ผลกระทบของความเข้มข้นของแก๊สออกซิเจนต่อปฏิกิริยาออกซิเดชันของ 2-โพรพานอล ในเฟสแก๊สบนตัวเร่งปฏิกิริยาไททาเนียมซิลิกาไลต์-1

นาย พิชิต ทิศทวีรัตน์

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EFFECT OF OXYGEN CONCENTRATION ON THE GAS PHASE OXIDATION OF 2-PROPANOL OVER TS-1 CATALYST

Mr. Pichit Thitthaweerut

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By	Mr. Pichit Thitthaweerut
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Thesis Advisor	Associate Professor Tharathon Mongkhonsi, Ph.D.

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……………………………….Dean of the Faculty of Engineering
(Professor Direk Lavansiri, Ph.D.)

THESIS COMMITTEE

……………………………………………… Chairman
(Associate Professor Suttichai Assabumrungrat, Ph.D.)

……………………………………………… Thesis Advisor
(Associate Professor Tharathon Mongkhonsi, Ph.D.)

Bunjerd Jongsomjit
……………………………………………… Member
(Assistant Professor Bunjerd Jongsomjit, Ph.D.)

Amornchai Arpornwichanop
……………………………………………… Member
(Amornchai Arpornwichanop, D.Eng)

พิชิต ทิศทวีรัตน์ : ผลของความเข้มข้นของแก๊สออกซิเจนต่อปฏิกิริยาออกซิเดชันของ 2-โพรพานอล ในเฟสแก๊สบนตัวเร่งปฏิกิริยาไททาเนียม ซิลิกาไลต์-1
(EFFECT OF OXYGEN CONCENTRATION ON THE GAS PHASE OXIDATION OF 2-PROPANOL OVER TS-1 CATALYST)
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ทำการศึกษาผลของความเข้มข้นต่อปฏิกิริยาออกซิเดชันของ 2-โพรพานอล บนตัวเร่งปฏิกิริยาไททาเนียม ซิลิกาไลต์-1 โดยความเข้มข้นของออกซิเจนในสายป้อนเข้าอยู่ในช่วง 2-16 % โดยปริมาตร โดยความเข้มข้น 2-โพรพานอลอยู่ที่ 5 % โดยปริมาตร ในช่วงอุณหภูมิ 100 ถึง 500 องศาเซลเซียสและความดันบรรยากาศ งานวิจัยนี้พบว่า ค่าการเปลี่ยนแปลงของ 2-โพรพานอล ในช่วงอุณหภูมิต่ำ (150 ถึง 300 องศาเซลเซียส) มีค่าเพิ่มขึ้นเล็กน้อยเมื่อความเข้มข้นของออกซิเจนเพิ่มขึ้น สำหรับช่วงอุณหภูมิสูง (350 ถึง 500 องศาเซลเซียส) พบว่าความเข้มข้นของออกซิเจนไม่มีส่วนสำคัญต่อค่าการเปลี่ยนแปลงของ 2-โพรพานอล นอกจากนี้ความเข้มข้นของออกซิเจนที่เพิ่มขึ้นในช่วงอุณหภูมิตั้งแต่ 300 ถึง 500 องศาเซลเซียสส่งผลต่อค่าการเลือกเกิดของโพรพิลีนที่ลดลง ส่วนค่าการเลือกเกิดของอะซีโตนและคาร์บอนไดออกไซด์เพิ่มขึ้นเมื่อเพิ่มความเข้มข้นของออกซิเจนในช่วง 0-8 % โดยปริมาตรที่ช่วงอุณหภูมิเดียวกัน ในทางตรงกันข้ามเมื่อเพิ่มความเข้มข้นของออกซิเจนมากกว่า 8 % โดยปริมาตรจะพบว่าค่าการเลือกเกิดของอะซีโตนเพิ่มขึ้นและลดลงเมื่ออุณหภูมิมากกว่า 350 องศาเซลเซียส ในขณะที่ค่าการเลือกเกิดของคาร์บอนไดออกไซด์เพิ่มขึ้นอย่างต่อเนื่อง

ภาควิชา…………..วิศวกรรมเคมี……..… ลายมือชื่อนิสิต……พิชิต ทิศทวีรัตน์……….
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This research studies effect of oxygen concentration on the gas phase oxidation of 2-propanol over TS-1 catalyst with the oxygen concentration in the feed gas varies from 2 to 16 vol% and 5 vol% of 2-propanol in the reaction temperature ranging from 100 to 500°C and atmospheric pressure. The research found that 2-propanol conversion in the low reaction temperature range (150-300 °C) slightly increases with the increase of oxygen concentration. For the high reaction temperature range (350 -500 °C), the 2-propanol conversion is independent on the oxygen concentration. In addition, increasing the oxygen concentration, from 2 to 8 vol% adversely affects the selectivity of propylene in reaction temperature ranging from 300 to 500 °C. On the other hand, when the oxygen concentration is increased above 8 vol%, the selectivity to acetone rises and then drops when the reaction temperature raised beyond 350 °C whereas the selectivitiy to CO_2 increases continually.

Department……Chemical Engineering… Student's signature…Pichit Thitthaweerut……

Field of study….Chemical Engineering… Advisor's signature……………………...

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Finally, he would like to dedicate the achievement of this work to his parents, who have always been the source of his support and encouragement.

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CHAPTER I

INTRODUCTION

Selective oxidation using air or oxygen is an area of immense industrial importance because the oxidation processes manufacture many petrochemical commodities and precursors for various chemicals. Most attention has been given to noble metal and transition metal oxide catalysts which are effective for the oxidation of many organic compounds.

Among the oxidation reaction, the oxidation of alcohols is a possible route to produce oxygenated products. It is known that alcohols can lose hydrogen atoms to form an aldehyde or a ketone depend on the alcohol reactant. Furthermore, these alcohols can be converted into a corresponding alkene by dehydration. In recent years, selective oxidation of alcohols using different catalysts is being interested [Pestryakov and Lunin (2000), Scire et al. (2003)]. In these cases, the gas phase oxidation is preferred because the gas phase oxidation already requires a low reactant concentration to avoid creating explosive mixture. In addition, the catalyst must not to reactive. Otherwise the C-C bonds of the product formed may be destroyed. Therefore, a sutiable catalyst has yet to be explored.

Titanium silicalite-1 (TS-1), which is a zeolite catalyst like ZSM-5 structure containing framework titanium atoms instead of aluminium atoms, was first discovered by Taramasso and co-worker in 1983. TS-1 is usually synthesized by using tetraethylorthotitanate (TEOT) as Ti source, tetraethylorthosilicate (TEOS) as Si source and tetrapropylammoniumhydroxide (TPAOH). It has very interesting properties as a catalyst for several important oxidation reactions such as the olefin epoxidation, the phenol hydroxylation and oxidation of alcohols. A variety of oxidation reaction carried out in liquid phase using TS-1 have been reported. The application of TS-1 in gaseous phase oxidation, however, is very limited. This is the area that is waiting to be explored.

Because of the above mentioned reasons. This research is set up to study the potential of TS-1 as a new gas phase oxidation catalyst. The oxidation of 2-propanol is selected as the test reaction. 2-propanol is selected as the reactant due to several reasons. For example, 2-propanol molecule contains only a hydroxyl group (-OH) which is more active than the methyl ($-CH_3$) group. Thus, the starting point of reaction pathway can be easily determined. Secondly, the primary oxidation product of 2-propanol is acetone, which is rather inactive than 2-propanol. The further oxidation of acetone requires more powerful active sites than those require for the oxidation of 2-propanol. Therefore, the products is formed from the oxidation of 2-propanol can indicate the power of the oxidizing site. If the oxidizing site is not too powerful, less acetone should appear in the product stream while the amount of the combustion products should increase.

In a previous research (Kedsuda C., 2005), The gas phase oxidation of various alcohols (eg. methanol, ethanol, 1-propanol, and 2-propanol) has been carried out over TS-1. Though the previous research showed that the oxidation of the alcohols could produce oxygenates, the oxygen concentration used was rather too high (8-21 %). This leads to the over oxidation of the oxygenates to CO_2. The present work covers the oxygen concentration region lower than the previous research to prevent the excessive oxidation of the oxygenate formed.

This research has been scoped as follows:

1) Preparation of TS-1 catalysts by using the hydrothermal method.

2) Characterization of TS-1 catalysts by using the following techniques.

- Determination of bulk composition of Si/Ti by X-ray Flourescene (XRF).
- Determination of specific surface area by N_2 adsorption based on BET method (BET).
- Determination of structure and crystallinity of catalysts by X-ray Diffractrometer (XRD).

- Determination of incorporation of Ti atoms as a framework element by IR Spectroscopy (IR).
- Determination of acid property by NH_3 Temperature Programmed Desorption (NH_3-TPD)

3) Catalytic reaction testing using the gas phase oxidation of 2-propanol at 100 - 500°C and atmospheric pressure for 2 vol%, 4 vol%, 6 vol%, 8 vol%, 12vol% and 16vol% of oxygen concentrations in the feed gas to determine catalytic activity

This present work is organized as follows:

The background and scopes of the research are described in chapter I.

Chapter II presents literatures relate to TS-1 catalysts and oxidation of 2-propanol on various reaction in the past and comments on previous work.

The theory of this research, studies about the oxidation reaction and its possible mechanism, and the properties of TS-1 catalysts are presented in chapter III.

Chapter IV consists of procedures of catalyst preparation, catalyst characterization and catalytic reaction in the gas phase oxidation of 2-propanol.

The experimental results of the characterization of TS-1 catalyst, and 2-propanol oxidation reactions over these catalysts, including an expanded discussion, are described in chapter V.

Chapter VI contains the overall conclusions emerging from this research and some recommendations for future work.

Finally, the sample of calculation of catalyst preparation, external and internal diffusion limitations, calibration curves from area to mole of acetones, propylene, 2-propanol and the others, and data of the experiments which had emerged from this research are included in appendices at the end of this thesis.

CHAPTER II

LITERATURE REVIEW

The invention of TS-1 catalyst, opened a new field in heterogeneously catalyzed various oxidation reaction such as the epoxidation of alkenes, the oxidation of alcohols, the phenol hydroxylation etc. in both gas and liquid phases. Some TS-1 catalyzed processes are advantageous from the environmental point of view as the oxidant is aqueous H_2O_2, which turns into water, and the reactions, operated in liquid phase under mild conditions, show very high selectivities and yields reducing problems and cost of by-product treatment. In addition, TS-1 can catalyze a variety of useful oxidation reactions in the presence of O_2 as the oxidant, carried out in gas phase.

This chapter divides the reviewed works into two parts, i.e., (a) the preparation, characterization of the TS-1 catalyst and the oxidation of organic compound over the TS-1, (b) the oxidation of organic compound by using the various catalysts. An attempt will also be made to summarise the present knowledge and understanding of various factors influencing the conversion of the oxidation of organic compounds (such as alkenes, alcohols). In the last section of this review, comments on previous studies that have directly influenced the aims of this study are given.

2.1 Literature reviews

2.1.1 The preparation, characterization of the TS-1 catalyst and the oxidation of organic compound over the TS-1.

Taramasso et al. (1983) invented a new catalyst material constituted by silicon and titanium oxide. The material was given the name titanium silicalite-1 or TS-1, and corresponds to the following formula $xTiO_2.(1-x)SiO_2$. The material was prepared by using a source of silicon oxide and a source of titanium oxide. The reaction took place in the aqueous phase at a temperature of 130˚C to 200˚C, and the solid product obtained was calcined in air at 550˚C.

Kraushaar-Czarnetzki and van Hooff (1989) reported that TS-1 could also be obtained from [Al]ZSM-5 by dealumination and subsequent treatment with titanium tetrachloride. The obtained TS-1 exhibited the same catalytic properties as hydrothermally synthesized TS-1 of high purity. Moreover, their experimental result showed that the selectivity of their catalyst was strongly affected by the presence of small amounts of non-framework titania.

Van der Pol et al. (1992) synthesized and investigated TS-1 samples of different particle size. Smaller particles were more active than larger particles. From calculation of the Weisz modulus it could be concluded that large zeolite particle were not fully utilized because of pore diffusion limitations. The product distribution was also influenced by particle size.

Duprey et al. (1997) characterized two titanium silicalite-1 samples which similar particle size by powder X-ray diffraction, FT-IR and FT-Raman spectroscopy, UV-visible diffuse reflectance spectroscopy (DRS), transmission electron microscopy with X-ray energy dispersion spectrometry, and xenon-129 NMR. In addition, the activity and selectivity for the epoxidation of the oct-1-ene by phosphate-free 30% aqueous hydrogen peroxide have also been investigated. The critical factors concerning the activities of the samples with molar rations Si:Ti ~ 39 and 32 were reported to be the distribution of titanium within the microporous materials and within the extraframework titania. Xenon-129 NMR chemical shifts depended dramatically on extraframework impurities and Ti(IV) dispersion. They reported that pure silicalite and nearly perfect TS-1 were not differentiated by xenon-129 NMR, a fact which was tentatively attributed to the "atomic dispersion" of the titanium, as evidenced by X-ray EDS and by the channel dimension.

