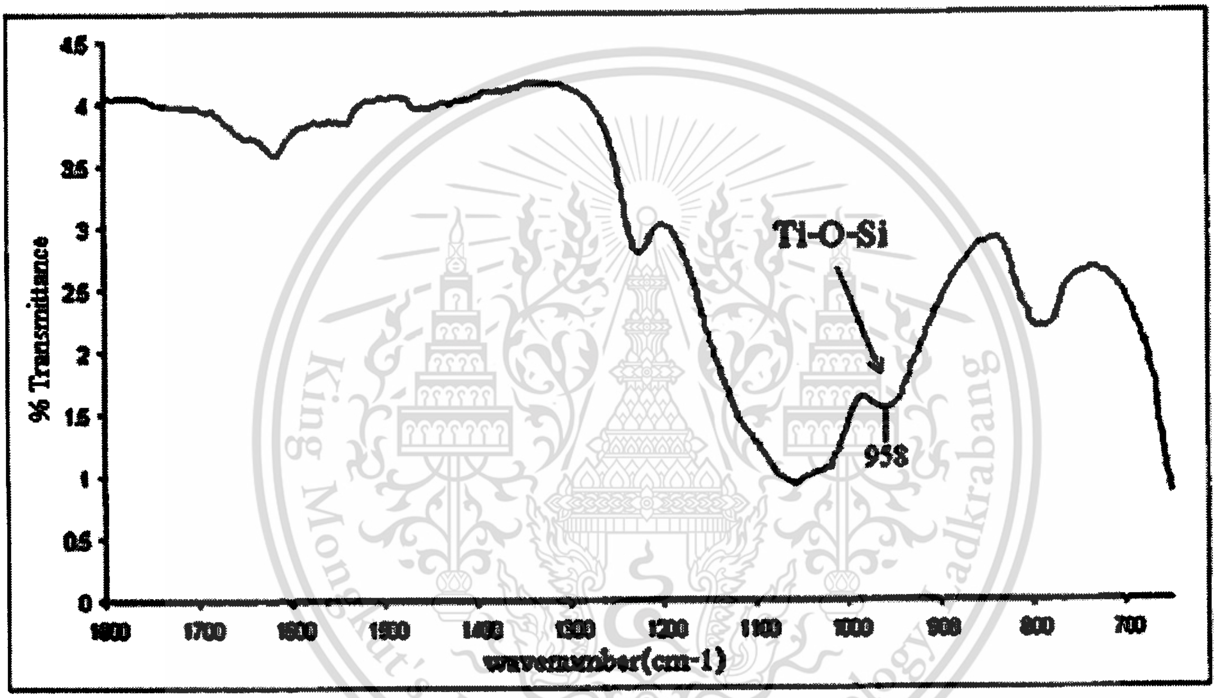


Figure 4.11 Fourier transformed IR spectra of TS-1 575°C calcination after acid treatment

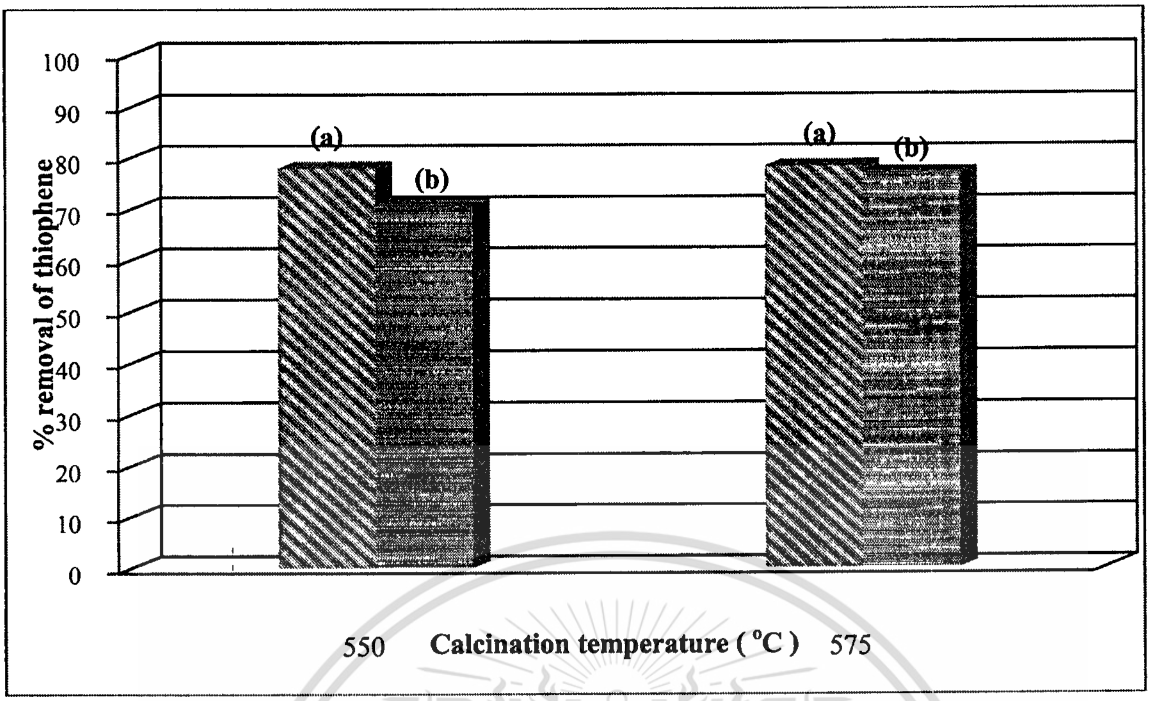


Figure 4.12 % Removal of thiophene from the study of calcination temperature using (a) fresh and (b) reused catalyst. Reaction condition: reaction temperature; 60°C, solvent; methanol, H_2O_2; 4.1 mmol, W/F; 775 $g_{catalyst}$ hr mol^{-1}, reaction time; 480 min.

The FT-IR of the catalyst calcined at 575°C (Figure 4.11) shows an absorption band at about 960 cm^{-1} indicating that the framework titanium (Si-O-Ti) of this catalyst was retained. Also, it can be seen for Figure 4.12 that the catalyst calcined at 575°C gives the same activity as that calcined at 550°C. This suggests that the increased calcination temperature up to 575°C does not give a significant change in TS-1 structure and activity. In addition, (Fig.4.12) there was no significant change in % removal of thiophene between the fresh (Si/Ti = 31) and the reused (Si/Ti = 35) catalyst calcined at 575°C. This indicates that the leaching of titanium active site was not readily promoted over the catalyst calcined at 575°C, as confirmed by XRF. In addition, the intensity of peak at 2θ = 7.89 and 8.84 was increased (Figure 4.13), indicates that the crystallinity of TS-1 is increased when calcined at 575°C. The activity can be reserved when the catalyst was used over a long period of time. It can be concluded at this state that the stability of tetrahedral titanium active site (Scheme 4.1) can be improved by increasing the calcination temperature up to 575°C.

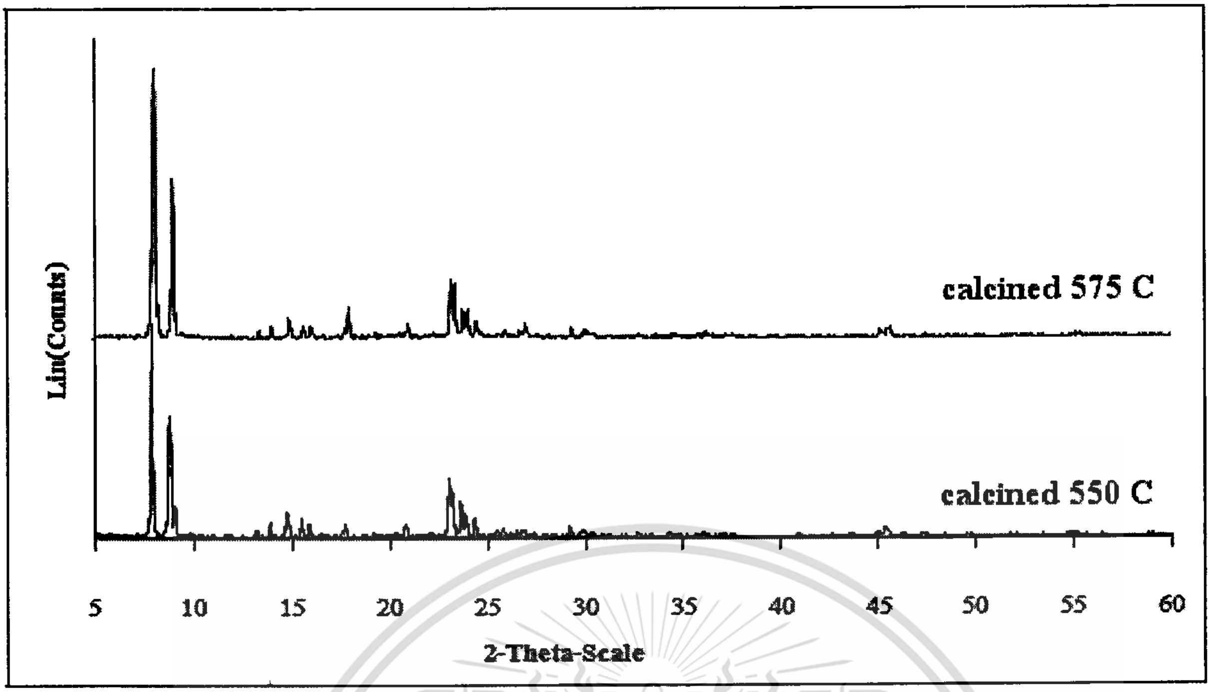


Figure 4.13 X-ray diffraction pattern of TS-1 calcined 575°C

4.3.3 Effect of Catalyst Content

The % removal of thiophene from the reaction without catalyst and using TS-1 1.0 and 1.8 gram in continuous process are shown in Figure 4.14.

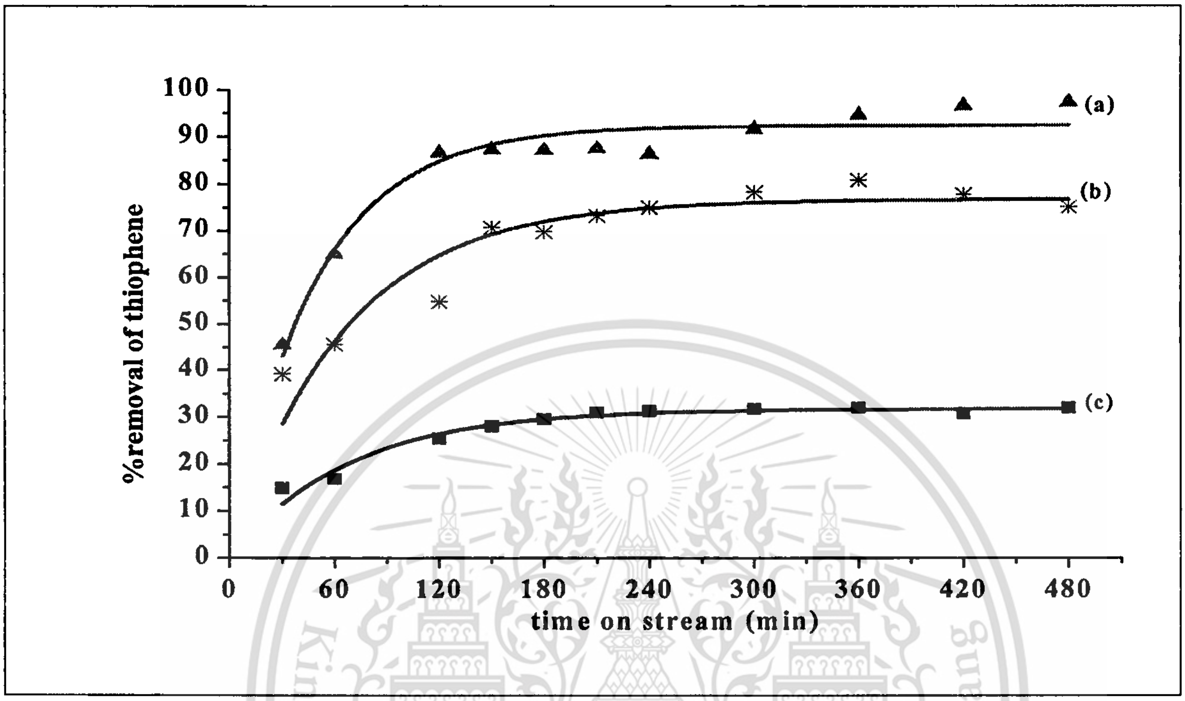


Figure 4.14 The % removal of thiophene from the study of content of TS-1 using (a) 1.8 g, (b) 1.0 g and (c) without catalyst. Reaction condition: temperature; 60°C, solvent; methanol, H_2O_2; 4.1 mmol, reaction time; 480 min, feed rate; 14.22 ml hrs^{-1}.