Davies et al. (2001) compared the study of the crotyl alcohol using hydrogen peroxide and *tert*-butyl hydroperoxide as oxidants with TS-1, Ti-β, Ti-MCM-41 and Ti-grafted-MCM-41 as catalysts. With hydrogen peroxide as oxidant, significant Ti-leaching was observed with all the catalysts except TS-1 (Ti-Alβ > Ti-grafted-MCM-

41 > Ti-MCM-41 > Tiβ > Ti-Al-MCM-41 >> TS-1). For Ti-Alβ, Ti-grafted-MCM-41 and Ti-Al-MCM-41, initial heterogeneously catalyzed formation of the epoxide was observed. The formation of a Ti-species in solution was shown to contribute to competing homogeneously catalyzed formation of ether diols and triol. Using *tert*-butyl hydroperoxide as oxidant the Ti-leaching was minimized and selective epoxide formation was observed with Ti-β, Ti-Alβ Ti-MCM-41 as heterogenous catalysts, although, with Ti-Alβ, the ether diols and triol products dominated due to acid catalyzed sovolysis of the epoxide.

Schuster et al. (2001) investigated the activity of titanium and vanadium containing zeolitic and non-zeolitic materials in the oxidative dehydrogenation of propane to propene. Using TS-1 as the catalyst showed the optimum performance. The propane and oxygen partial pressure had no influence on the selectivity, and the mass transport limitation in the macro- and mesopores could be neglected. The addition of water caused a decrease in the conversion, but increased the selectivity, probably due to a competitive adsorption of the water molecules and the reactant molecules on the active site. They assumed that the reaction probably took place on the outer surface of the TS-1 crystallites on Lewis acid sites, the exact reaction mechanism nor the exact active site were not yet clear. In addition, increasing the Lewis acidity by a sulfation of TS-1 in both the gas phase and the liquid phase prior to the reaction resulted in an increase of the conversion of up to 17% with a selectivity about 74% which were the best results up to now.

Wang et al. (2003) investigated the effect of preparation, treatment method of the Ag/TS-1 catalyst and the reaction conditions on propylene epoxidation using oxygen as the oxidant in a fixed-bed quartz glass reactor. The result of effect of preparation condition was divided into three parts. The first one, the effect of Ag loading, showed the amount of Ag loading had an important effect on the catalytic properties. With an increase in the Ag loading, the propylene conversion increased significantly, and then leveled off, but the selectivity to propylene oxide decreased significantly with an excessive increase of Ag loading. The optimum catalytic activity for Ag loading was 2%. The second one, the effect of support reported the effects of supports, ie. Ag/TiO_2, Ag/SiO_2, Ag/silicalite-1, Ag/HZSM-5, and Ag/TS-1. They observed that the catalytic activities for the epoxidation of propylene were different.

Only TS-1 was the suitable support, and there was a synergy between Ag and TS-1 in the gas phase epoxidation of propylene. The third one was the effect of Si/Ti ratio of TS-1. They found that the Si/Ti ratio of TS-1 had a great effect on the propylene epoxidaton. With an increase in the Si/TI ratio of TS-1, both the propylene conversion and the selectivity to propylene oxide increased. The Si/Ti ratio was 64, the catalyst exhibited optimum performance, 0.92% propylene conversion and 91.21% propylene oxide selectivity.

Moreover, they also studied the effect of pretreatment condition of Ag/TS-1 catalysts. The results showed that an increase in the calcination temperature, both the propylene conversion and the selectivity to propylene oxide increased. The catalyst calcined at 450°C, exhibited the optimum performance. In case of the effect of calcinations methods of Ag/TS-1 catalysts, they presented that calcinations methods had an important effect on the reaction. The optimum activity showed when the catalyst calcined in air at 450°C. The optimum Ag/TS-1 catalyst, by passing a reactant mixture of C_3H_6, O_2, H_2, and N_2 at 150°C at a volume ratio of 1:2:3:12 with a space velocity of 4,000 h^{-1}, exhibited the best result. At this condition, after 70 min reaction the conversion of propylene and the selectivity to propylene oxide was 1.37 and 93.51%, respectively. The results of the characterization showed that the oxidized Ag species without single electrons played an important role in the epoxidation of propylene.

Yap et al. (2004) studied the direct vapor-phase epoxidation of propylene using hydrogen and oxygen over gold particles prepared by the deposition-precipitation method on various modified titanium silicalite- (TS-1) supports. The reaction was carried out over a reaction time of 24-36 hrs at a space velocity of 7000 $mlg_{cat}^{-1}h^{-1}$ and temperatures of 140, 170, and 200 °C. The results showed that gold deposition at pH 9-10 allowed for a consistent amount of 1-3 wt% of the gold available in solution to be deposited, while still maintaining gold particle diameters in the 2-5 nm range, as observed by TEM. Au/TS-1 catalysts achieved propylene conversions of 2.5-6.5% and propylene oxide selectivities of 60-85% at 170 ºC, with dilute Au and Ti catalysts exhibiting good stability. They explained that propylene oxide rates were not highly influenced by the TS-1 particle size and are thus not proportional to the specific external surface area of the support.

The conclusion that activity may reside in the channels of the TS-1 was supported by the finding that the observable gold particles decorating the TS-1 particle only account for about 30% of the total gold content of the catalyst. Increasing the gold loading up to 0.74 wt% did not increase the propylene oxide rates proportionally, suggesting that the active Au-Ti propylene oxide-forming centers are limited. In contrast to the prevailing interpretation of this catalyst that a critical Au particle diameter of 2-5 nm was essential for propylene oxide activity, their results are consistent with a molecular cluster model where extremely small gold clusters located near Ti sites inside the TS-1 pores or on the external surface were active for propylene epoxidation.

Wang et al. (2004) investigated the effect of calcinations atmosphere of the Ag/TS-1 catalyst and other Ti-containing supports on propylene epoxidation in the presence of hydrogen and oxygen. The results showed calcinations atmosphere has an important effect on the catalytic properties. The catalyst, which was calcined in air, exhibited the optimum catalytic activity 0.43% propylene conversion with 92.75% propylene oxide selectivity. However, the catalyst, which was calcined in nitrogen or hydrogen, exhibited obviously activity decrease. The framework titanium species played an important role in the reaction, but the extra framework titanium species (centered at about 280-290 nm) also had weak epoxidation activity. They concluded that excessive extra framework titanium species (hexahedral) could decrease the propylene oxide selectivity and the oxidized silver ions are the main active sites for the gas-phase epoxidation of propylene.

2.1.2 The oxidation of organic compound by using the various catalysts.

Yao (1984) studied the catalytic oxidation of ethanol at low concentrations by Pt, Pd, Rh, Ag and the first row transition metal oxide catalysts supported on Al_2O_3. The results presented $CuO/\gamma\text{-}Al_2O_3$ and $Mn_2O_3/\gamma\text{-}Al_2O_3$ gave the highest activity for total oxidation to CO_2. Ethylene was found to be the only reaction product over $\gamma\text{-}Al_2O_3$. The amount of acetaldehyde formed was generally higher with the base metal oxide catalysts than with Pt or Pd. Dehydration by $NiO/\gamma\text{-}Al_2O_3$ produced ethylene was predominant.

Ozkan et al. (1990) reported the oxidation of methanol over transition metal oxide catalysts (oxides of Cr, Mn, Fe, Co, Ni, Cu) which supported on γ-Al_2O_3. The results showed that all the catalysts exhibited similar activities for methanol conversion but Cu catalyst was found to be considerably more selective to CO_2.

Rekoske and Barteau (1997) determined the steady-state kinetics of 2-propanol decomposition on oxidized anatase TiO_2 at temperatures ranging from 175 to 325°C and 2-propanol partial pressures from 8.9 to 102.7 Torr. The effects of the addition of O_2 and water to the carrier gas were also investigated. The steady-state reaction resulted primarily in the formation of a dehydration product, propylene, and a dehydrogenation product, acetone, with small amounts of carbon oxides also being observed. Depending on the reaction conditions, the selectivity to either propylene or acetone could range between 5 and 95%. The rate of dehydrogenation increased dramatically with the addition of both O_2 and water, while the dehydration rate was unaffected by their presence. Accordingly, the kinetics of 2-propanol decomposition were investigated using both air and an inert carrier. Using air as the carrier gas, the dehydration and dehydrogenation reactions were determined to be approximately one-half order with respect to 2-propanol partial pressure. The activation energies determined for the two processes are substantially different, 68 kJ mol^{-1} for dehydrogenation and 130 kJ mol^{-1} for dehydration, as evidenced by the strong temperature dependence of the decomposition selectivity. Using an inert carrier, the reaction kinetics depended in a complex fashion on the conversion of 2-propanol. The dependence on conversion was found to arise from the influence of water on the dehydrogenation kinetics. The presence of water, whether produced by 2-propanol dehydration or added independently, was found to increase the rate of 2-propanol dehydrogenation. The results of the present study can be reconciled with previously reported steady-state and temperature-programmed desorption investigations of 2-propanol on TiO_2 by recognizing the influence of both surface hydroxyls and the use of an oxidizing carrier gas on the dehydrogenation and dehydration pathways at steady state.

Mongkhonsi *et al.* (2000) investigated the selective oxidation reaction of ethanol and 1-propanol over V-Mg-O/TiO_2 catalyst. Ethanol and 1-propanol could be selectivity oxidized to ethanal and propanal, respectively. Aldehyde yield up to 73%

and 66% for ethanal and propanal, respectively, were achieved in the temperature range 200-250^{o}C. The catalyst was rather inactive for the further oxidation of aldehyde products to carboxylic acid.

Pestryakov and Lunin (2000) studied the active electronic states of the supported metal catalysts (Ag, Cu, Au) in the processes of alcohol partial oxidation by physicochemical methods. Comparison of the obtained catalytic and spectroscopic data revealed that one-charged cations M^+ were the active sites of the local interaction on the metal catalyst surface in the processes of alcohol oxidation. The catalyst selectivity strongly depends on the effect charge of the surface active sites.

Laufer and Hoelderich (2001) investigated direct oxidation of propylene and other olefins on precious metal containing Ti-catalysts. For the direct oxidation of propylene to propylene oxide, the best results could be obtained by carrying out the reaction in a semi-batch process at 40-45 ^{o}C by using of O_2:H_2 ratios of 1:1 to 2:1. The addition of small amounts of salt to the reaction mixture had appositive influence on the catalytic performance by improving the H_2O_2 direct synthesis. The oxidation of other olefins like styrene or terpenes led to very low product yields and selectivities.

Mongkhonsi et al. (2001) studied the reactivity of Co-Mg-O catalyst in the gas phase selective oxidation of methanol, ethanol, 1-propanol and 2-propanol by using a tubular flow reactor. The Co-Mg-O system has shown the potential as a selective oxidation catalyst for the production of aldehydes from ethanol and 1-propanol. They found that another advantage of this catalyst system is the other by-products form in a small amount and can be removed from the product stream by any conventional process. The oxidation of methanol and 2-propanol does not produce any oxygenate compound. Oxidation of methanol produced mainly CO_2 while the major products for the oxidation of 2-propanol was propene.

Mongkhonsi et al. (2002) investigated the oxidation of 1-propanol and 2propanol by Co-Mg-O catalysts supported on TiO_2 and Al_2O_3. The reaction condition carried out in gas phase by using oxygen as the oxidant. They found that the catalytic activity of the supported Co-Mg-O catalysts depended on the reactant. Propanal was the primary product of 1-propanol oxidation reaction. In the case of 2-propanol oxidation, the primary product at low reaction temperature was propene, while at high reaction temperatures, propanal began to appear as others main product. The direct oxidation of propene confirmed that the catalysts could directly oxidize propene to propanal. The sequence of cobalt and magnesium loading had no observable effect on the structure or catalytic performance of the catalysts studied.

Unnikrishnan and Endalkachew (2002) studied selective oxidation of various primary and secondary alcohols in a gas-phase photochemical reactor using immobilized TiO_2 catalyst. An annular photoreactor was used at 190°C with an average contact time of 32 second. The system was found to be specifically suited for the selective oxidation of primary and secondary aliphatic alcohols to their corresponding carbonyl compounds. Benzylic alcohols gave higher conversions, however, with more secondary reaction products. The reaction mechanism for various products formed is explained. The effects of different reaction parameters, such as O_2/alcohol ratio, water vapor, UV light, and contact time, were studied. The presence of oxygen was found to be critical for the photooxidation. Water vapor in the feed was also found to be helpful in the reaction, although it was not as critical as in hydrocarbon oxidation, where it was necessary for hydroxylating the catalyst surface and sustaining its activity. In alcohol oxidation, surface hydroxylation could be partially provided by the hydroxyl groups of the alcohol itself. Catalyst deactivation was also observed and is attributed to the surface accumulation of reaction products. However, the catalyst regained its original activity after regeneration by calcination in air for 3 hr at 450°C.

Scire et al. (2003) investigated the gold/cerium oxide catalyst, which was prepared by coprecipitation and deposition-precipitation on the catalytic combustion of some representative volatile organic compounds, such as 2-propanol, methanol and toluene by using oxygen as the oxidant. From the results, deposition-precipitation method has been found to be more suitable than coprecipitation to obtain highly active Au/CeO_2 catalysts, because the deposition-precipitation method leds to gold nanoparticles, which were preferentially located on the surface of ceria. The high activity of the Au/CeO_2 system might be related to the capacity of gold nanoparticles to weaken the Ce-O bond, thus increasing the mobility or reactivity of the surface lattice oxygen, which was involved in the volatile organic compounds oxidation through a Mars-van Krevelen reaction mechanism.

Sato et al. (2003) investigated the selective dehydration of 1,3-diols into allylic alcohols at 300-375˚C by using CeO_2 catalyst in a usual fixed bed flow reactor. In the dehydration of 1,3-propanediol over pure CeO_2, 2-propen-1-ol was produced with the maximum selectivity of 98.9 mol% at 325˚C. In the dehydration of 1,3-butanediol, 2-butane-1-ol and 3-buten-2-ol were produced with the sum of the selectivity >99 mol% over CeO_2, which showed attractive catalytic performance without decay at temperature <375˚C. In the reaction of 2-buten-1-ol, 1,2- and 1,4-butanediol, little dehydrated products were detected over the CeO_2.

Takehira *et al.* (2005) studied Nickel containing Mg-Al hydrotalcite-type anionic clay catalyst for the oxidation of alcohols with molecular oxygen. They founded that Octahedrally coordinated and isolated Ni(II) sites formed by the Ni substitution of Mg(II) sites in Mg-Al HT and revealed a high activity in the liquid-phase oxidation of alcohols with molecular oxygen. Moreover Benzyl alcohol was the most effectively oxidized to benzaldehyde, the yield of which increased significantly with increasing nickel content up to 7.6 wt%. Using non-polar solvents, such as toluene, was favorable for this oxidation reaction. Alcohols were oxidized on the $Mg_{2.5}Ni_{0.5}AL$ HT heterogeneous catalyst which Ni(II) worked as the active site by activating molecular oxygen assisted by Mg(II) as a base as well as by activating alcohols on the Al(III) as a Lewis acid

2.2 Comment on previous works

From the reviewed literatures, TS-1 can catalyze for the reaction both in gas phase and liquid phase. However there are only some researches about the oxidation of hydrocarbon compounds by O_2 in gas phase and some researches concern the oxidation of alcohol by H_2O_2 in liquid phase. This review can be inferred that TS-1 can improve the conversion and product selectivities of the various reactions.

From the previous studies about the reaction, there are few researches studied the gas phase oxidation of alcohol such as methanol, ethanol, 1-propanol and 2-propanol over TS-1. It is proved that TS-1 played role as an effective catalyst for alcohol oxidation reactions in the gas phase. For the same condition, 2-propanol oxidation posses higher catalytic performance compare to the other alcohol oxidation.

However there are some researches about the selective oxidation of 2-propanol using oxygen as oxidant over other catalyst. Thus, in this study will be expanded to studied the effect of oxygen concentration for the gas phase oxidation of 2-propanol over TS-1 catalyst.

CHAPTER III

THEORY

3.1 Reactions of alcohols

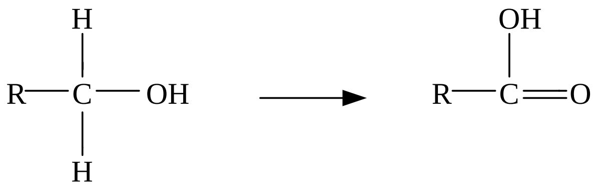
Reactions of an alcohol can involve the breaking of either of two bonds: the C-OH bond, with removal of the -OH group; or the O-H bond, with removal of -H bond. Either kind of reaction can involve substitution, in which a group replaces the -OH or -H, or elimination, in which a double bond is formed.

3.1.1 Oxidation

The oxidation of an alcohol involves the loss of one or more hydrogens (α-hydrogens) from the carbon bearing the -OH group. The kind of product that is formed depends upon how many of this α-hydrogens the alcohol contains, that is, upon whether the alcohol is primary, secondary, or tertiary.

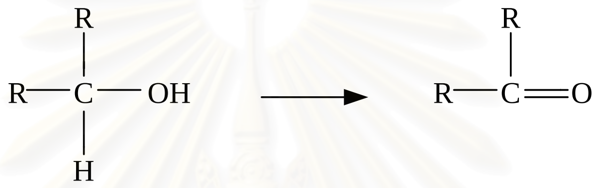
A primary alcohol contains two α-hydrogens, and can either lose one of them to form an aldehyde,

or both of them to form a carboxylic acid.



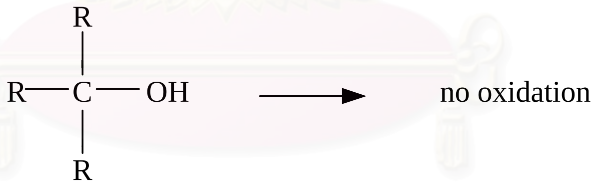
A 1^{o} alcohol A carboxylic acid

A secondary alcohol can lose its only α-hydrogen to form a ketone.



A 2^{o} alcohol A ketone

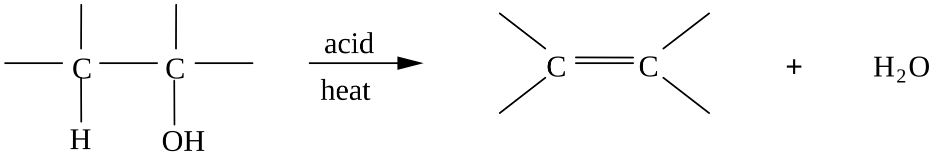
A tertiary alcohol contains no α-hydrogen and is not oxidized. (An acidic oxidizing agent can, however, dehydrate the alcohol to an alkene and then oxidized this).



A 3^{o} alcohol

3.1.2 Dehydration

Dehydration requires the presence of an acid and the application of heat. It is generally carried out in either of two ways: (a) by heating the alcohol with sulfuric or phosphoric acid; or (b) by passing the alcohol vapor over a catalyst, commonly alumina (Al_2O_3), at high temperature. An alcohol is converted into an alkene by dehydration (elimination of a molecule of water).



Alcohol Alkene Water

The various classes of alcohols differ widely in ease of dehydration, the order of reactivity being

Ease of dehydration of alcohol $3^o > 2^o > 1^o$

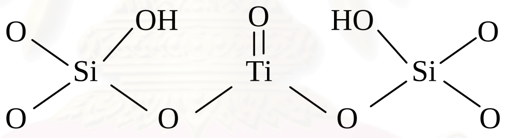
3.2 **Titanium silicalite** [Notari (1989)]

Titanium silicalite is an interesting material obtained by isomorphic substitution of trivalent metals or tetravalent metals in the framework of crystalline aluminosilicates or silicates. Titanium silicalites with MFI (TS-1) and MFI/MEL (TS-2) structures have been used in several oxidation reactions with H_2O_2 as the oxidizing agent [Centi et al. (2001)].

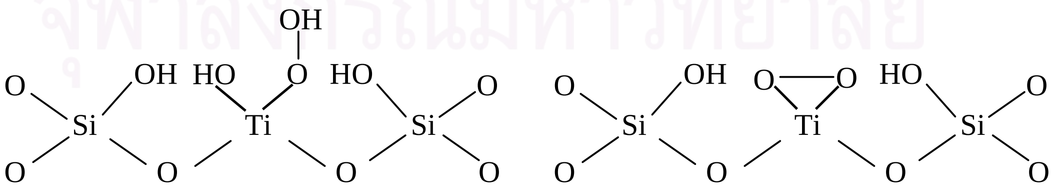
Titaniun has a stable valence of 4 and in an oxidizing medium it is very likely that this valence is maintained. An examination of the chemistry of Ti^{IV} compounds immediately shows that Ti^{IV} has a strong tendency to assume a high coordination number: with oxygen, six groups in octahedral coordination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

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

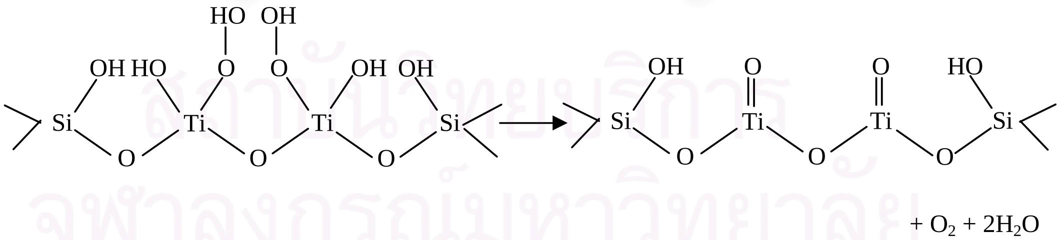
Finally, near neighbour positions of Ti^{IV} are occupied by Si^{IV} which in a field of $O^{=}$ is stable only in tetrahedral coordination. A simple representation of the sites where substitution has occurred which takes into consideration the various pieces of experimental evidence could be



Other more elaborated and detailed representations could be given, should the present model prove inadequate to interpret all experimental facts. Ti^{IV} in TS-1 maintains the strong affinity of soluble Ti^{IV} salts for H_2O_2 and in fact the addition of H_2O_2 gives rise to a strong yellow colour which can be attributed to the formation of surface titaniunperoxocompounds which can be in the hydrated or dehydrated form and which constitutes the actual oxidants.



Work carried out on Mo(VI) and W(VI) peroxocompounds [Amato et al. (1986)] has demonstrated that peroxocompounds can act as oxidants in stoichiometric epoxidations involving a nucleophilic attack of the substrate to the peroxidic oxygen: in the presence of excess H_2O_2 the peroxo compound is regenerated and this accounts for the catalytic nature of the reaction. It seems reasonable to assume that a similar mechanism operates in the case of Ti(IV) peroxocompounds. The relevance of isolated Ti^{IV} and the connection with catalytic performances appears to hold also for the TiO_2/SiO_2 catalyst. In fact high epoxide selectivities are obtained when TiO_2 is distributed on high surface area SiO_2 and its concentration is limited to 2% [Sheldon, (1980)]. It is very likely that at this low concentration Ti^{IV} are isolated and surrounded by Si^{IV}. Furthermore, SiO_2 or TiO_2 alone, or physical mixtures of SiO_2 and TiO_2 or various metal titanates exhibit no significant activity. Similarly, supporting TiO_2 on carriers different from SiO_2 like Al_2O_3, MgO or ZrO_2 leads to catalysts whose activity is lower or nil. One piece of evidence seems very convincing: when the TiO_2 concentration on the catalyst is reduced from 4% to 0.4%, all other conditions being equal, an increase in epoxide selectivity is obtained. The only effect that a reduction in the concentration of TiO_2 can have is an increase in the degree of dispersion of each Ti^{IV}: chances for each Ti^{IV} of having Si^{IV} as near neighbours increase, as does the selectivity of the catalyst. The correlation between the isolated Ti^{IV} and selectivity of the catalyst in epoxidation could be due to the fact that on Ti^{IV} having other Ti^{IV} as near neighbours, a mechanism proceeding through a bimolecular interaction of surface peroxo species could be operating which would give rise to a high decomposition rate of H_2O_2 or hydroperoxides to O_2. This mechanism could not operate on perfectly isolated Ti^{IV}.



Low decomposition of H_2O_2 (or hydroperoxides as well) means greater stability of titanium peroxo compound whose reduction can only be carried out by the organic substrate with increased yields of useful oxidized products. When the different results between TS-1 and TiO_2/SiO_2 in the hydroxylation of phenol are analyzed the existence of a “restricted transition state selectivity” must be assumed to explain the small amount of tars formed.

CHAPTER IV

EXPERIMENTAL

This chapter consists of experimental systems and procedures used in this study. The chapter is divided into three sections such as catalyst preparation, catalyst characterization and catalytic reaction. The chemicals, apparatus and procedures for catalyst preparation are explained in section 4.1. The composition, structure and surface properties of the catalyst characterized by various techniques such as XRF, XRD, BET, NH_3-TPD, and FT-IR are discussed in section 4.2. Finally, the details of the catalytic reaction are illustrated in section 4.3.