From Figure 4.14, it can be seen that a relatively higher % removal of thiophene was obtained when the amount of TS-1 was increased. This is obviously shown that, for a certain retention volume, when the amount of catalyst was increased, more titanium active sites were available. The thiophene can be readily oxidized and removed from the oil phase. It was found that the % removal of thiophene is increased to 95 % using 1.8 gram catalyst.

4.3.4 Effect of Feed Rate

From previous section, it can be seen that when the amounts of catalyst was increased, a higher % removal of thiophene was obtained. The % removal of thiophene may also be improved by reducing feed rate. The effect of feed rate was tested using 10, 14, 25 ml hrs^{-1} as shown in Figure 4.15.

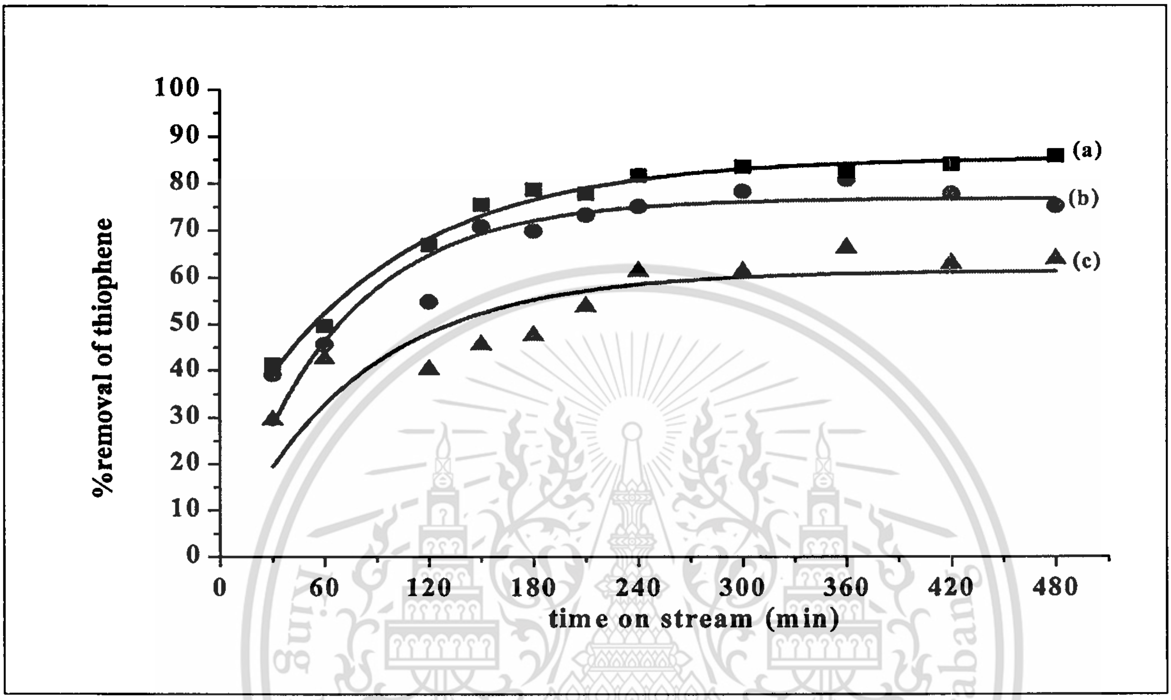


Figure 4.15. The % removal of thiophene from the study of feed rate using (a) 10 ml hrs^{-1}, (b) 14 ml hrs^{-1} and (c) 25 ml hrs^{-1}. Reaction condition: reaction temperature; 60°C, solvent; methanol, H_2O_2; 4.1 mmol, reaction time; 480 min.

When the feed rate was reduced to 10 ml hrs^{-1}, the % removal of thiophene was enhanced to about 85%. As the feed rate was decreased (Figure 4.15), the opportunity for thiophene to be in contact with the catalyst was increased (high contact time) and the oxidized product can be removed to oil phase. In addition, it would take a relatively longer to fill the retention volume of the reactor when feed rate is reduced. Consequently, a steady state for the reaction using lower feed rate was relatively delayed.

4.3.5 Effect of Feed Concentration

Effect of feed concentration on the % removal of thiophene were investigated by the reaction using 1 and 3 % wt thiophene, as shown in Figure 4.16.

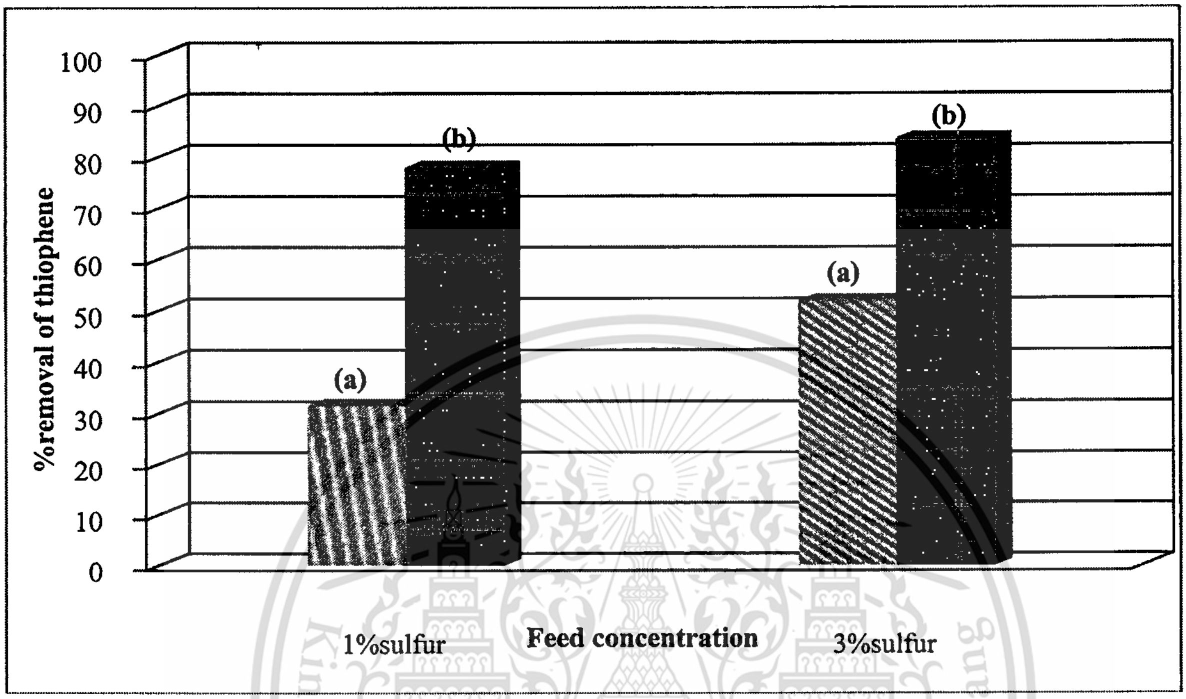


Figure 4.16 % Removal of thiophene from the study of concentration of thiophene using (a) extraction and (b) TS-1. Reaction condition: reaction temperature; 60°C, solvent; methanol, H_2O_2; 4.1 mmol, reaction time; 480 min, feed rate; 14.22 ml hr^{-1}.

It can be seen that the % removal of thiophene was increased with the thiophene concentration in feed (Figure 4.16). This can be explained that the increase in the thiophene concentration can increase the thiophene adsorption on the catalyst surface. Consequently, the rate of the thiophene oxidation was increased leading to a higher % removal as observed. However, the increase in the % removal of thiophene is not caused only by the thiophene oxidation but also by the solvent extraction. When higher concentrate on of thiophene feed (3% wt) was used, the % removal of thiophene by extraction was increased. The amount of thiophene that can be removed by oxidation process, was also increased. Although, the % removal of thiophene appears to increase only *ca.* 5 %, the amount of thiophene actually removed for 3% thiophene concentration is much higher than that from the reaction with 1 % thiophene feed. This is due to the higher initial concentration of thiophene leading to a higher rate of oxidation. The observed % removal is the result of fractional conversion which cannot clearly determine the actual activity when the initial concentration is different.

CHAPTER 5

CONCLUSION AND SUGGESTION

5.1 Conclusion

The removal of thiophene from a model of sulfur contained diesel can be achieved by both (i) direct solvent extraction and (ii) oxidation of thiophene followed by solvent extraction of the oxidized products (oxidative extraction). 30-45 % Thiophene can be homogeneously transferred to the solvent phase (i) and additional 40% removal is derived from the oxidative extraction (ii) as shown in figure 4.5 and table 4.2. In fact, thiophene was highly stable organosulfur compound. It cannot be efficiently oxidized by hydrogen peroxide alone. However, TS-1 was an active catalyst for the oxidation of thiophene using hydrogen peroxide as oxidizing agent under mild condition (60°C, atmospheric pressure). The oxidized product can be easily transferred to polar solvent by solvent extraction. Methanol was found to enhance the oxidative extraction of thiophene providing up to 75% removal. Methanol can facilitate the formation of the active titanium species, resulting in a more available active sites for thiophene oxidation. Furthermore, the oxidized products can be easily soluble in methanol. The % removal of thiophene using acetonitrile and acetic acid were 68 and 60%, respectively. These solvents can readily promote the formation of peroxoimidic acid (R-C-(=NH)-O-O-H) and peracetic acid (CH_3-(CO)-O-O-H), respectively. Such intermediates were good oxidizing agent for various organic substances. The activity using water was relatively lower, as compared to methanol, acetonitrile and acetic acid. This is because TS-1 is hydrophobic. Hence, the interaction between TS-1 framework and water is weak, resulting in a decreased formation of titanium hydroperoxo complex. The catalytic activity of TS-1 was increased with the solvent to oil ratio. The better dispersion of oil drop in solvent would increased by increasing in a amount of solvent. Accordingly, the oxidized products can be easily extracted to the solvent phase.

For continuous process, the well mixing of solvent, hydrocarbon and the catalyst were essentially required for an effective removal of thiophene. The continuous stirred tank reactor (CSTR) with specially designed agitator and feeding flow path can be successfully used for this reaction. The well mixing can enhance an opportunity of thiophene to react with the active sites. The higher % removal of thiophene can be achieved by increasing the contact time either by reducing the feed flow rate or increasing the catalyst content. With high contact time, thiophene have a higher possibility to react with titanium active sites and a higher % removal of thiophene can be obtained. The increased concentration of thiophene feed (3% wt) in the feed increases the % removal up to 84%. The higher thiophene concentration would increase thiophene adsorption on the catalyst surface. Hence, the rate of thiophene oxidation was increased. Over

12 hours on stream, the catalyst remains active as seen from a steady % removal. However, the leaching of titanium active site was observed in the reaction using catalyst calcined at 550°C. Titanium species can be partially dissolved into the reaction mixture during the reaction. The leaching of titanium active sites is diminished when the calcining temperature is raised to 575°C. Higher stability of titanium active sites can be obtained by treating TS-1 at high temperature before using as catalyst.

5.2 Suggestion for future studies

Considering the removal of thiophene in a continuous process, it is seen that the higher removal of thiophene from the oil feed using CSTR reactor, specially designed agitator and feeding flow path can be achieved. Therefore, the removal of real diesel using this process could be investigated.

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APPENDIXES

APPENDIX A

X-ray Diffraction Patterns of TS-1

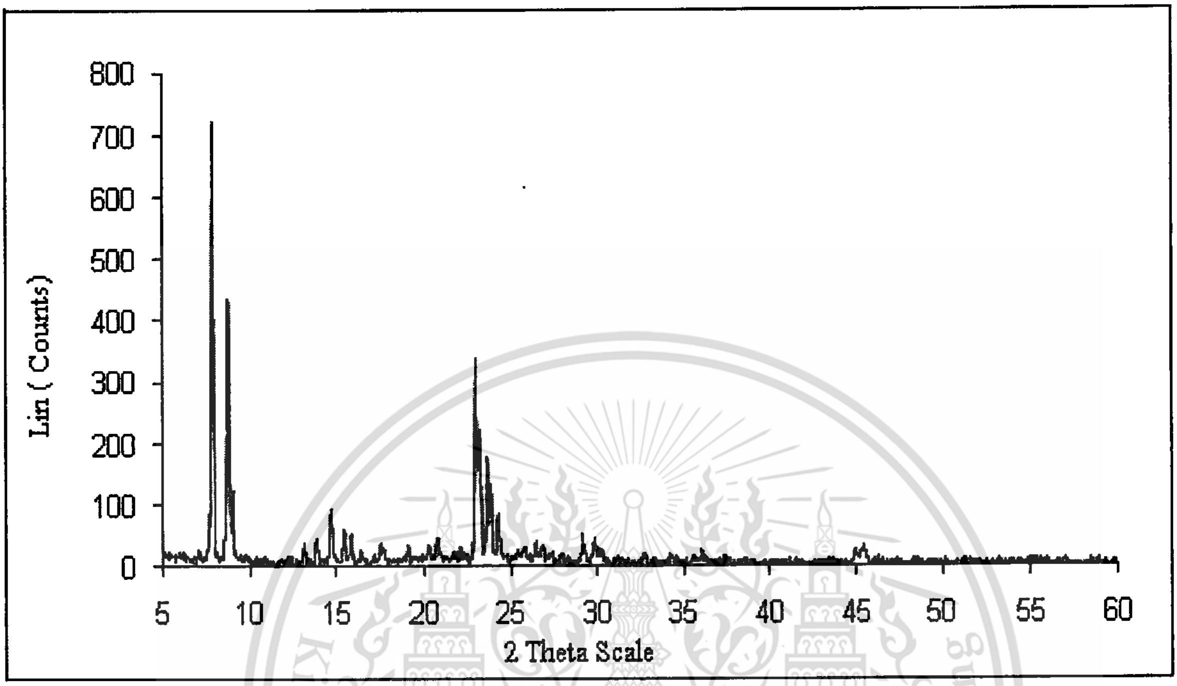


Figure A.1 X-ray diffraction pattern of TS-1 before acid treatment

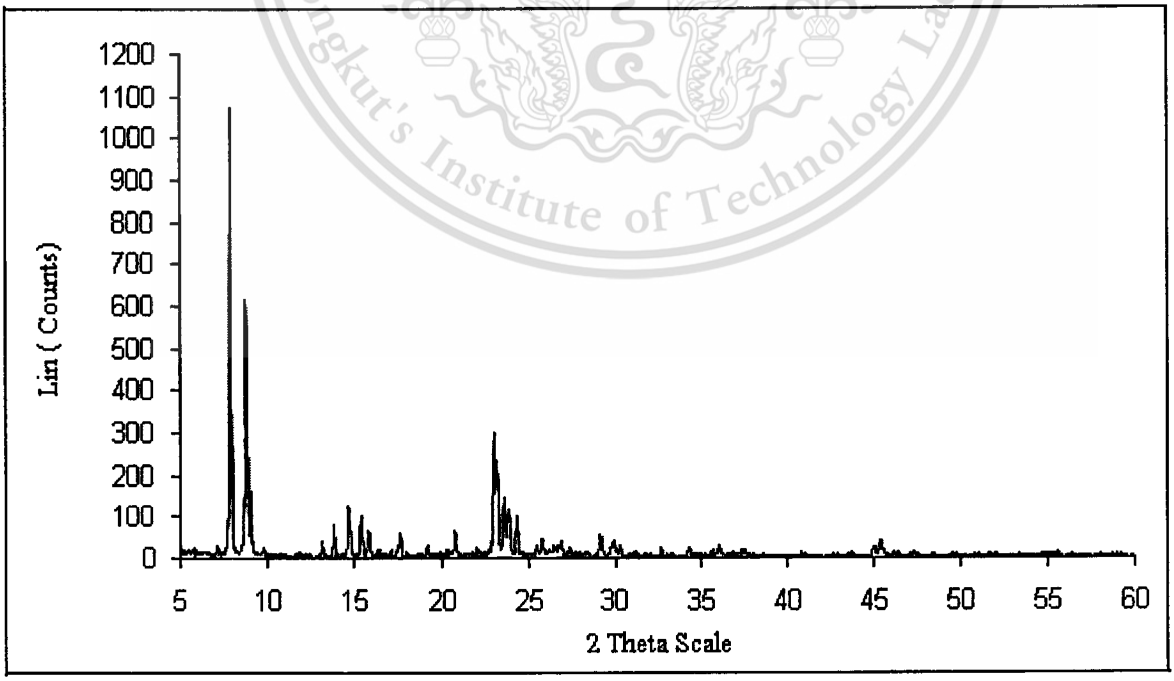


Figure A.2 X-ray diffraction pattern of TS-1 after acid treatment

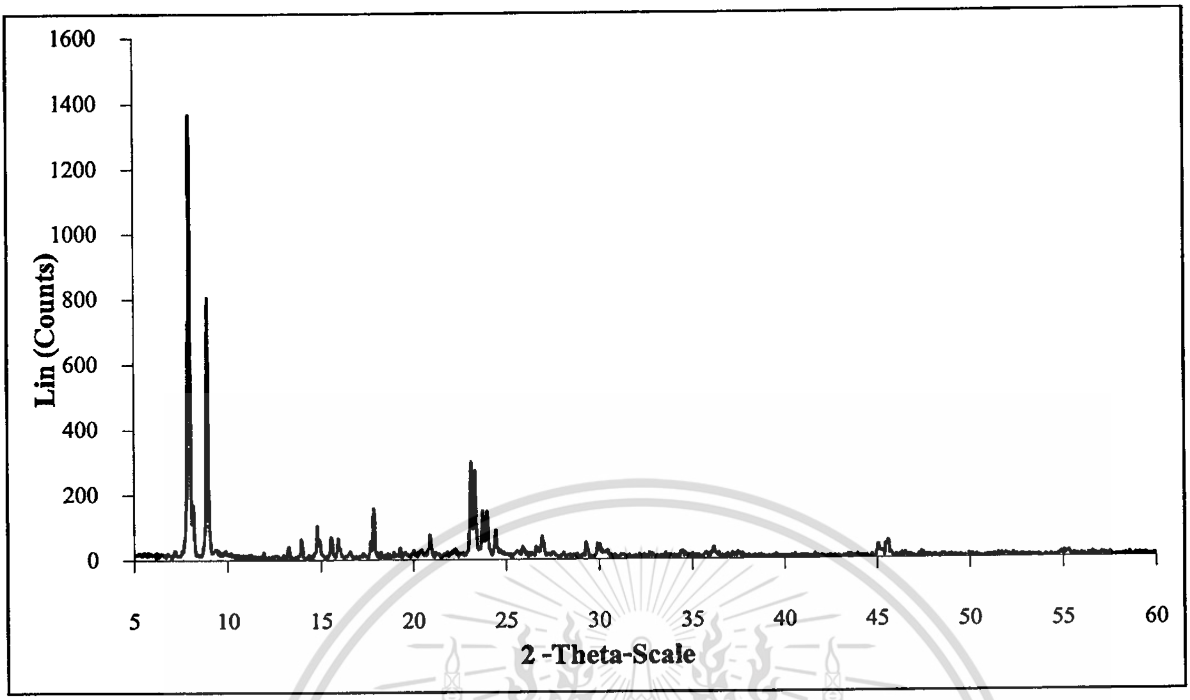


Figure A.3 X-ray diffraction pattern of TS-1 after calcined 575 °C

APPENDIX B

Scanning Electron Micrograph

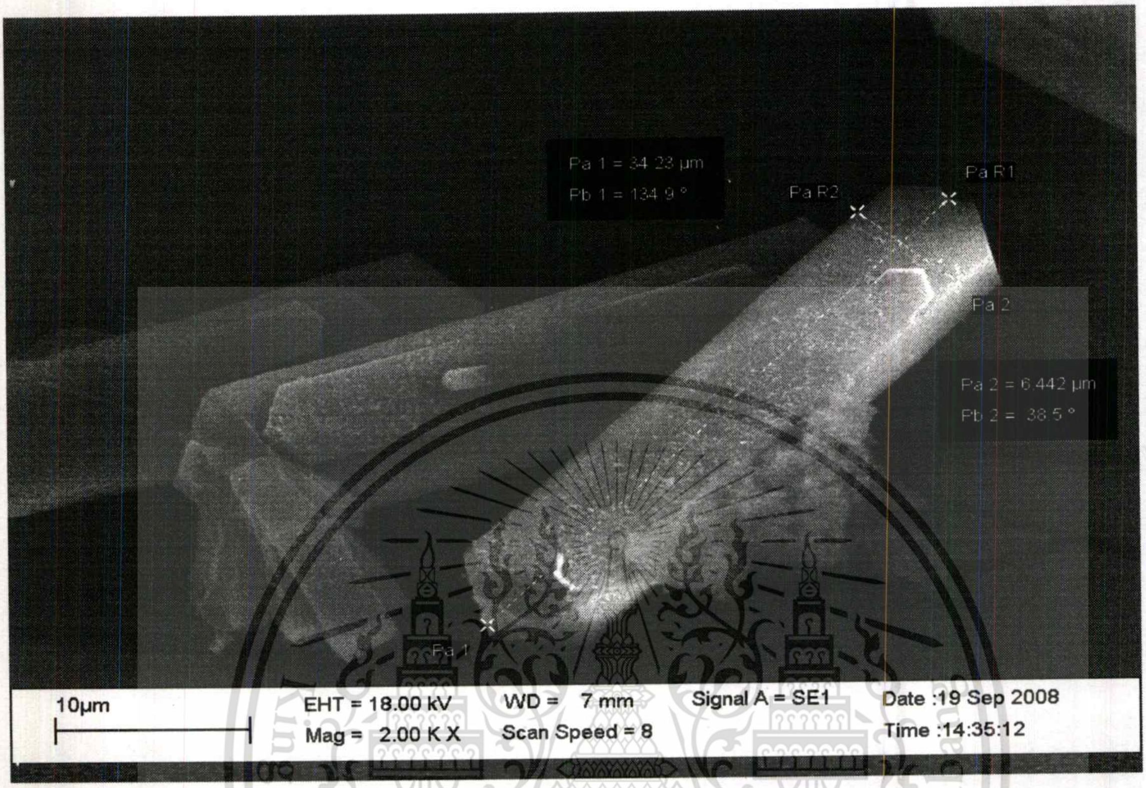


Figure B.1 Scanning electron micrograph of TS-1 before calcinations and acid treatment

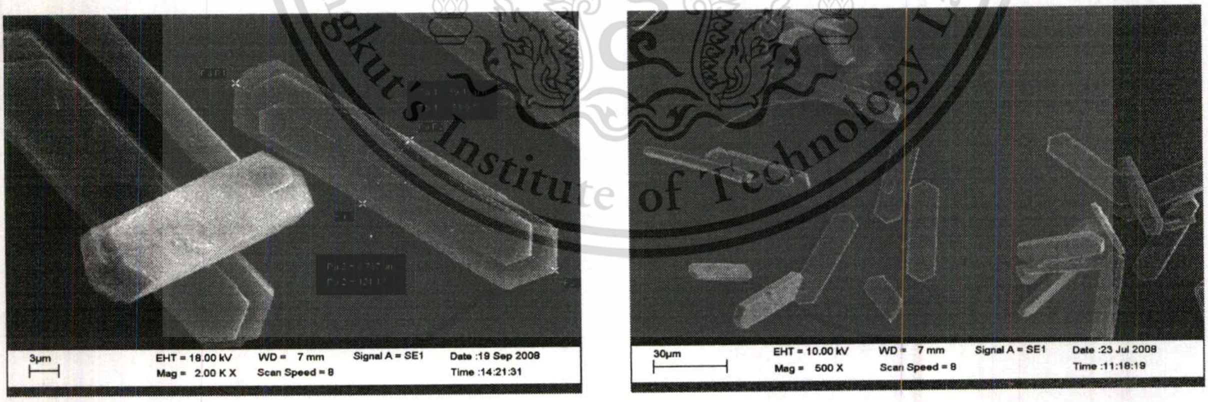
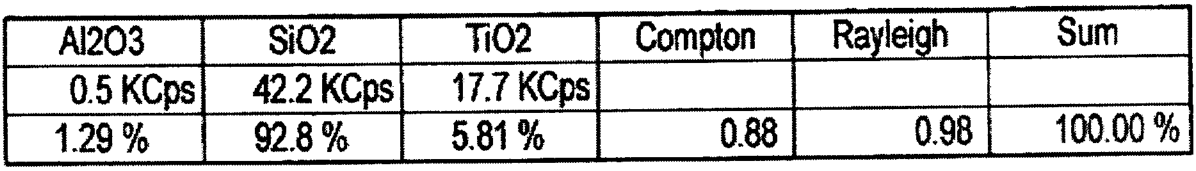