The scope of this study

The reaction conditions are chosen as follows:

Catalyst : Titanium silicalite-1 (TS-1)
Reactant : 2-Propanol
Feed composition : 2-Propanol 5 vol%, Oxygen 0-8 vol%, Argon balance
Flow rate of reactant : 100 ml/min
Reaction temperature : 100-500^{o}C
Space velocity : 60,000 $g^{-1}h^{-1}$

4.1 Catalyst preparation

4.1.1 Chemicals

The details of chemicals used in the preparation procedure of TS-1 are shown in Table 4.1.

Table 4.1 The chemicals used in the catalyst preparation

Chemical	Grade	Supplier
Tetrapropylammonium hydroxide, 1.0 M solution in water	-	Aldrich
Tetraethyl orthosilicate 98%	-	Aldrich
Tetraethyl orthotitanate 95%	For synthesis	Merk-Schuchardt

4.1.2 Preparation Procedures

Tinanium silicalite-1 (TS-1) was prepared from the hydrothermal procedure.

4.1.2.1 Preparation of Solution

All procedures in this section are operated in Ar atmosphere. Tetraethyl orthotitanate was added dropwise into tetraethyl orthosilicate and then the mixture solution was stirred at 35°C. To the clear solution, tetrapropylammonium hydroxide was added with stirring and then heating at 80°C for 1 hr. The clear gel was stirred at 80°C for 3 hrs to aid hydrolysis, during the procedure the volume of the mixture solution was controled by adding de-ionized water.

4.1.2.2 Crystallization

The mixture of solution was filled in a 250 ml pyrex glass. The glass container was placed in a stainless steel autoclave. The atmosphere in the autoclave was replaced by nitrogen gas and pressurized up to 3 kg/cm^2 gauge. The mixture was heated from room temperature to 175 ^{o}C with a heating rate of 2 ^{o}C/min and held at this temperature for 4 days while being stirred at 60 rpm, followed by cooling the mixture to room temperature in the autoclave overnight. The product crystals were washed with de-ionized water until the pH of the washing water decreased from about 10 to 7. Finally the crystals were dried in an oven at 110 ^{o}C for 24 h.

4.1.2.3 Calcination

The dry crystals were calcined in an air stream at 550 ^{o}C and held at that temperature for 6 h, by heating them from room temperature to 550 ^{o}C with heating rate 8.6 ^{o}C/min. The organic templates were burned off leaving cavities and channels in the crystals. Finally, the calcined crystals were cooled down to room temperature and stored in a dessicator for later use.

4.2 Catalyst characterization

4.2.1 Determination of composition content of catalysts

The chemical composition analysis of elements of the catalyst was performed by X-ray fluorescence (XRF) using Siemens SRS3400 at Scientific Intruments Service Centre, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang.

4.2.2 X-ray diffraction (XRD)

The crystallinity and X-ray diffraction patterns of the catalysts were performed by an X-ray diffractometer, SIEMENS D5000, using Cu Kα radiation with Ni filter. The operating conditions of measurement are shown below:

2θ range of detection:	6-40^{o}
Resolution:	0.04^{o}
Number of scan	10

4.2.3 BET surface area measurement

Procedure

The carrier gas which mixed with 30 % nitrogen and 70% helium flowed through the system at the flow rate 15 ml/min. The sample, 0.3 g, was placed in the unit cell, which was heated up to 200 °C and held at this temperature for 1 hour to remove water in the sample. Next step, the sample was cooled down to room temperature and ready to measure the surface area. There were two steps to measure the surface area.

(1) Adsorption step

The sample was dipped into a liquid nitrogen bath. Nitrogen was adsorbed on the surface of the sample until an equilibrium was reached. And then the equipment showed the adsorption peak area.

(2) Desorption step

A liquid nitrogen bath was moved away from the unit cell. In order to desorb nitrogen from the surface of sample ,the nitrogen-adsorbed sample was blowed with fan. When this step was completed, the equipment showed the desorption peak area obtain from the Micromeritics Chemisorb 2750 analyzer.

(3) The BET surface area means the desorption peak area divided by weight of sample.

4.2.4 Fourier transform Infrared (FT-IR)

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

4.2.5 NH_3 Temperature Programmed Desorption (NH_3-TPD)

Temperature programmed desorption of ammonia (NH_3-TPD) was used to determine the acid properties of catalysts. NH_3-TPD were carried out using a flow apparatus. The catalyst sample (0.1 g) was treated at 550^{o}C in helium flow for 1h and then saturated with 15 %NH_3/He mixture after cooling to 100 ^{o}C. After purging with helium at 100 ^{o}C for 1 h to remove weakly physisorbed NH_3, the sample was heated to 550 ^{o}C at therate of 10 ^{o}C/min in a helium flow of 50 ml/min. The amount of acid sites on the catalyst surface was calculated from the desorption amount of NH_3. It was determined by measuring the areas of the desorption profiles obtained from the Micromeritics Chemisorb 2750 analyzer

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

4.3 The catalytic activity measurements

4.3.1 Equipment

Flow diagram of the reaction system is shown in Figure 4.5. The system consists of a saturator, a microreactor, an automatic temperature controller, an electrical furnace and a gas controlling system. The liquid phase reactant was filled in the saturator. Ar is passed through the evaporator to evaporate the reactant and carried to the microreactor.

The microreactor is made from a stainless steel tube. Three sampling points are provided above and below the catalyst bed. Catalyst was placed between two quartz wool layers.

The gas supplying system consists of cylinders of ultra high purity argon and air, each equipped with pressure regulators (0-120 psig), on-off valves and mass-flow controller for adjusting the flow rate of these gases.

A Shimadzu GC8A gas chromatograph equipped with flame ionization detector measured the composition of oxygenate compounds in the feed and product streams.

A Shimadzu GC8A gas chromatograph equipped with a thermal conductivity detector was used to analyze permanent gases and water. Two columns, a 5A molecular sieve to separate oxygen and carbon monoxide and a Porapak-Q column to separate CO_2 and water were operated in parallel. The operating conditions are shown in the Table 4.4.

Table 4.2 Operating conditions for gas chromatograph.

Gas chromatograph	Shimadzu GC8A	Shimadzu GC8A
Detector	TCD	FID
Column	MS-5A, Porapak-Q	3% SP-1500
Carrier gas	He (99.999%)	N_2 (99.999%)
Carrier gas flow	25 ml/min	25 ml/min
Column temperature		
- Initial	100°C	70°C
- Final	100°C	120°C
Heating rate	-	4°C/min
Detector temperature	130°C	120°C
Injector temperature	130°C	120°C
Analyzed gas	CO_2, CO	Oxygenates

4.3.2 Oxidation procedure

The oxidation procedures are described in the detail below.

1. 0.1 gram of catalyst was packed in the middle of the stainless steel microreactor located in the electrical furnace.

2. The total flow rate was 100 ml/min. Flow rate of 2-propanol, argon and air were regulated by mass Flow controller. The gas mixtures for oxidation reaction were 5 vol% 2-propanol, 2-16 vol% oxygen and balance with argon.

3. The reaction temperature was between 100-500^{o}C. Before increasing the reaction temperature, the feed gas was analyzed by using the GC-FID in order to confirm the steady state operation of the system. The reaction temperature was increased by a 50 ^{o}C step and hold at this temperature for 10 minutes. The effluent gases were analyzed by using the GC-FID and GC-TCD gas chromatographs. The chromatograph data were changed into mole of propylene, 2-propanol, isopropyl ether, acetone and CO_2 by calibration curves in Appendix D.

4. The result of catalytic test was calculated in the term of

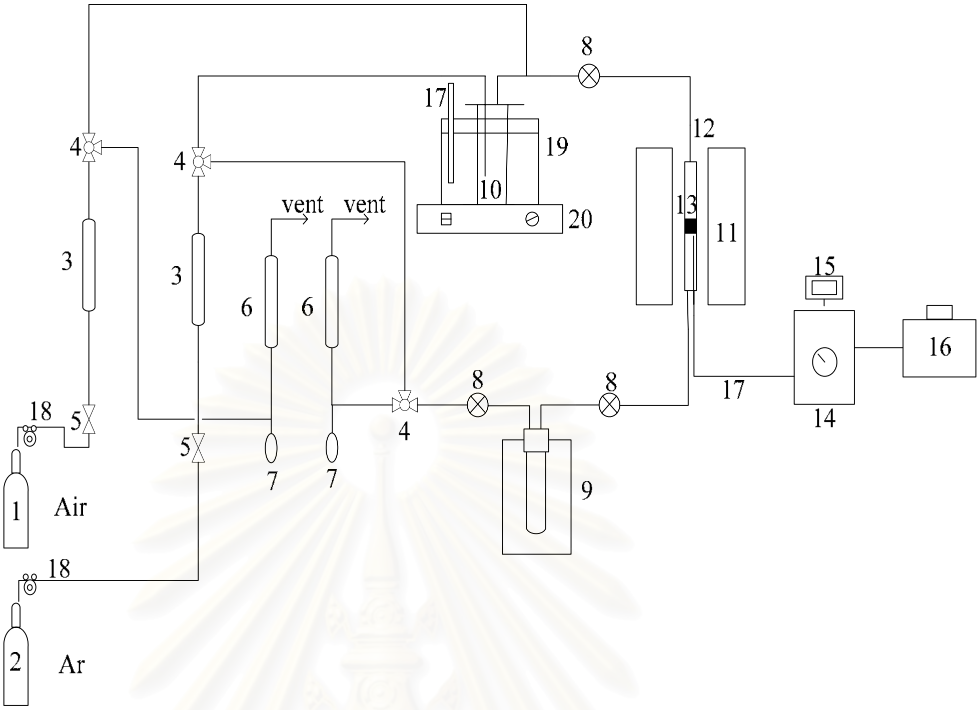
$$\%\ \text{A conversion (C)} = \frac{\text{mole of A converted}}{\text{mole of A in feed}}$$

$$\%\ \text{Selectivity (S) to B} = \frac{\text{mole of B formed}}{\text{mole of A converted}} \times \frac{\text{no. of C atom of B}}{\text{no. of C atom of A}} \times 100$$

$$\%\ \text{Yield (Y) to B} = \frac{\%\ \text{A conversion} \times \%\ \text{selectivity toB}}{100\%}$$

Where, A is reactant

B is product



1. Air cylinder
2. Ar cylinder
3. Mass Flow controller
4. Three-way-valve
5. Gate valve
6. Rotary meter
7. Rubber cock
8. Sampling point
9. Condense
10. Saturator
11. Furnace
12. Reactor
13.Catalyst bed
14. Temperature controller
15. Digital temperature indicator
16. Variable voltage transformer
17. Thermocouple/Thermometer
18. Pressure regulator
19. Water bath
20. Heating and Stirring controller

Figure 4.1 Flow diagram of oxidation reaction system.

CHAPTER V

RESULTS AND DISCISSION

In this chapter, results and discussion are divided into two parts the first one is the results of characterization of TS-1 sample, such as XRF, BET, XRD, FT-IR and NH_3-TPD. The second part is the results of catalytic activity of alcohol oxidation reactions.

5.1 Catalyst characterization

5.1.1 Determination of composition content and BET surface area of TS-1 sample

The results of mole ratio of Si/Ti and BET surface area of the TS-1 sample, which were analyzed by XRF and BET nitrogen adsorption method respectively, are represented in Table 5.1.

Table 5.1 The mole ratio of Si/Ti and BET surface area

Catalyst sample	Mole ratio of Si/Ti	BET surface area (m^2/g)
TS-1	32	181

5.1.2 X-ray Diffraction (XRD)

Figure 5.1 shows the XRD patterns of the synthesized TS-1. The XRD pattern showed six main characteristic peaks at 2θ as 8, 8.8, 14.8, 23.1, 24 and 29.5 degree, marked with dark circle.

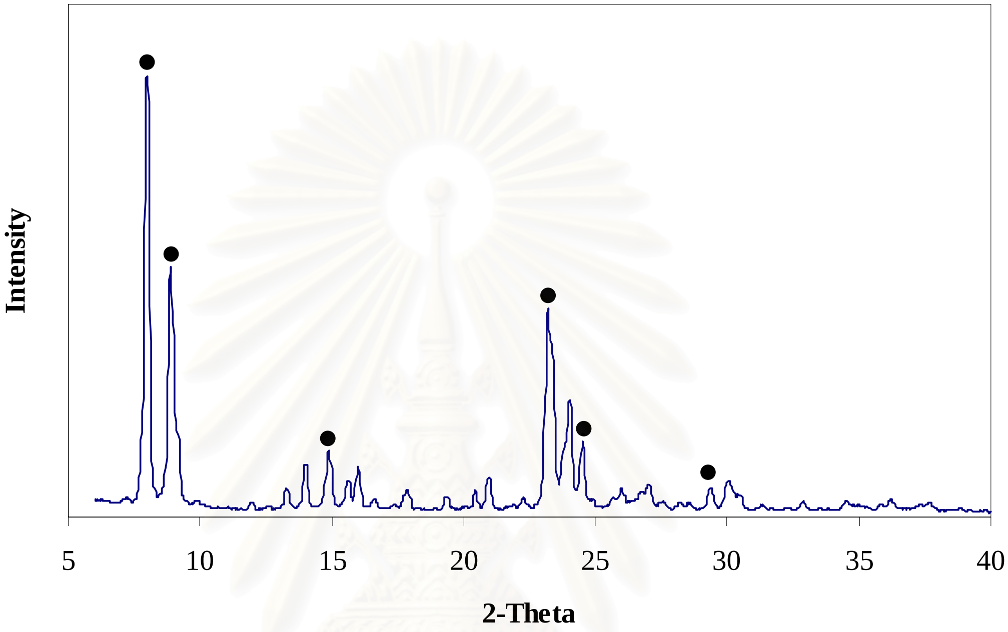


Figure 5.1 X-ray diffraction pattern of the synthesized TS-1

The pattern obtained is the pattern typical for a crystalline zeolite having a MFI structure. The result showed that the catalyst contained a well-defined single-phase XRD pattern and was consistent to those already reported for TS-1 [Taramasso et al. (1983)]. The incorporation of Ti^{4+} into the framework is indicated by the conversion of the monoclinic structure of silicalite-1 to an orthorhombic structure, evidenced by the disappearance of peaked splittings at 2θ = 24˚ and 2θ = 29.5˚ [Taramasso et al. (1983)]. Because of the low Ti content in the support materials (Ti < 3 wt%), additional TiO_2 crystalline phases, i.e., anatase (2θ = 25.5˚) and rutile (2θ = 48.2˚) [Yap et al. (2004)], did not appear in the XRD pattern.

5.1.3 Fourier Transform Infrared Spectroscopy (FT-IR)

General character

A comparative IR spectrometric study was performed to obtain information concerning the existence of framework titanium. The spectrum obtained in the region 700–1200 cm^{-1} is exhibited in figure 5.2. The vibrational spectrum of TS-1 is characterized by an absorption band in the 900–975 cm^{-1} region [Taramasso et al. (1983)]. It has been suggested that the presence of a 960–975 cm^{-1} band is a necessary, but not sufficient, condition for catalytic activity [Huybrechts et al. (1991)]. Thus, defective orthorhombic silicalites, with fully hydroxylated nanocavities generated by extraction of a few adjacent (SiO$_4$) units, have been characterized by an extra-broad IR absorption in the 960-975m^{-1} [Perego et al. (1986)] as shown in figure 5.2.

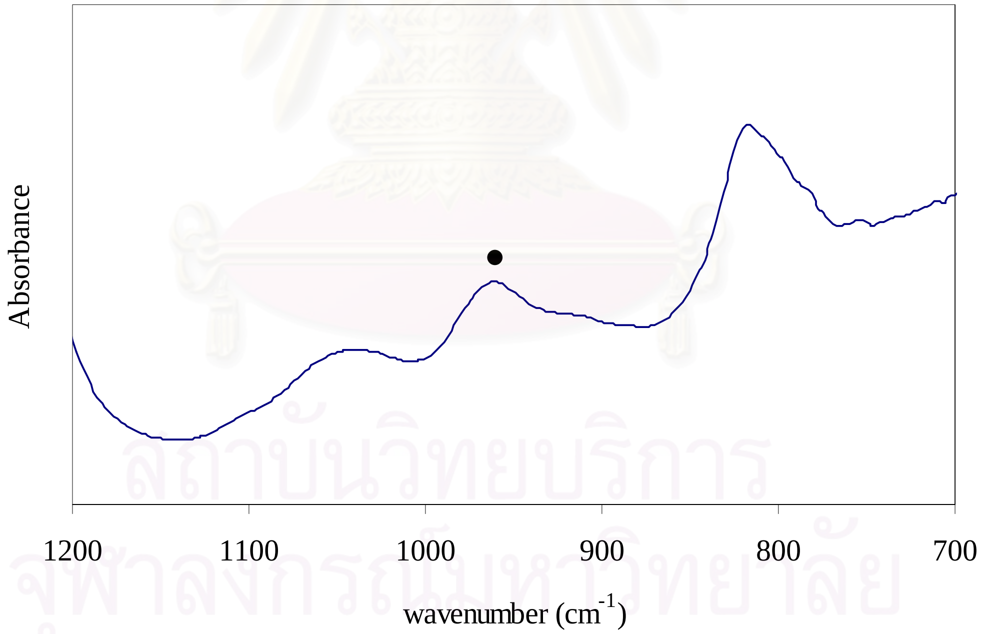


Figure 5.2 IR spectrum of the synthesized TS-1

5.1.3 NH_3 Temperature Programmed Desorption (NH_3-TPD)

NH_3-TPD characterization was conducted to survey the acid strength and the amount of acid site of TS-1. During the analysis it was observed that NH_3 began to desorb from the sample since 80 ^{o}C and nearly completely desorb at a temperature around 300 ^{o}C. From the result shown in figure 5.3a, it can be seen that only acid sites with acid strength around 148.5 ^{o}C exists on the surface of the synthesized TS-1. The total acid site on the surface of the synthesized TS-1 is 382 μmol/g which is calculated by dividing the amount of adsorped NH_3 (calculated form the peak area) with the weight of the catalyst (0.1 g).

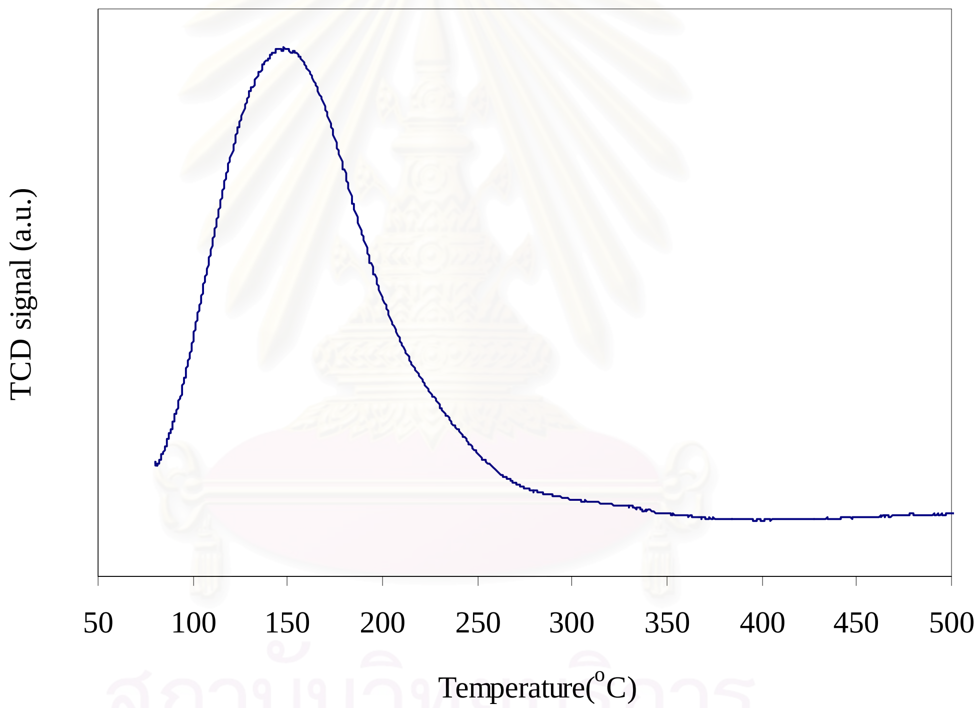


Figure 5.3a NH_3 temperature programmed desorption profile of the synthesized TS-1

An attempt has been made to deconvolute this peak, the deconvolution result (in figure 5.3b) can spilt the peak in figure 5.3a into 2 peaks at 145^{o}C and 228 ^{o}C, consecutively. From the reported peak area of the peak fitting program, ratio of each acid site on catalyst surface are 92.95 % and 7.05 % for the peaks at 145 ^{o}C and 228

^{o}C, respectively. Therefore the amount of the weak acid site (145 ^{o}C) is 361.64 μmol/g and the amount of the strong acid site (228 ^{o}C) is 20.36 μmol/g

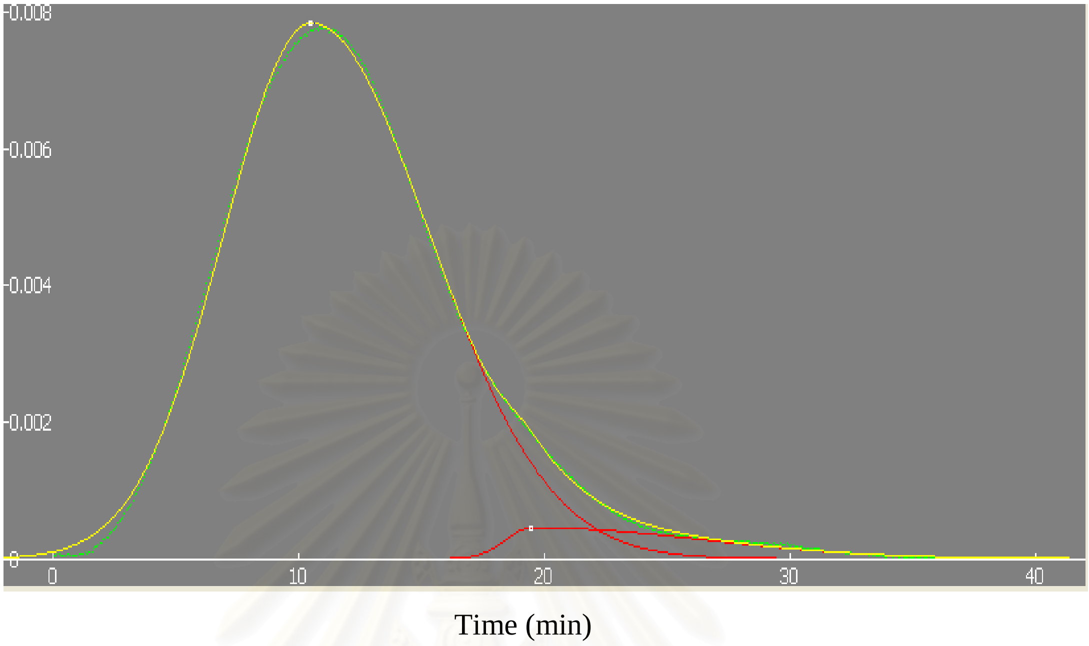


Figure 5.3b The deconvolution of NH_3 temperature programmed desorption profile of the synthesized TS-1 from peak fitting program

5.2 Catalytic activity

This part investigates the catalytic activity of the synthesized TS-1 for 2-propanol oxidation.

The results of catalytic performance of 2-propanol oxidation are presented in figures 5.4a-5.4d for 2 vol%, 4 vol%, 6 vol%, 8 vol%, 12vol% and 16vol% of oxygen concentration in the feed gas, respectively.

For 2 vol% of oxygen concentration (figure 5.4a), the conversion of 2-propanol becomes observable at the reaction temperature about 150 ^{o}C and increases up to 100% at about 300 ^{o}C. In the reaction temperature region below 300 ^{o}C, the major product formed is propylene with selectivity higher than 90% while the rest is acetone. When the reaction temperature is increased from 300 ^{o}C to 350 ^{o}C, the selectivity to propylene drops about 20% with an abrupt increase of acetone selectivity. In addition, CO_2 also appears in a significant amount. At 500 ^{o}C, the selectivity of propylene drops to a value about 56% while the selectivity to acetone increases to about 42%. The selectivity to CO_2 still remains below 2%.

The result of 2-propanol oxidation in a gas stream containing 4 vol% oxygen is illustrated in figure 5.4b. The product distribution of this system is similar to the 2 vol% oxygen system. In this system, less propylene and more acetone formed at high reaction temperature. The selectivity to carbon dioxide also slightly increases.

When the oxygen concentration is another 2 vol% increased (from 4 vol% to 6 vol%), the conversion of 2-propanol (see figure 5.4c) rapidly increases from nearly zero at 150 up to 100% at about 250 ^{o}C. Between 250-400 ^{o}C, the selectivity to propylene rapidly drops whereas the selectivity to acetone substantially increases. The selectivity to CO_2 increases up to a level at the reaction temperature about 400 ^{o}C and stays at this level up to the reaction temperature 500 ^{o}C. The oxidation result obtained from using 8 vol% oxygen is also similar to the 6 vol% oxygen system.

It should be noted here that, when the oxygen concentration in the feed gas is 8 vol% or lower, the selectivity to acetone keeps increasing as the reaction temperature increases.