Figure B.2 Scanning electron micrograph of TS-1 after calcinations and acid treatment

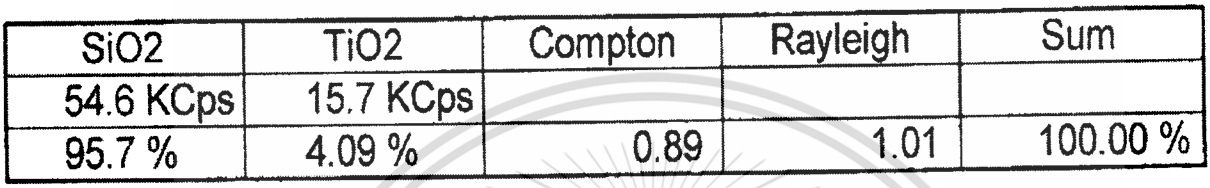
APPENDIX C

X-ray Fluorescence of TS-1



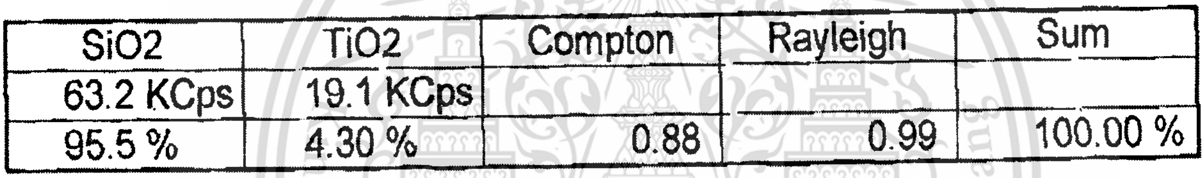
Al2O3	SiO2	TiO2	Compton	Rayleigh	Sum
0.5 KCps	42.2 KCps	17.7 KCps			
1.29 %	92.8 %	5.81 %	0.88	0.98	100.00 %

Figure C.1 Percentage of SiO_2 and TiO_2 of TS-1 before acid treatment



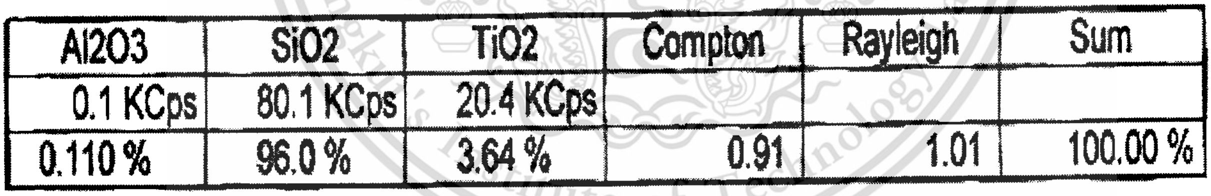
SiO2	TiO2	Compton	Rayleigh	Sum
54.6 KCps	15.7 KCps			
95.7 %	4.09 %	0.89	1.01	100.00 %

Figure C.2 Percentage of SiO_2 and TiO_2 of TS-1 after acid treatment was calcined temperature at 550°C



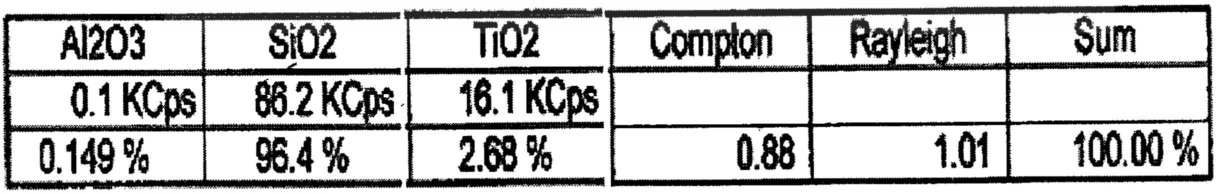
SiO2	TiO2	Compton	Rayleigh	Sum
63.2 KCps	19.1 KCps			
95.5 %	4.30 %	0.88	0.99	100.00 %

Figure C.3 Percentage of SiO_2 and TiO_2 of TS-1 after acid treatment was calcined temperature at 575°C



Al2O3	SiO2	TiO2	Compton	Rayleigh	Sum
0.1 KCps	80.1 KCps	20.4 KCps			
0.110 %	96.0 %	3.64 %	0.91	1.01	100.00 %

Figure C.4 Percentage of SiO_2 and TiO_2 of TS-1 575°C calcinations after using in reaction

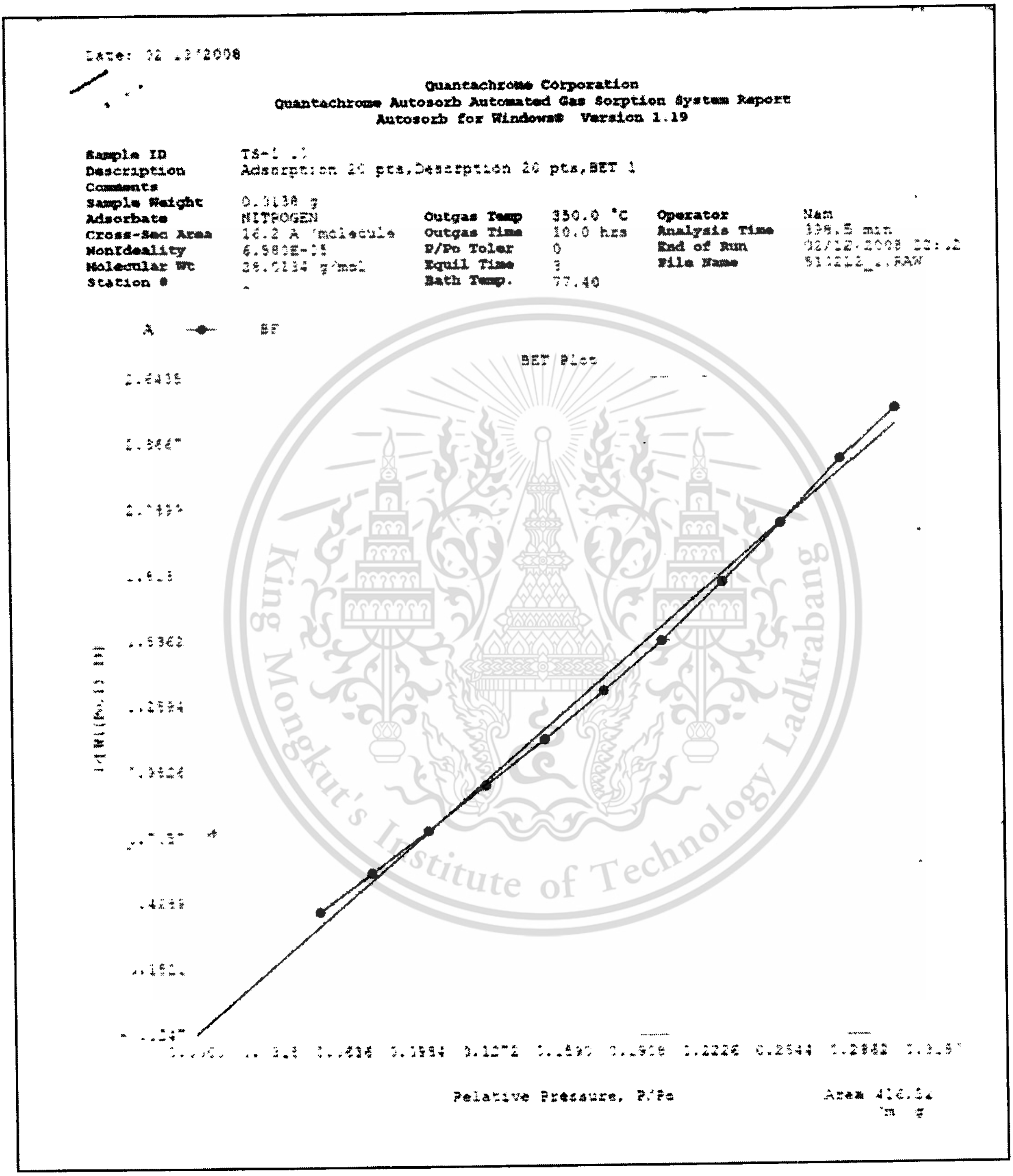


Al2O3	SiO2	TiO2	Compton	Rayleigh	Sum
0.1 KCps	86.2 KCps	16.1 KCps			
0.149 %	96.4 %	2.68 %	0.88	1.01	100.00 %

Figure C.5 Percentage of SiO_2 and TiO_2 of TS-1 550°C calcinations after regenerated

APPENDIX D

Surface Area and BET Plot from Gas Adsorption Analyzer

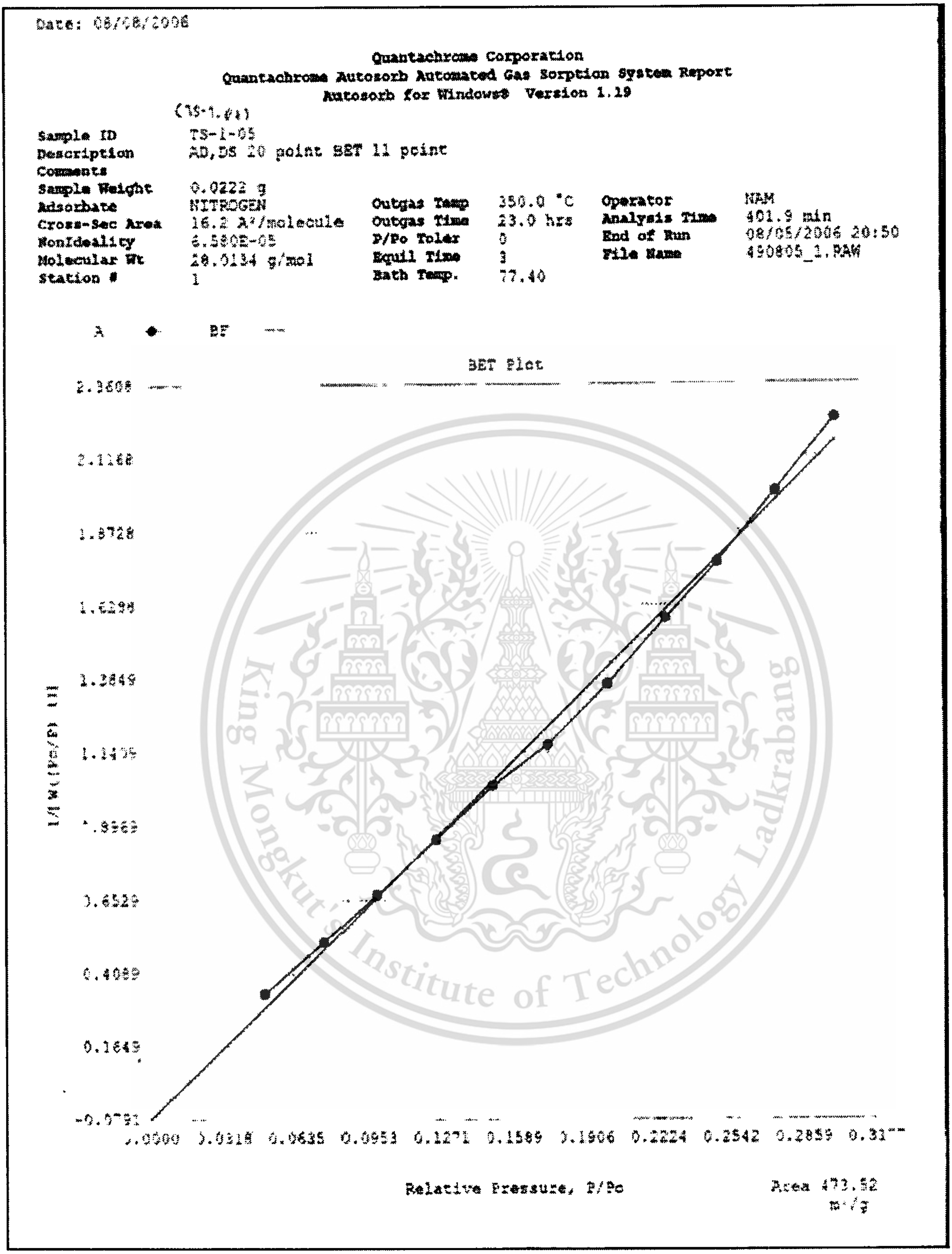


```
Date: 02 12 2008

                    Quantachrome Corporation
     Quantachrome Autosorb Automated Gas Sorption System Report
              Autosorb for Windows®  Version 1.19

Sample ID         TS-1 .1
Description       Adsorption 20 pts,Desorption 20 pts,BET 1
Comments
Sample Weight     0.0130 g
Adsorbate         NITROGEN            Outgas Temp    350.0 °C    Operator          Nam
Cross-Sec Area    16.2 A /molecule    Outgas Time    10.0 hrs    Analysis Time     398.5 min
NonIdeality       6.580E-05           P/Po Toler     0           End of Run        02/12/2008 20:12
Molecular Wt      28.0134 g/mol       Equil Time     3           File Name         S11212_1.RAW
Station #         1                   Bath Temp.     77.40
```