Figure 5.4e shows the oxidation of 2-propanol in a 12 vol% oxygen system. The conversion of 2-propanol increases rapidly between 150 and 250 ^{o}C. The major products in this reaction temperature region are propylene (selectivity 80% or higher) and acetone (selectivity 20% or lower). Between 300-350 ^{o}C, the selectivity of propylene abruptly drops from the 80% level to the 20% level, or 60% drops. On the contrary, in this reaction temperature region, the selectivity of acetone also suddenly increases, but only about 35-40%. Another product suddenly increases its amount is in this temperature region is CO_2. The selectivity to CO_2 jumps from near 0% to about 20% when the reaction temperature is increased only 50 ^{o}C. When the reaction temperature is further raises beyond 350 ^{o}C, the selectivity to acetone reversely changes into the other direction. The selectivity of acetone drops after reaching a maximum at 350 ^{o}C while the selectivity to CO_2 continually increases. The selectivity to propylene, however, remains unchanged in this reaction temperature region.

The case of 16 vol% oxygen concentration (figure 5.4f) is similar to the 12 vol% oxygen case. More acetone is formed in the reaction temperature between 300-350 °C. From 350 to 500 °C, the selectivities of both acetone and propylene drop to a level around 10% while the selectivity to CO_2 increases up to 80%.

It should be noted here that the formation of CO_2 is not occurred significantly when the reaction temperature is not higher than 300 °C, independent from the oxygen concentration in the feed gas. The rate of CO_2 formation increases rapidly when the reaction temperature and oxygen concentration are increased. The effects of reaction temperature and oxygen concentration are discussed below.

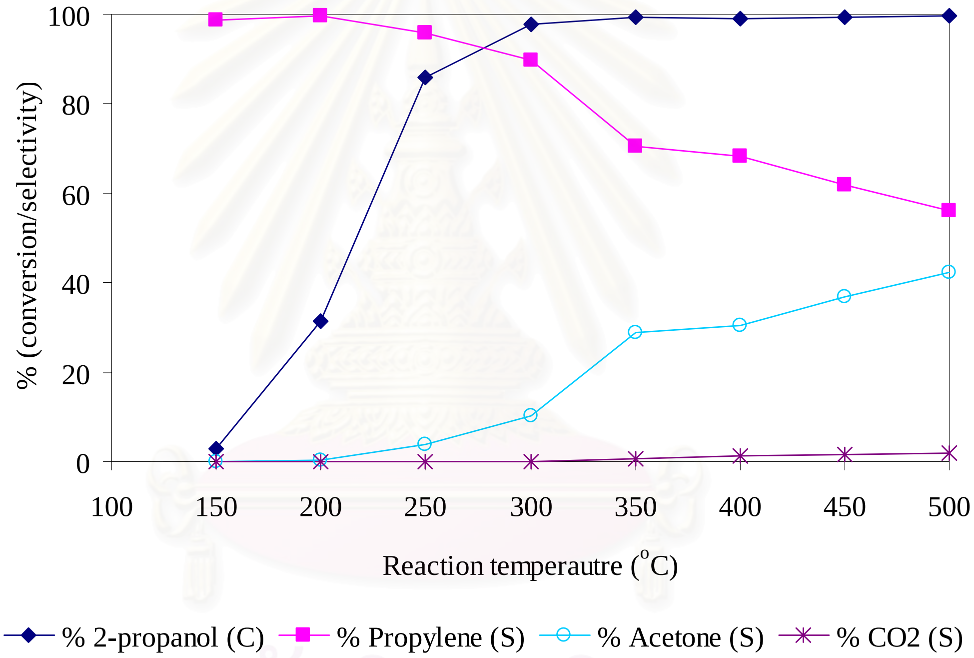


Figure 5.4a Product selectivities of 2-propanol over TS-1 for 2 vol% O_2 system (C : conversion and S : selectivity)

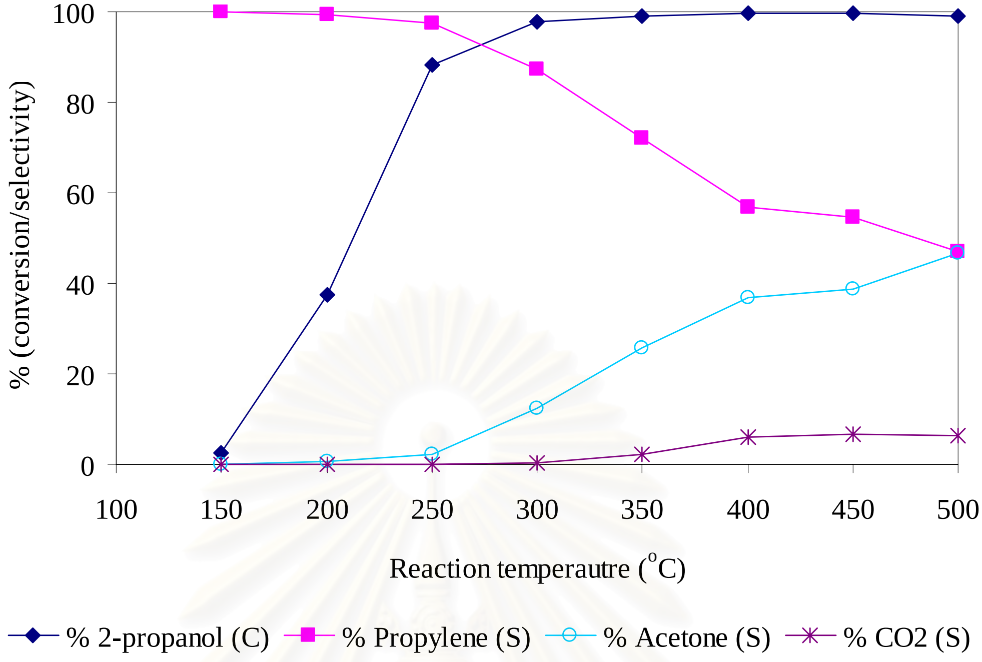


Figure 5.4b Product selectivities of 2-propanol over TS-1 for 4 vol% O_2 system (C : conversion and S : selectivity)

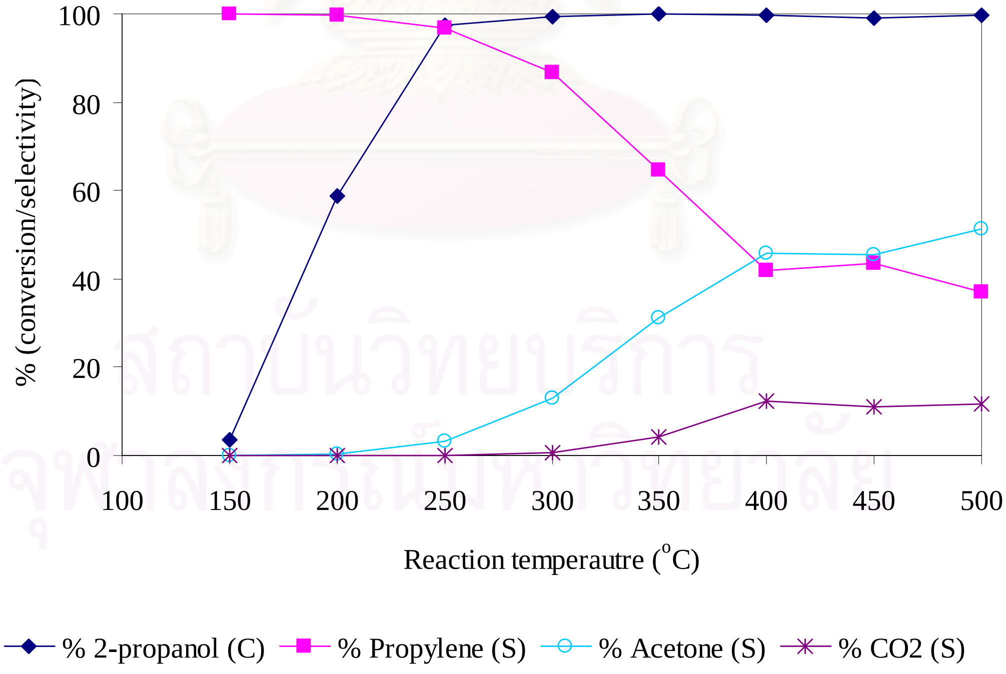


Figure 5.4c Product selectivities of 2-propanol over TS-1 for 6 vol% O_2 system (C : conversion and S : selectivity)

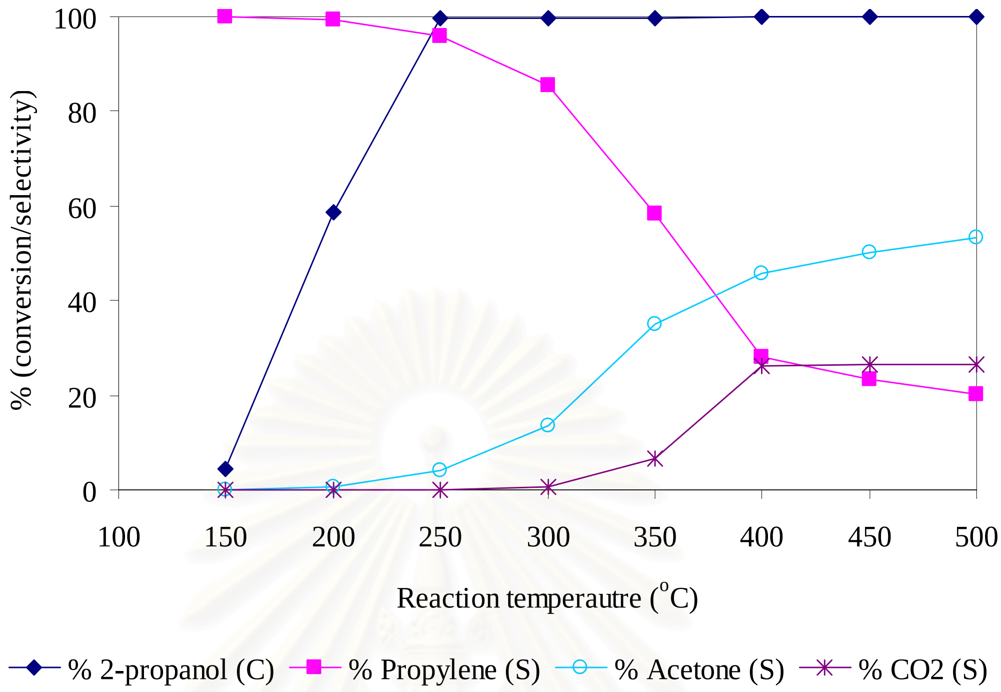


Figure 5.4d Product selectivities of 2-propanol over TS-1 for 8 vol% O_2 system (C : conversion and S : selectivity)

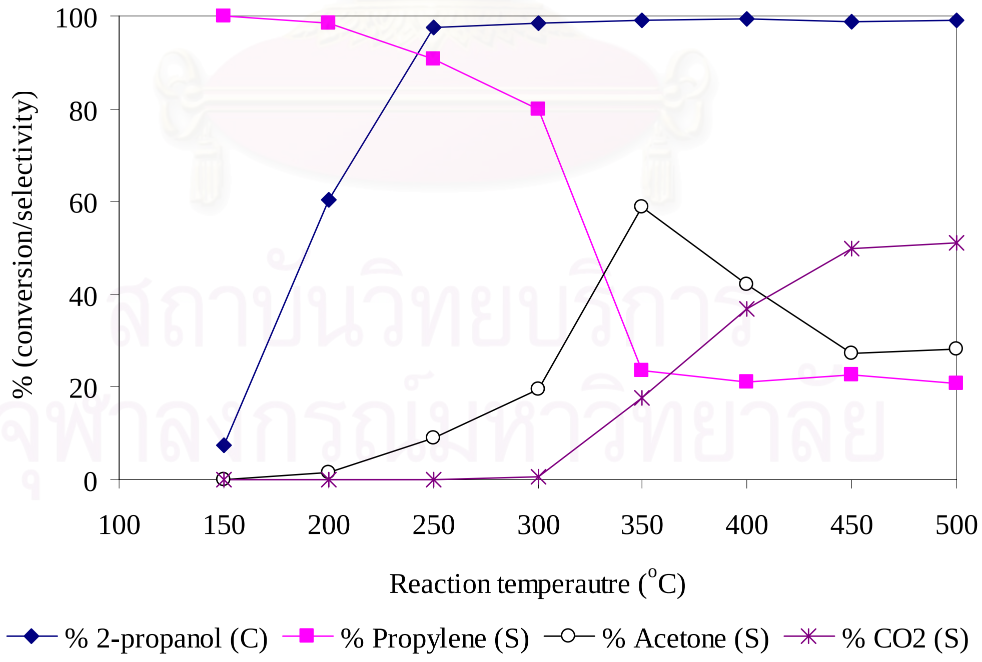


Figure 5.4e Product selectivities of 2-propanol over TS-1 for 12 vol% O_2 system (C : conversion and S : selectivity)

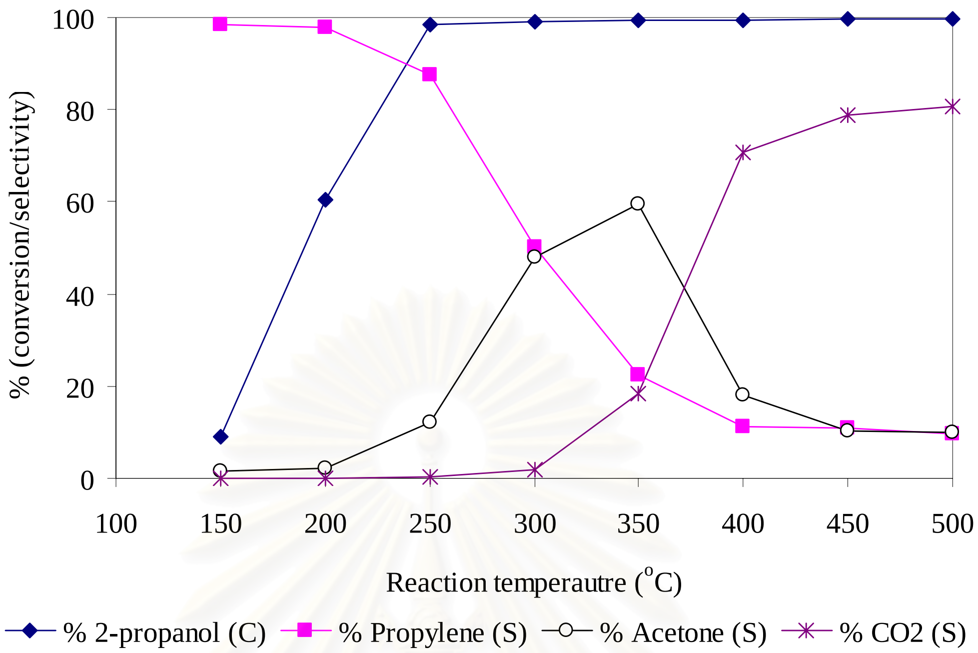


Figure 5.4f Product selectivities of 2-propanol over TS-1 for 16 vol% O_2 system (C : conversion and S : selectivity)

The results shown in figures 5.4a to 5.4f and described above indicate that 2-propanol can be dehydrated to propylene and oxidized to acetone. The dehydration reaction is dominant in the low reaction temperature region (i.e. not higher than 300 °C) while the oxidation reaction becomes dominant in the high reaction temperature region (at 350 °C and beyond).

Theoretically, acetone can also be produced from the oxidation of propylene. To check the formation of acetone via the propylene oxidation route, the oxidation of propylene (figure 5.5) in the presence of oxygen (5 vol% propylene, 8 vol% oxygen) was carried out. The result shows that, over the TS-1, the oxidation of propylene produces a lot of organic compounds which, at this moment, cannot be labeled. But it can be confirmed that among those organic compounds, then is no acetone formed. Another major product is CO_2 which becomes dominant at the reaction temperature about 350 °C and beyond. Thus, all the acetone formed in the previous results should come from the oxidation of 2-propanol.

The formation of CO_2 via the oxidation of acetone route is also investigated. The result is showed in figure 5.6. The concentration of acetone is 5 vol% and the concentration of oxygen is 8 vol%. It can be seen that acetone can also be further oxidized to CO_2 with a slightly higher rate than the oxidation of propylene to CO_2. The oxidation of acetone also produces some organic species but less than the oxidation of propylene. The selectivity to CO_2 rises up to nearly 100% at the reaction temperature about 450 ^{o}C. CO_2 observed in each experiment, thus, should come from the further oxidation of propylene and acetone, in which more CO_2 is generated from acetone than propylene.

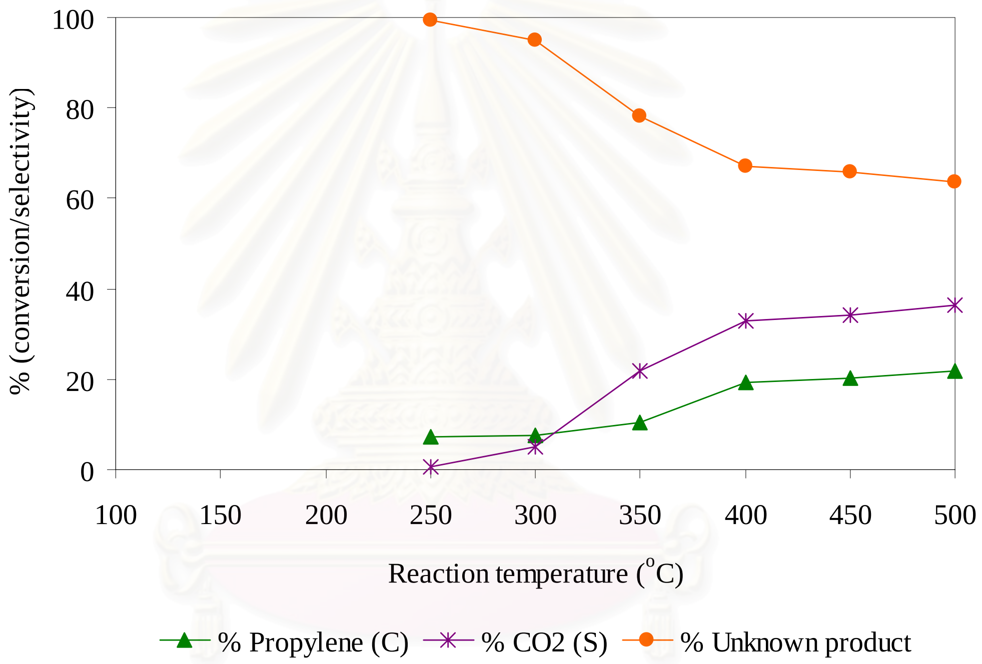


Figure 5.5 Product selectivities of Propylene over TS-1 for 8 vol% O_2 system (C : conversion and S : selectivity)

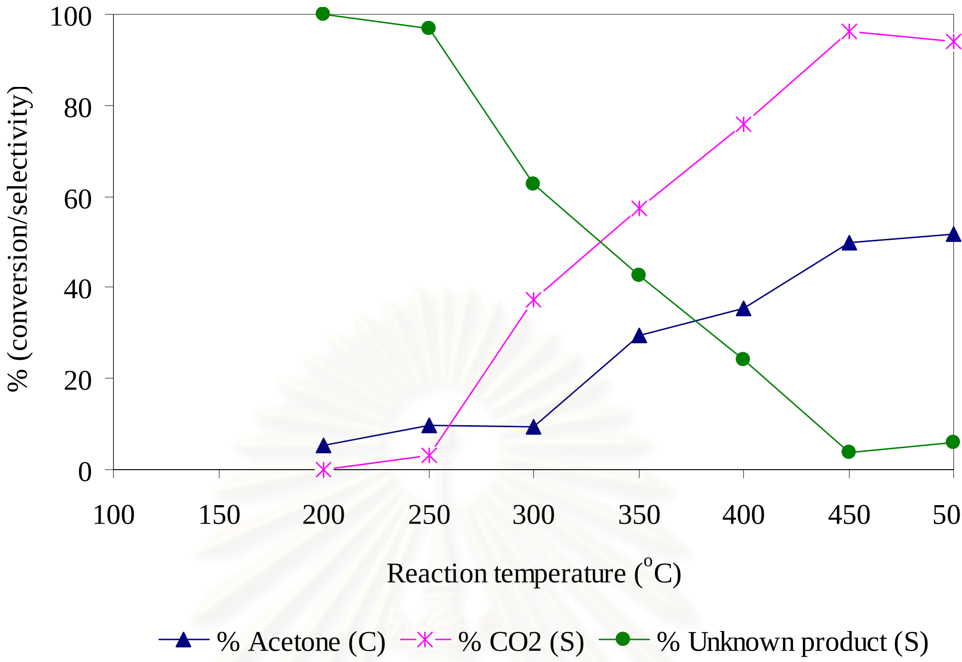


Figure 5.6 Product selectivities of acetone over TS-1 for 8 vol% O_2 system (C : conversion and S : selectivity)

In a previous research [Kedusda C., 2005], the oxidation of propylene produces mainly acetone (with selectivity nearly 100%) and a small amount of CO_2. The catalytic activity of the catalyst and in the previous research, as can be seen from the conversion of propylene, was higher than the activity of the catalyst and in the present study. The difference between the catalysts used in both studies is the amount of the strong acid site. The catalyst used in the present study has much less amount of the strong acid site. Since the strong acid site possesses higher oxidation activity than the weaker acid site, the appearance of such unidentified organic compounds observed in the present study is probably the result of the disability of the synthesized TS-1 to complete the total oxidation process and/or produces another reaction pathway.

The 2-propanol conversion for all oxygen concentrations is summarized in figure 5.7. It is found that, the higher oxygen concentration, the higher the 2-propanol conversion. This is the result of the summation of 2 reactions i.e., the dehydration to propylene and the oxidation of 2-propanol to acetone. The dehydration of 2-propanol to propylene does not require oxygen but the oxidation does. The increase conversion of 2-propanol is, therefore, the result of the increase in the oxidation reaction (i.e., the production of acetone and CO_2). Beyond 300 ^oC, the conversion of 2-propanol reaches the maximum value about 100 % and is independent on the oxygen concentration.

The selectivities to propylene, acetone, and CO_2 for all oxygen concentration are summarized in figures 5.8, 5.9, and 5.10, consecutively. It is observed that the selectivity to propylene is independent on the oxygen concentration below 300 ^oC. The summation of selectivities to acetone and CO_2 increases with the increase in oxygen concentration in the reaction temperature range 250-500 ^oC whereas the selectivity to propylene decreases. The less of propylene formation shows that the oxidation and combustion well occurs than the dehydration. Moreover, it indicates that the selectivity shifts from the dominance of an oxidation path in an oxygen-poor condition to combustion dominance in an oxygen-rich environment beyond 350 ^oC. These behaviors indicate that the oxygen concentration affects the amount of 2-propanol consumed in the various reactions over TS-1.

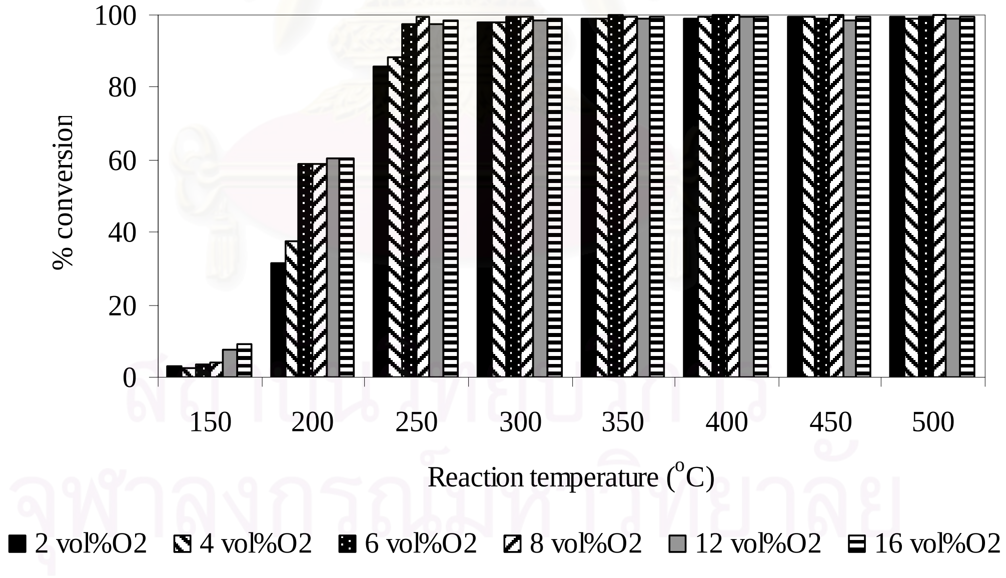


Figure 5.7 The 2-propanol conversion of 2-propanol oxidation over TS-1 for various concentration of oxygen (2, 4, 6, 8, 12, and 16 vol%, respectively)

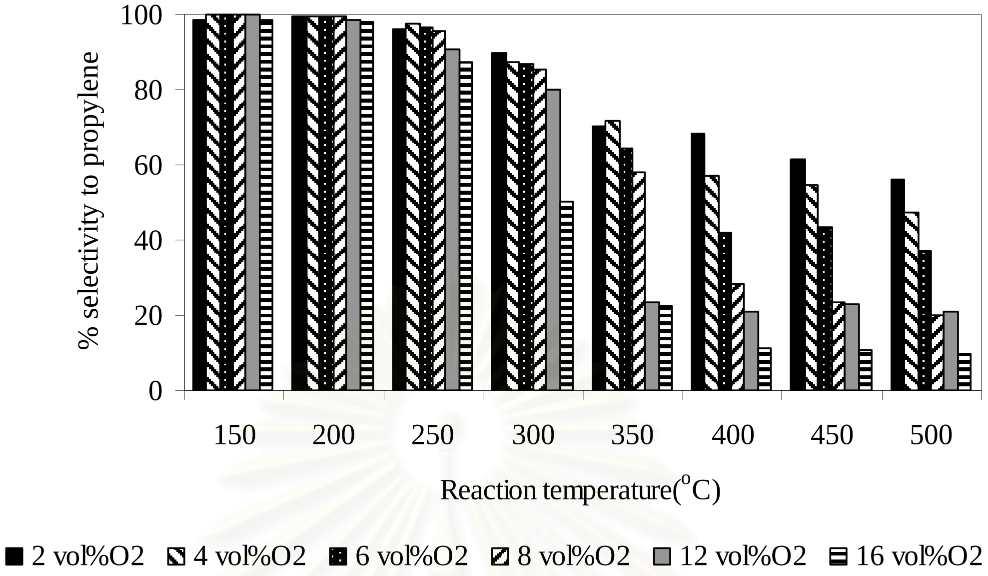


Figure 5.8 The selectivity to propylene of 2-propanol oxidation over TS-1 for various concentration of oxygen (2, 4, 6, 8, 12, and 16 vol%, respectively)