Figure D.1 BET plot of TS-1 before acid treatment



```
Date: 08/08/2006

                    Quantachrome Corporation
     Quantachrome Autosorb Automated Gas Sorption System Report
               Autosorb for Windows®  Version 1.19
            (TS-1.01)
Sample ID       TS-1-05
Description     AD,DS 20 point BET 11 point
Comments
Sample Weight   0.0222 g
Adsorbate       NITROGEN           Outgas Temp   350.0 °C   Operator        NAM
Cross-Sec Area  16.2 Å²/molecule   Outgas Time   23.0 hrs   Analysis Time   401.9 min
NonIdeality     6.580E-05          P/Po Toler    0          End of Run      08/05/2006 20:50
Molecular Wt    28.0134 g/mol      Equil Time    3          File Name       490805_1.RAW
Station #       1                  Bath Temp.    77.40
```

Area 473.52 m²/g

Figure D.2 BET plot of TS-1 after acid treatment

APPENDIX E

The Fourier Infrared Spectrum

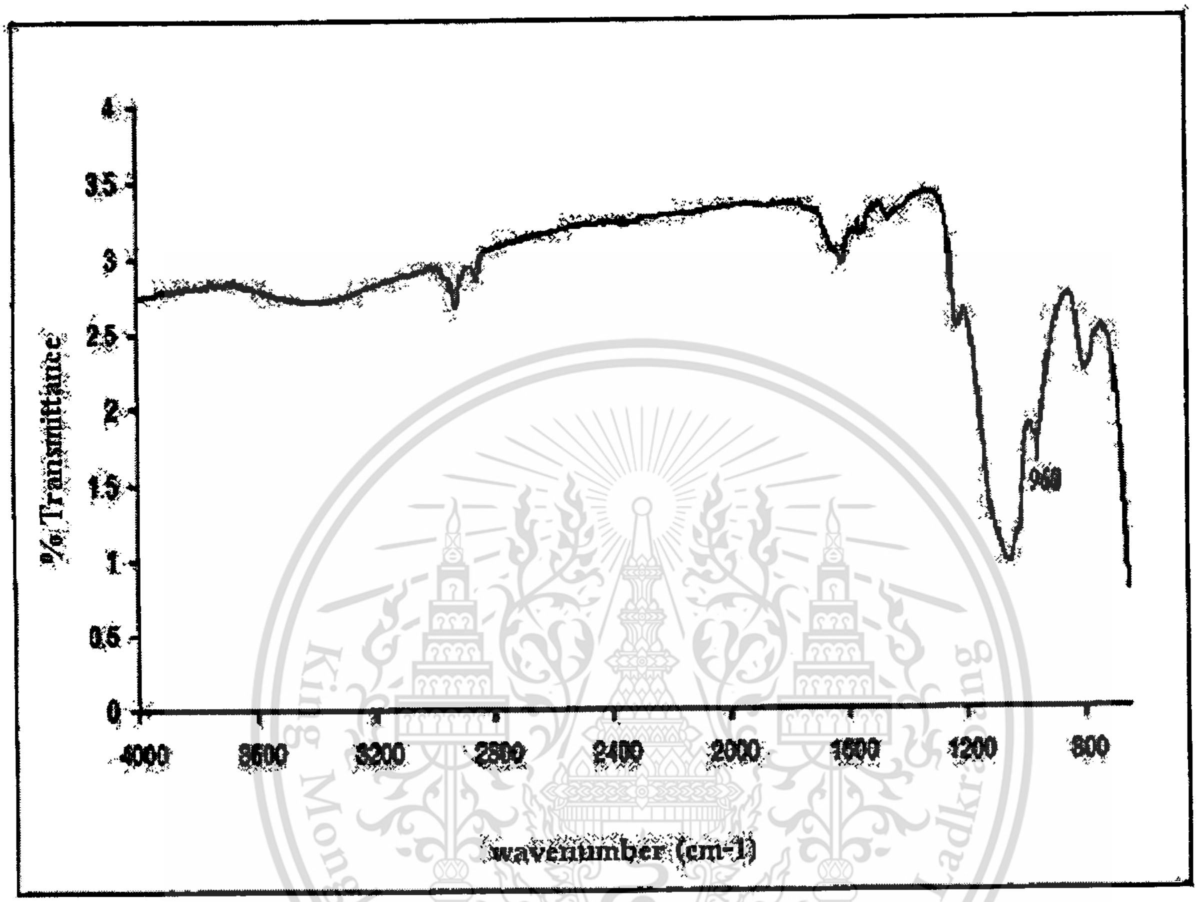


Figure E.1 Fourier IR spectrum of TS-1 before acid treatment

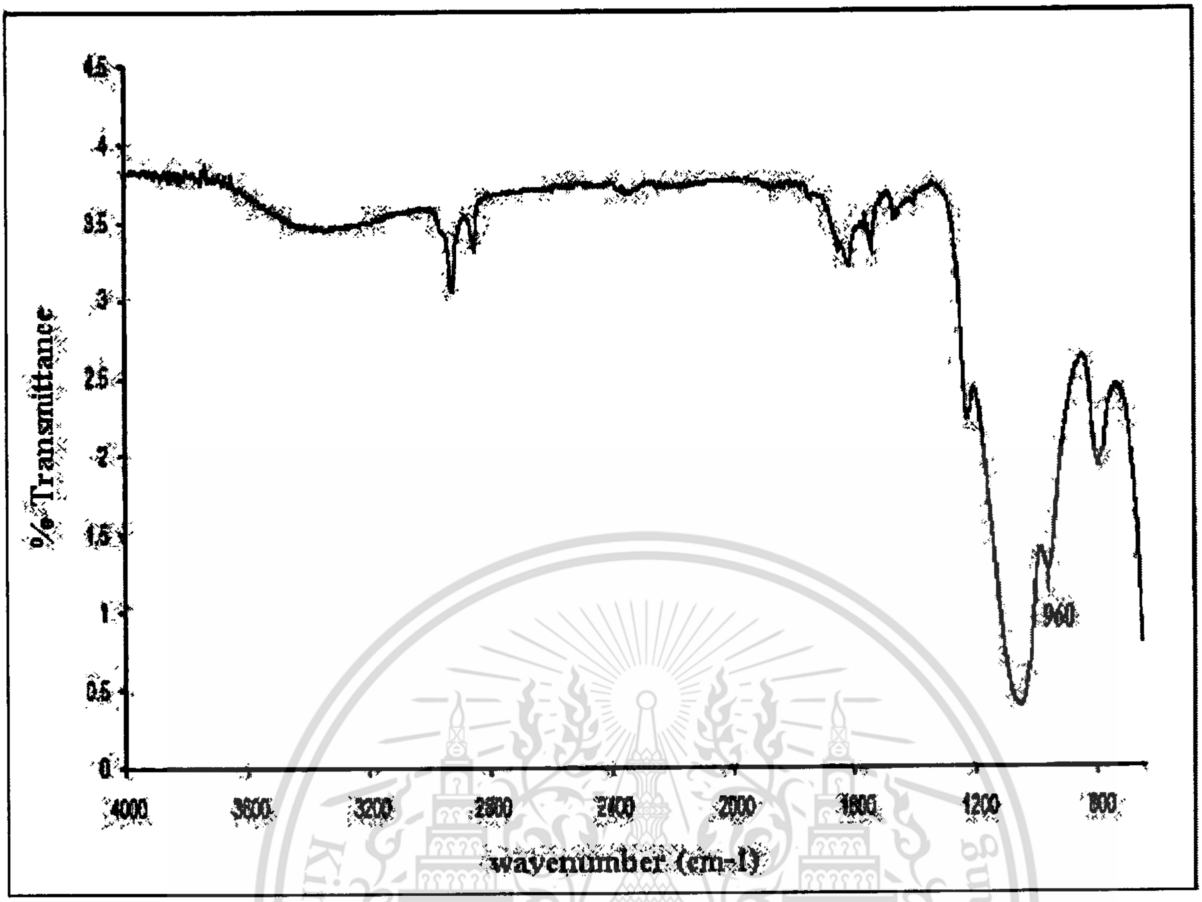


Figure E.2 Fourier IR spectrum of TS-1 after acid treatment

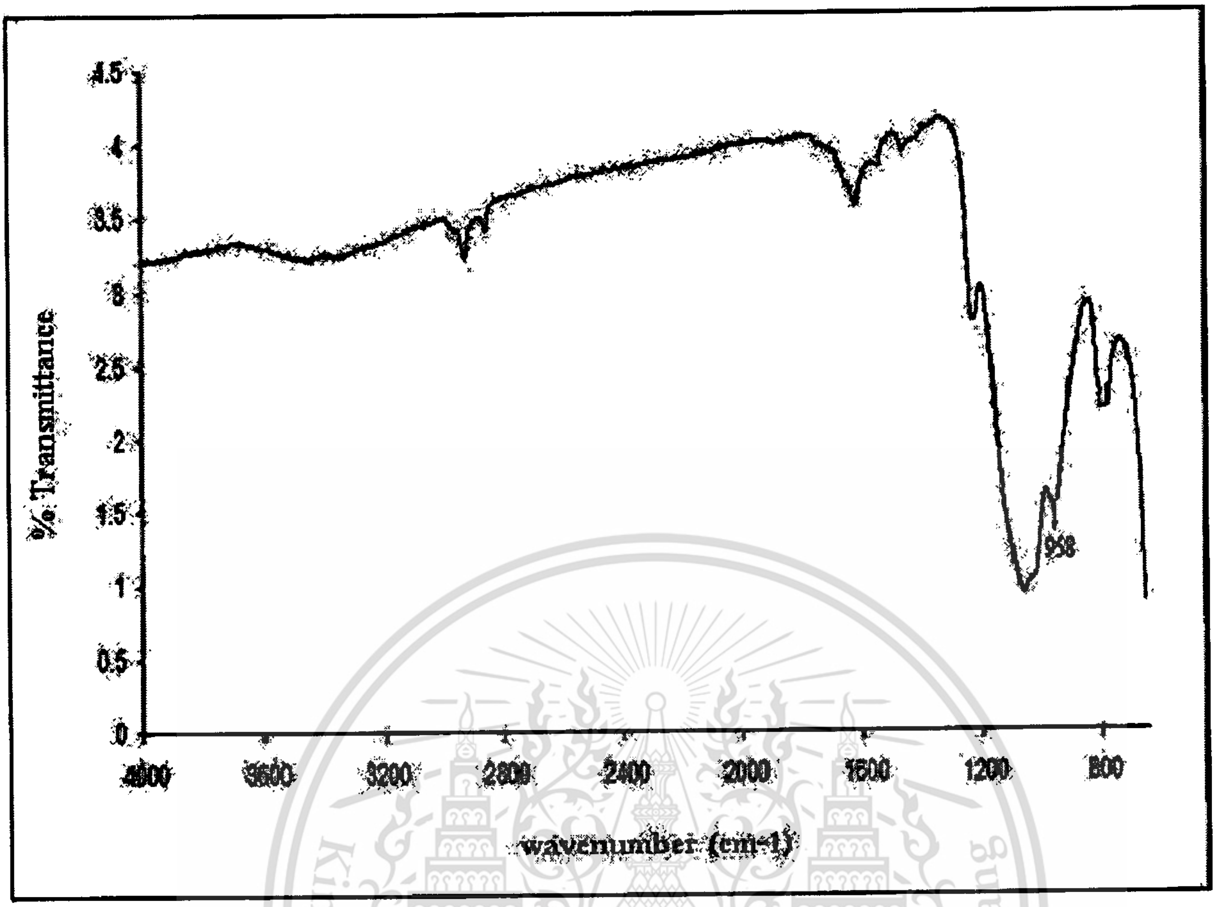


Figure E.3 Fourier IR spectrum of TS-1 575°C calcination after acid treatment

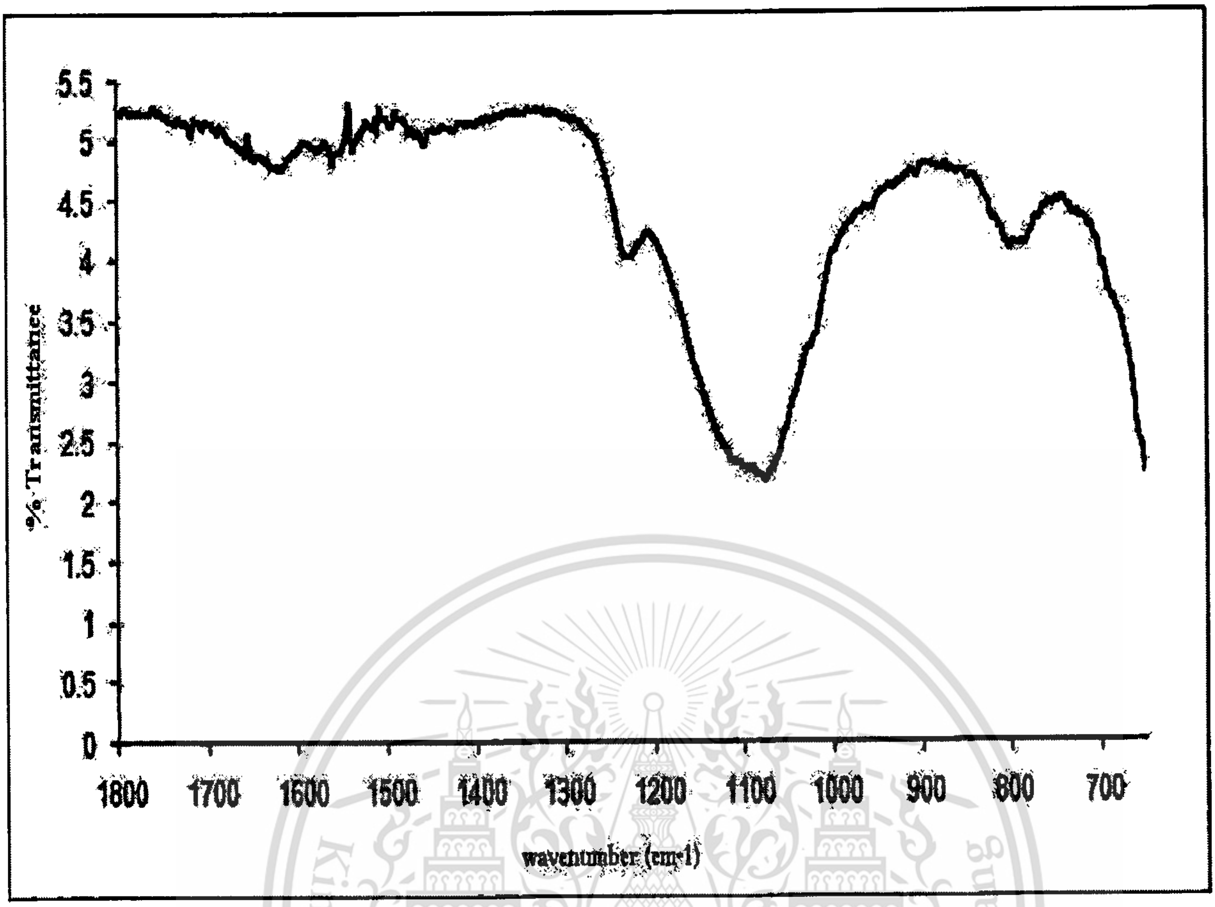


Figure E.4 Fourier IR spectrum of silicalite

APPENDIX F

Gas

Chromatogram

```
=====================================================================
Injection Date  : 31/1/2008 14:19:58 PM
Sample Name     :                                  Location : Vial 1
Acq. Operator   : nam
Acq. Instrument : Instrument 1                   Inj Volume : Manually
Method          : C:\HPCHEM\1\METHODS\NAM.M
Last changed    : 9/12/2007 17:56:47 PM
```

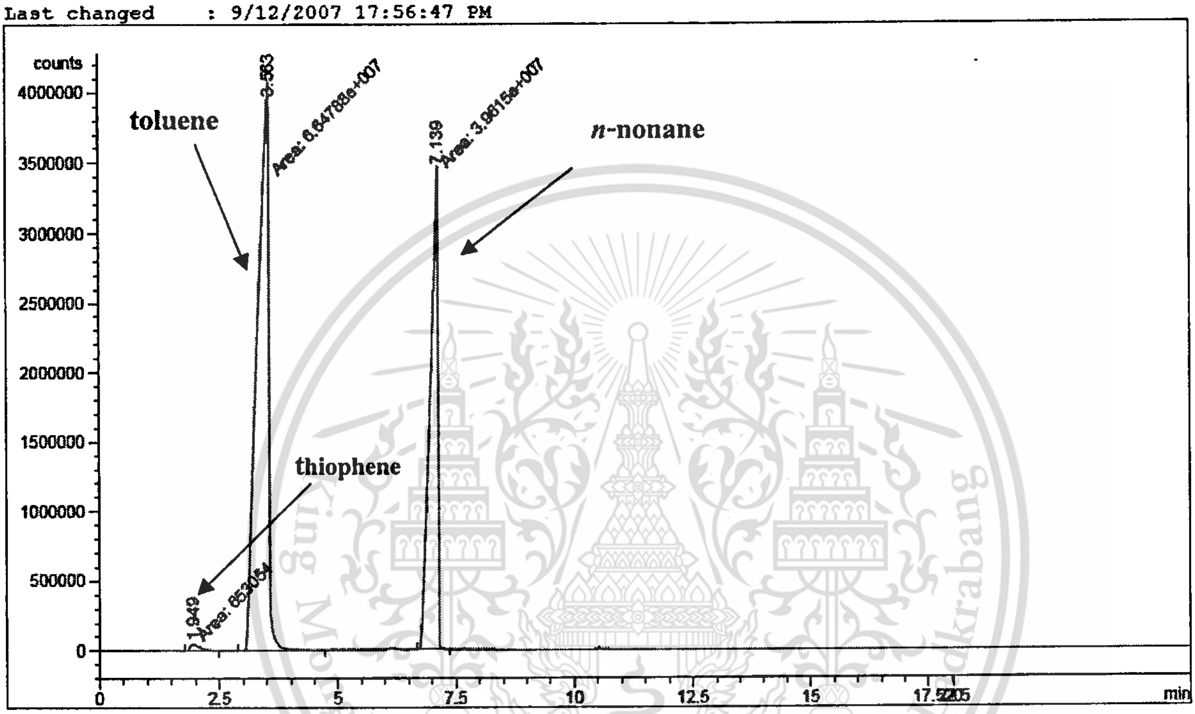
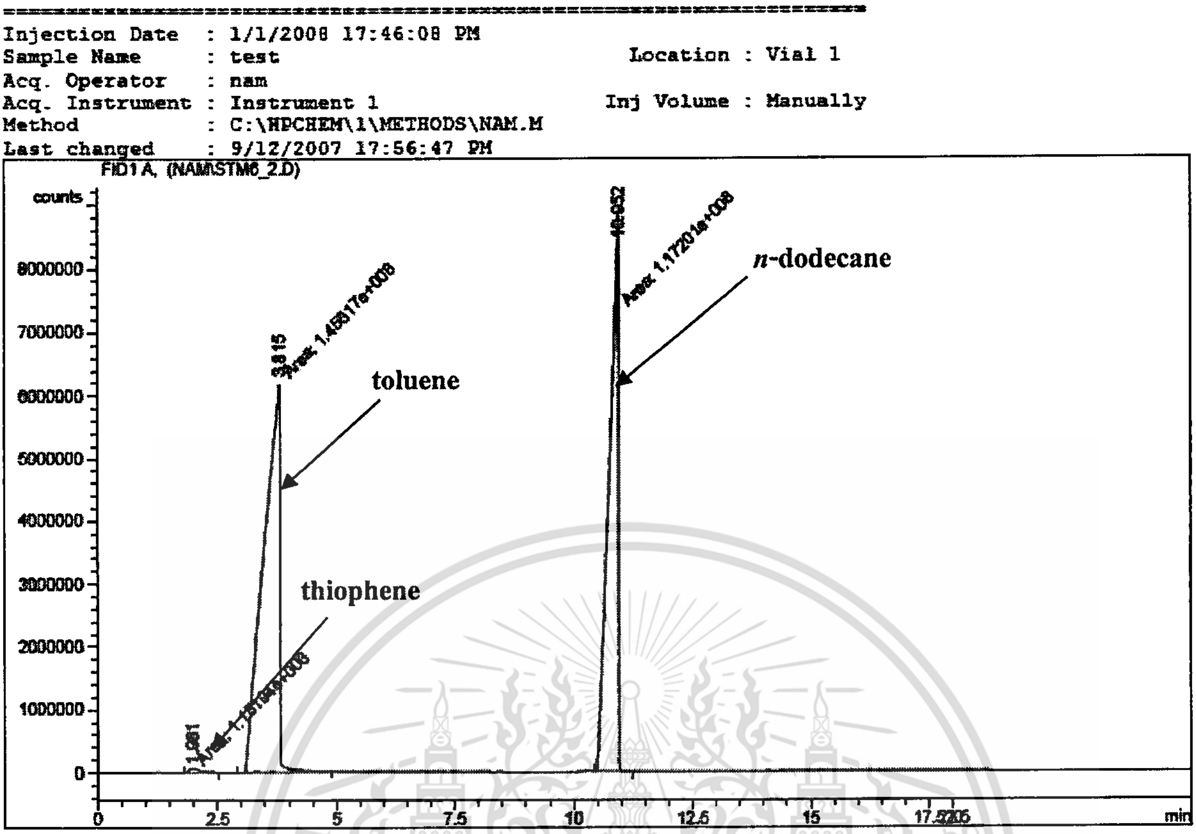


Figure F.1 Gas chromatogram from the oxidative extraction of thiophene at 60°C in n-nonane using TS-1 as catalyst.



```
Injection Date  : 1/1/2008 17:46:08 PM
Sample Name     : test                          Location : Vial 1
Acq. Operator   : nam
Acq. Instrument : Instrument 1                Inj Volume : Manually
Method          : C:\HPCHEM\1\METHODS\NAM.M
Last changed    : 9/12/2007 17:56:47 PM
```

Figure F.2 Gas chromatogram from the oxidative extraction of thiophene at 60°C in n-dodecane using TS-1 as catalyst.

APPENDIX G

Correction Factor Curve for Gas Chromatography Analysis and Product Calculation

Correction Factor Curve Preparation

The standard curve for correcting the area percentage from gas chromatography analysis to the relative percent concentration of sample, was prepared by analysis of the standard solution containing thiophene using chromatography. Standard concentration percentage was plotted with the area percentage of the sample.

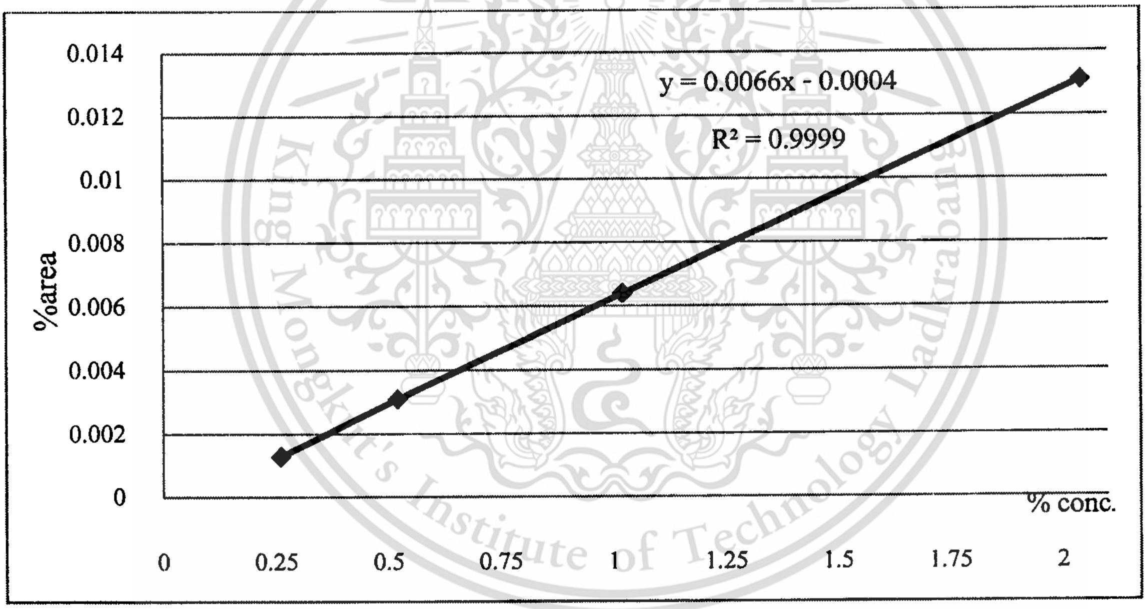


Figure G.1 Correction factor curve of thiophene in *n*-nonane

Equation fitted the correction factor curve of relative molar concentration of thiophene is shown below

$$y = 0.0066x - 0.0004$$

- x is relative % concentration of thiophene
- y is the area percentage of thiophene in a sample

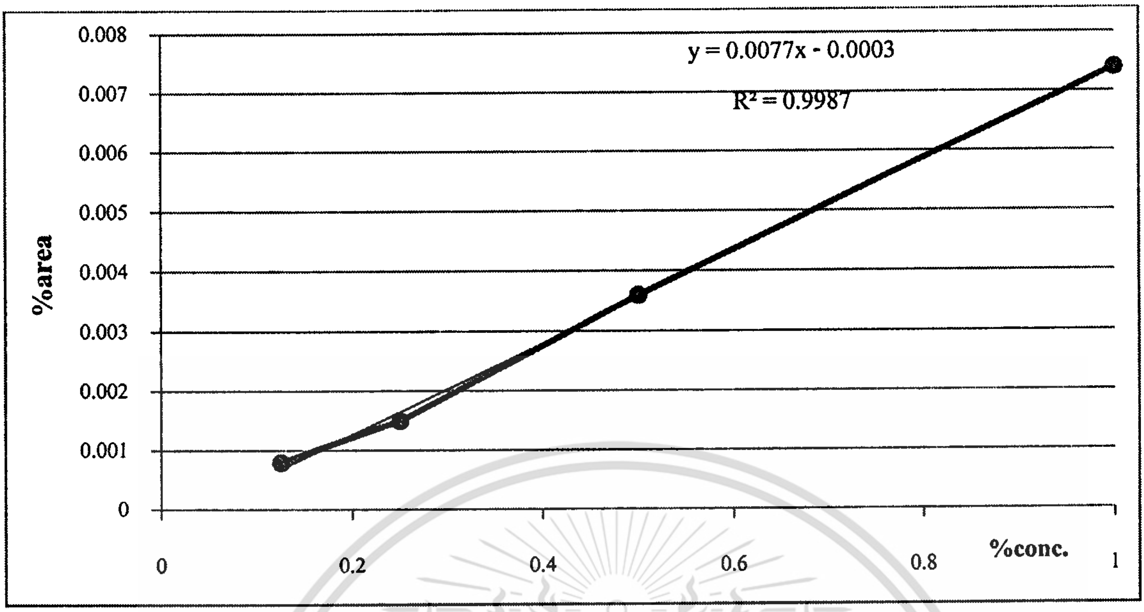


Figure G.2 Correction factor curve of thiophene in *n*-dodecane

Equation fitted the correction factor curve of relative molar concentration of thiophene is shown below

$$y = 0.0077x-0.0003$$

- x is relative % concentration of thiophene
- y is the area percentage of thiophene in a sample

% Removal of thiophene

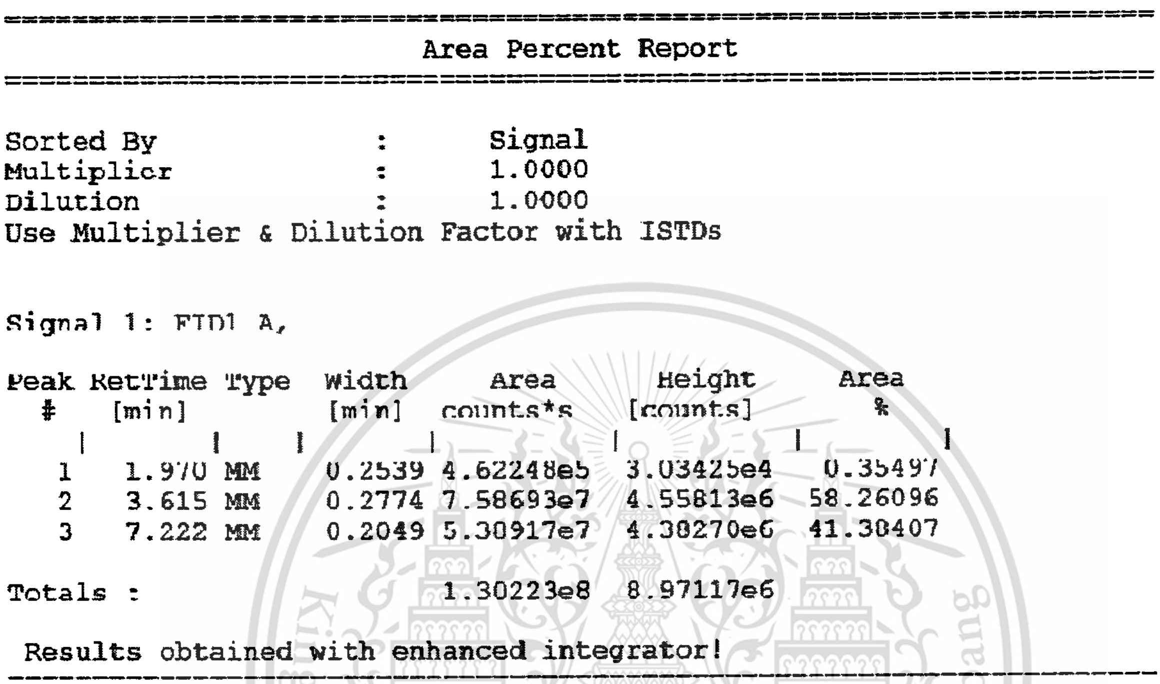
The removal of thiophene can be calculate from the remaining thiophene in the reaction. It can be expressed as following.

$$\% \text{ removal} = \frac{C_o - C_t}{C_o} \times 100$$

- C_0 is initial concentration of thiophene in feed
- C_t is concentration of thiophene in oil phase after t min

Example

The removal of thiophene was calculated from GC result. For example, the area percentage before used in the reaction in *n*-nonane as oil phase.



```
==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   counts*s   [counts]      %
   |       |     |       |          |          |         |
   1   1.970 MM    0.2539 4.62248e5  3.03425e4   0.35497
   2   3.615 MM    0.2774 7.58693e7  4.55813e6  58.26096
   3   7.222 MM    0.2049 5.30917e7  4.38270e6  41.38407

Totals :                  1.30223e8  8.97117e6

 Results obtained with enhanced integrator!
------------------------------------------------------------------
```

Figure G.3 Area percentage of thiophene before used in reaction from gas chromatography

The retention time 1.970 is thiophene, 3.615 is toluene and 7.222 is *n*-nonane.

The relative percent concentration of thiophene remaining in *n*-nonane = $\dfrac{(6.09\text{x}10^{-3}) + 0.0004}{0.0066}$

$= 0.9838\ \%$

The area percentage from the reaction using zeolite TS-1 as catalyst in methanol for 180 min is shown in Figure G.4

```
---------------------------------------------------------------------
                         Area Percent Report
=====================================================================

Sorted By            :      Signal
Multiplier           :      1.0000
Dilution             :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]  counts*s    [counts]       %
----|-------|----|-------|----------|----------|--------|
   1   1.976 MM    0.2989 1.83862e5  1.02516e4   0.06408
   2   3.823 MM    0.4082 1.51298e8  6.17739e6  52.72909
   3   7.435 MM    0.3167 1.35452e8  7.12744e6  47.20683

Totals :                  2.86934e8  1.33151e7

 Results obtained with enhanced integrator!
=====================================================================
```

Figure G.4 Area percentage of thiophene remaining in *n*-nonane reaction from gas chromatography

The retention time 1.976 is thiophene, 3.823 is toluene and 7.435 is *n*-nonane.

$$\text{The relative percent concentration of thiophene remaining in n-nonane} = \frac{(1.22\text{x}10^{-3}) + 0.0004}{0.0066}$$

$$= 0.2447\ \%$$

Then;

$$\%\ \text{removal of thiophene} = \frac{(0.9838 - 0.2447)}{0.9838} \text{ x } 100$$

$$= 75.48\ \%$$

The removal of thiophene was calculated from GC result. For example, the area percentage before used in the reaction using *n*-dodecane and methanol as oil phase and solvent phase.

```
----------------------------------------------------------------------
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   counts*s   [counts]      %
----|-------|----|-------|----------|----------|--------|
   1   1.945 MM    0.2666 1.43210e6  8.95410e4   0.54853
   2   3.707 MM    0.3281 1.48379e8  7.53687e6  56.83317
   3  10.876 MM    0.1837 1.11267e8  1.00934e7  42.61830

Totals :                  2.61078e8  1.77199e7

 Results obtained with enhanced integrator!
======================================================================
```

Figure G.5 Area percentage of thiophene before used in reaction from gas chromatography

The retention time 1.945 is thiophene, 3.707 is toluene and 10.876 is *n*-dodecane

The relative percent concentration of thiophene remaining in dodecane $= \frac{(9.65\text{x}10^{-3}) + 0.0003}{0.0077}$

$= 1.2924\ \%$

The area percentage from the reaction using zeolite TS-1 as catalyst in methanol for 180 min is shown in Figure G.6

```
---------------------------------------------------------------------
                        Area Percent Report
=====================================================================

Sorted By                :      Signal
Multiplier               :      1.0000
Dilution                 :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   counts*s   [counts]     %
----|-------|----|-------|----------|----------|--------|
   1   1.957 MM    0.2631 3.26486e5  2.06854e4   0.11540
   2   3.752 MM    0.3394 1.56314e8  7.67706e6  55.24912
   3  10.918 MM    0.1979 1.26286e8  1.06344e7  44.63548

Totals :                  2.82926e8  1.83322e7

 Results obtained with enhanced integrator!
```

Figure G.6 Area percentage of thiophene remaining in *n*-dodecane reaction from gas chromatography

The retention time 1.957 is thiophene, 3.752 is toluene and 10.918 is n-dodecane.

The relative percent concentration of thiophene remaining in dodecane $= \dfrac{(2.089 \times 10^{-3}) + 0.0003}{0.0077}$

$= 0.3062\ \%$

Then;

$$\%\ \text{removal of thiophene} = \frac{(1.2924 - 0.3062)}{1.2924} \times 100$$

$= 76.30\ \%$

APPENDIX H

Result from Gas Chromatography

Table H.1 Result from the study of temperature

Time (min)	Temperature	% removal of thiophene
60	Room-temperature	30.72
120	Room-temperature	32.47
180	Room-temperature	33.20
240	Room-temperature	35.32
300	Room-temperature	35.71
360	Room-temperature	35.01
60	60°C	37.26
120	60°C	35.11
180	60°C	40.20
240	60°C	44.52
300	60°C	43.72
360	60°C	44.42

Reaction condition : (1%wt TH) *n*-nonane; 2.5 ml, acetic acid; 2.5 ml, reaction time; 360 min

Table H.2 Result from the study of catalyst

Time (min)	Condition	% removal of thiophene
60	n-extraction	37.26
120	n-extraction	38.47
180	n-extraction	40.20
240	n-extraction	44.52
300	n-extraction	43.72
360	n-extraction	44.42
60	H_2O_2 without TS-1	36.33
120	H_2O_2 without TS-1	40.65
180	H_2O_2 without TS-1	45.33
240	H_2O_2 without TS-1	44.13
300	H_2O_2 without TS-1	44.78
360	H_2O_2 without TS-1	50.20

Reaction condition : (1%wt TH) *n*-nonane; 2.5 ml, acetic acid; 2.5 ml, hydrogen peroxide (30% w/w); 4.1 mmol, TS-1; 0.06, temperature; 60°C , reaction time 360 min

Table H.3 Result from the study of catalyst

Time (min)	condition	% removal of thiophene
60	H_2O_2, TS-1	55.65
120	H_2O_2, TS-1	61.54
180	H_2O_2, TS-1	60.16
240	H_2O_2, TS-1	57.31
300	H_2O_2, TS-1	58.27
360	H_2O_2, TS-1	61.87

Reaction condition : (1%wt TH) *n*-nonane; 2.5 ml, acetic acid; 2.5 ml, hydrogen peroxide (30% w/w); 4.1 mmol, TS-1; 0.06, temperature; 60°C , reaction time 360 min

Table H.4 Result from the oxidative extraction of thiophene using TS-1 as catalyst in various solvents

Time (min)	solvent	% removal of thiophene
60	Water	5.91
120	Water	17.46
180	Water	31.50
240	Water	30.00
300	Water	29.29
360	water	35.40

Reaction condition: (1%wt TH) *n*-nonane; 2.5 ml, solvent; 2.5 ml, hydrogen peroxide (30% w/w); 4.1 mmol, TS-1; 0.06 g; temperature; 60°C; reaction time; 360 min

Table H.5 Result from the oxidative extraction of thiophene using TS-1 as catalyst in various solvents

Time (min)	solvent	% removal of thiophene
60	Acetic acid	55.65
120	Acetic acid	61.54
180	Acetic acid	60.16
240	Acetic acid	55.31
300	Acetic acid	58.27
360	Acetic acid	61.87
60	acetonitrile	66.81
120	Acetonitrile	68.39
180	Acetonitrile	68.85
240	Acetonitrile	69.44
300	Acetonitrile	72.75
360	acetonitrile	69.40

Reaction condition : (1%wt TH) *n*-nonane; 2.5 ml, solvent; 2.5 ml, hydrogen peroxide (30% w/w); 4.1 mmol, TS-1; 0.06 g; temperature; 60°C; reaction time; 360 min.

Table H.6 Result from the oxidative extraction of thiophene using TS-1 as catalyst in various solvents

Time (min)	solvent	% removal of thiophene
60	Methanol	64.95
120	Methanol	75.19
180	Methanol	75.48
240	Methanol	77.42
300	Methanol	84.83
360	Methanol	84.11

Reaction condition: (1%wt TH) *n*-nonane; 2.5 ml, solvent; 2.5 ml, hydrogen peroxide (30% w/w); 4.1 mmol, TS-1; 0.06 g; temperature; 60°C; reaction time; 360 min

Table H.7 Result from the oxidative extraction of thiophene using TS-1 as catalyst in a various solvent to oil ratio

Time (min)	ration	% removal of thiophene
180	0.2	56.09
180	0.4	62.00
180	0.6	65.38
180	0.8	71.71
180	1.0	75.48

Reaction condition : hydrogen peroxide (30% w/w); 4.1 mmol, TS-1; 0.06 g, temperature; 60°C, reaction time; 180 min

Table H.8 Result from the oxidative extraction of thiophene using TS-1 as catalyst in a various hydrocarbon chain length

Time (min)	solvent	% removal of thiophene
180	Water	36.74
180	Acetic acid	63.61
180	Acetonitrile	73.77
180	Methanol	76.30

Reaction condition : (1%wt TH) *n*-dodecane; 2.5 ml, methanol; 2.5 ml, hydrogen peroxide (30%w/w); 4.1 mmol, temperature; 60°C, TS-1; 0.06 g, reaction time; 180 min

Table H.9 Result from the oxidative extraction of thiophene using TS-1 as catalyst for the catalyst stability in continuous process

Time (min)	% removal of thiophene
60	45.63
120	54.76
180	69.79
240	75.06
300	78.28
360	80.85
420	77.76
480	75.13
540	81.23
600	79.82
660	82.01
720	75.71
780	76.86

Reaction condition : temperature; 60°C, solvent; methanol, hydrogen peroxide(30 %w/w); 4.1 mmol, time on stream; 780 min, W/F; 775 $g_{catalyst}$hr mol^{-1}

Table H.10 Result from the oxidative extraction of thiophene using TS-1 as catalyst for the leaching of titanium framework in continuous process

Time (min)	catalyst	% removal of thiophene
60	Fresh catalyst	45.63
120	Fresh catalyst	54.76
180	Fresh catalyst	69.79
240	Fresh catalyst	75.06
300	Fresh catalyst	78.28
360	Fresh catalyst	80.85
420	Fresh catalyst	77.76
480	Fresh catalyst	75.13
60	Reused catalyst	42.72
120	Reused catalyst	56.84
180	Reused catalyst	62.32
240	Reused catalyst	71.07
300	Reused catalyst	71.24
360	Reused catalyst	70.61
420	Reused catalyst	71.23
480	Reused catalyst	69.89

Reaction condition : temperature; 60°C, solvent; methanol, hydrogen peroxide(30 %w/w); 4.1 mmol, time on stream; 480 min, W/F; 775 $g_{catalyst}hr\ mol^{-1}$

Table H.11 Result from the oxidative extraction of thiophene using TS-1 as catalyst for the leaching of titanium framework in continuous process

Time (min)	catalyst	% removal of thiophene
60	Regenerated catalyst	40.85
120	Regenerated catalyst	53.31
180	Regenerated catalyst	60.66
240	Regenerated catalyst	65.85
300	Regenerated catalyst	68.80
360	Regenerated catalyst	67.06
420	Regenerated catalyst	65.69
480	Regenerated catalyst	70.82

Reaction condition : temperature; 60°C, solvent; methanol, hydrogen peroxide(30 %w/w); 4.1 mmol, time on stream; 780 min, W/F; 775 $g_{catalyst}hr\ mol^{-1}$

Table H.12 Result from the oxidative extraction of thiophene using TS-1 as catalyst for the calcinations temperature in continuous process

Time (min)	Temperature	% removal of thiophene
360	550°C (fresh catalyst)	80.85
420	550°C (fresh catalyst)	77.76
480	550°C (fresh catalyst)	75.13
360	550°C (reused catalyst)	70.61
420	550°C (reused catalyst)	71.23
480	550°C (reused catalyst)	69.89
360	575°C (fresh catalyst)	76.60
420	575°C (fresh catalyst)	78.49
480	575°C (fresh catalyst)	79.45
360	575°C (reused catalyts)	77.81
420	575°C (reused catalyts)	76.32
480	575°C (reused catalyts)	76.61

Reaction condition : temperature; 60°C, solvent; methanol, hydrogen peroxide (30% w/w); 4.1 mmol, reaction time; 480 min, W/F; 775 $g_{catalyst}$hr mol^{-1}

Table H.13 Result from the oxidative extraction of thiophene using TS-1 as catalyst for the catalyst content in continuous process

Time (min)	Catalyst	% removal of thiophene
60	Without catalyst	16.78
120	Without catalyst	25.42
180	Without catalyst	29.48
240	Without catalyst	31.27
300	Without catalyst	31.67
360	Without catalyst	31.94
420	Without catalyst	30.63
480	Without catalyst	31.87
60	1 grams	45.63
120	1 grams	54.76
180	1 grams	69.79
240	1 grams	75.04
300	1 grams	78.28
360	1 grams	80.85
420	1 grams	77.76
480	1 grams	75.13

Reaction condition : temperature; 60°C, solvent; methanol, hydrogen peroxide (30 % w/w); 4.1 mmol, feed rate; 14.22 ml hr^{-1}, reaction time; 480 min

Table H.14 Result from the oxidative extraction of thiophene using TS-1 as catalyst for the catalyst content in continuous process

Time (min)	catalyst	% removal of thiophen
60	1.8 grams	64.99
120	1.8 grams	86.62
180	1.8 grams	87.17
240	1.8 grams	86.32
300	1.8 grams	91.56
360	1.8 grams	94.61
420	1.8 grams	96.62
480	1.8 grams	97.30

Reaction condition : temperature; 60°C, solvent; methanol, hydrogen peroxide (30 % w/w); 4.1 mmol, feed rate; 14.22 ml hr^{-1}, reaction time; 480 min

Table H.15 Result from the oxidative extraction of thiophene using TS-1 as catalyst in the various feeding rate in continuous process

Time (min)	Feed rate (ml/hr)	% removal of thiophene
60	10.52	49.54
120	10.52	66.82
180	10.52	78.65
240	10.52	81.62
300	10.52	83.51
360	10.52	82.46
420	10.52	83.98
480	10.52	85.76
60	14.22	45.63
120	14.22	54.76
180	14.22	69.79
240	14.22	75.06
300	14.22	78.28
360	14.22	80.85
420	14.22	77.76
480	14.22	75.13

Reaction condition : temperature; 60^{o}C, solvent; methanol, hydrogen peroxide (30 % w/w); 4.1 mmol, TS-1; 1.0 g, reaction time; 480 min

Table H.16 Result from the oxidative extraction of thiophene using TS-1 as catalyst in the various feeding rate in continuous process

Time (min)	Feed rate (ml/hrs)	% removal of thiophene
60	25	42.54
120	25	40.32
180	25	47.53
240	25	61.29
300	25	61.16
360	25	66.19
420	25	62.89
480	25	63.80

Reaction condition : temperature; 60°C, solvent; methanol, hydrogen peroxide (30 % w/w); 4.1 mmol, TS-1; 1.0 g, reaction time; 480 min

Table H.17 Result from the oxidative extraction of thiophene using TS-1 as catalyst in the various concentration of feed in continuous process

Time (min)	concentration	% removal of thiophene
360	Extraction (1%sulfur)	31.94
420	Extraction (1%sulfur)	30.63
480	Extraction (1%sulfur)	31.87
360	Extraction (3%sulfur)	52.34
420	Extraction (3%sulfur)	50.32
480	Extraction (3%sulfur)	52.86
360	TS-1 (1%sulfur)	80.85
420	TS-1 (1%sulfur)	77.76
480	TS-1 (1%sulfur)	75.13
360	TS-1 (3%sulfur)	87.49
420	TS-1 (3%sulfur)	82.34
480	TS-1 (3%sulfur)	80.77

Reaction condition : temperature; 60^{o}C, solvent; methanol, hydrogen peroxide (30 % w/w); 4.1 mmol, W/F; 775 $g_{catalyts}$hr mol^{-1}, reaction time; 480 min

AUTHOR BIOGRAPHY

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