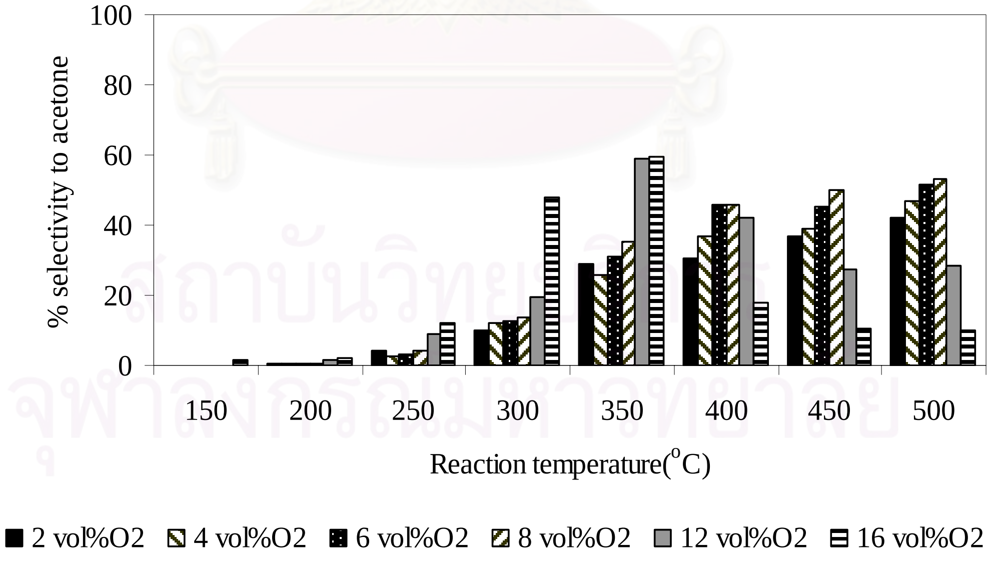


Figure 5.9 The selectivity to acetone of 2-propanol oxidation over TS-1 for various concentration of oxygen (2, 4, 6, 8, 12, and 16 vol%, respectively)

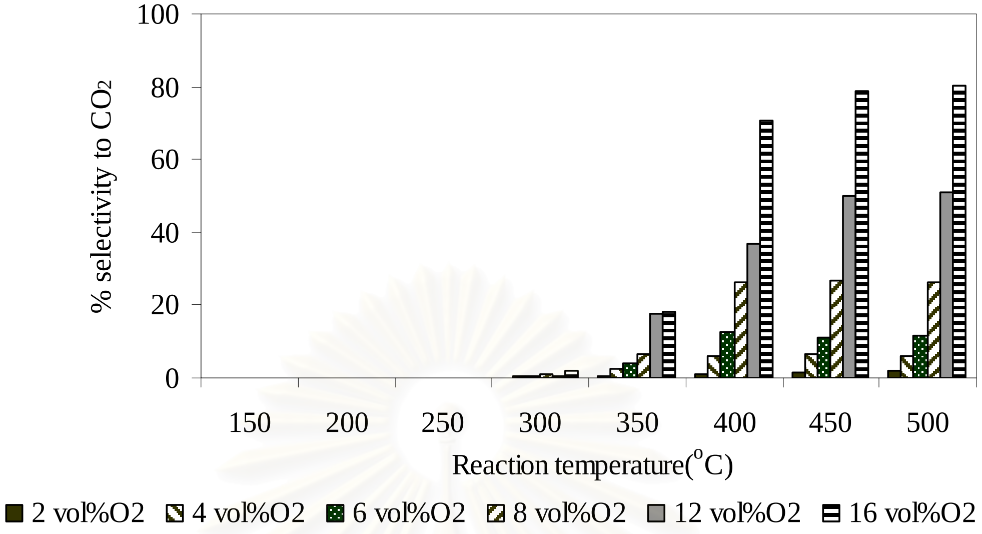


Figure 5.10 The selectivity to CO_2 of 2-propanol oxidation over TS-1 for various concentration of oxygen (2, 4, 6, 8, 12, and 16 vol%, respectively)

It should be noted here that the synthesized TS-1 of the present study has one property differences from those used in the previous study [Kedsuda C., 2005] or the other co-current studies [Eakawut P., Darunee S., Rattamwalee S., Nitiporn S., 2006]. The difference is the amount of the weak and the strong acidic site is much lower than the previous and the co-current studies. Because of this reason, the selectivity to propylene observed in the present study is higher than the selectivity to acetone. This finding confirms that the major role of the weak acid site is the dehydration reaction. The weak acid site may be able to play as the oxidation site, but not a good one. Otherwise, the selectivity to acetone and CO_2 must be higher than that are observed here.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

From the results exhibited and discussed in Chapter V, the following conclusions of the present research can be summarized as follows:

1. The reaction temperature influences the conversion and product selectivities of the reaction of 2-propanol over TS-1. Propylene is the main product in the low reaction temperature range. Acetone becomes the major product in the high reaction temperature range and low oxygen concentration. At high oxygen concentration and high temperature, CO_2 becomes the prominent reaction product.

2. In the low reaction temperature range, the increase in oxygen concentration promotes the oxidation of 2-propanol to acetone. This leads to the increase in the selectivity to acetone accompany with the decrease in the selectivity of propylene because there is less 2-propanol to be dehydrated.

3. The oxidation of propylene requires the site with higher acid strength than the oxidation of acetone. The weak acid site of the catalyst investigated in the present work has no enough reactivity to oxidized propylene to CO_2 while it can still destroy acetone to the combustion product. CO_2 observed, therefore, in this study mainly comes from the further oxidation of acetone.

6.2 Recommendations for future studies

From the previous conclusions, the following recommendations for future studies are proposed.

1. Because the property of catalyst (such as acid site, type of acid site, the structure) influences the catalytic property, therefore the effect of synthesis of TS-1

on the gas phase of 2-propanol oxidation using oxygen as oxidant on should be further studied.

2. Because the water content affect on the oxidation of 2-propanol, therefore the addition of water in the gas phase of 2-propanol oxidation using oxygen as oxidant over TS-1 should be further studied

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APPENDICES

APPENDIX A

CALCULATION FOR CATALYST PREPARATION

Calculation of Si/Ti Atomic Ration for TS-1

The calculation is based on weight of tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$) for Si source.

Molecular Weight of Si = 28.0855
Molecular Weight of TEOS = 208.330
Weight percent of Si in TEOS = 98

Using TEOS 17.208 g

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

$$= 17.208 \times (98/100) \times (1/208.330)$$

$$= 0.0809$$

For example, to prepare TS-1 at Si/Ti atomic ratio of 32 by using tetraethyl orthotitanate (TEOT, $C_8H_{20}O_4Ti$) for Ti source.

Molecular Weight of Ti = 47.88
Molecular Weight of TEOT = 228.15
Weight percent purity of TEOT = 95

Si/Ti atomic ratio = 32

mole of TEOT required = 0.0809/32
= 2.53×10^{-3} mole

amount of TEOT = $2.53 \times 10^{-3} \times 228.15 \times (100/95)$
= 0.608 g

which used in Topic 4.1.2.1.

APPENDIX B

CALCULATION OF DIFFUSIONAL LIMITATION EFFECT

External diffusion limitation

The alcohol oxidation reactions are considered to be an irreversible first order reaction occurred on the pore surface of catalyst particles in a fixed bed microreactor. Assume isothermal operation for the reaction.

In the experiment, 5 vol% 2-propanol, 0-8 vol% oxygen balance with nitrogen were investigated, in this case using 5 vol% 2-propanol, 8 vol% oxygen and balance with nitrogen was used as an example system calculation. Molecular weight of 2-propanol, nitrogen and oxygen (8 vol%) are 60.09, 28.02 and 31.98 respectively. Thus, the average molecular weight of the gas mixture was calculated as follows:

$$\begin{aligned} M_{AB} &= (0.05\times60.09) + 0.95\times((0.92\times28.02)+(0.08\times31.98)) \\ &= (0.05\times60.09) + (0.95\times28.34) \\ &= 29.928 \text{ g/mol} \end{aligned}$$

Calculation of reactant gas density

Consider the 2-propanol oxidation is operated at low pressure and high temperature. We assume that the gases are respect to ideal gas law. The density of such gas mixture reactant at various temperatures is calculated in the following.

$$\rho = \frac{PM}{RT} = \frac{1.0\times10^{5}\times29.928\times10^{-3}}{8.314T}$$

We obtained : $\rho = 0.761$ kg/m^3 at T = 200°C

$\rho = 0.688$ kg/m^3 at T = 250°C

$\rho = 0.628$ kg/m^3 at T = 300°C

$\rho = 0.578$ kg/m^3 at T = 350°C

Calculation of the gas mixture viscosity

The simplified methods for determining the viscosity of low pressure binary are described anywhere [Reid (1988)]. The method of Wilke is chosen to estimate the gas mixture viscosity.

For a binary system of 1 and 2,

$$\mu_m = \frac{y_1\mu_1}{y_1 + y_2\Phi_{12}} + \frac{y_2\mu_2}{y_2 + y_1\Phi_{21}}$$

Where, μ_m = viscosity of the mixture

μ_1, μ_2 = pure component viscosity

y_1 , y_2 = mole fractions

$$\phi_{12} = \frac{\left[1 + \left(\frac{\mu_1}{\mu_2}\right)^{1/2}\left(\frac{M_1}{M_2}\right)^{1/4}\right]^2}{\left[8\left(1 + \frac{M_1}{M_2}\right)\right]^{1/2}}$$

$$\phi_{21} = \phi_{12}\left(\frac{\mu_2}{\mu_1}\right)\left(\frac{M_1}{M_2}\right)$$

Where, M_1, M_2 = molecular weight

Let 1 refer to 1-propanol and 2 to air (O_2 8%)

M_1 = 60.09 and M_2 = 28.34

From Perry the viscosity of pure 2-propanol at 200ºC, 250ºC, 300ºC and 350ºC are 0.0124, 0.0135, 0.015 and 0.0162 cP, respectively. The viscosity of pure air at 200°C, 250°C, 300°C and 350°C are 0.0248, 0.0265, 0.0285 and 0.030 cP, respectively.

At 200°C :

$$\phi_{12} = \frac{\left[1+\left(\frac{0.0124}{0.0248}\right)^{1/2}\left(\frac{28.34}{60.09}\right)^{1/4}\right]^2}{\left[8\left(1+\frac{60.09}{28.34}\right)\right]^{1/2}} = 0.503$$

$$\phi_{21} = 0.503\left(\frac{0.0248}{0.0124}\right)\left(\frac{60.09}{28.34}\right) = 2.133$$

$$\mu_m = \frac{0.05\times 0.0124}{0.05+0.95\times 0.503} + \frac{0.95\times 0.0248}{0.95+0.05\times 2.133} = 0.0235\text{cP} = 2.35\times 10^{-5}\,\text{kg/m}-\text{sec}$$

At 250°C :

$$\phi_{12} = \frac{\left[1+\left(\frac{0.0135}{0.0265}\right)^{1/2}\left(\frac{28.34}{60.09}\right)^{1/4}\right]^2}{\left[8\left(1+\frac{60.09}{28.34}\right)\right]^{1/2}} = 0.507$$

$$\phi_{21} = 0.507\left(\frac{0.0265}{0.0135}\right)\left(\frac{60.09}{28.34}\right) = 2.110$$

$$\mu_m = \frac{0.05\times 0.0135}{0.05+0.95\times 0.507} + \frac{0.95\times 0.0265}{0.95+0.05\times 2.110} = 0.0251\text{cP} = 2.51\times 10^{-5}\,\text{kg/m}-\text{sec}$$

At 300°C :

$$\phi_{12} = \frac{\left[1+\left(\frac{0.015}{0.0285}\right)^{1/2}\left(\frac{28.34}{60.09}\right)^{1/4}\right]^2}{\left[8\left(1+\frac{60.09}{28.34}\right)\right]^{1/2}} = 0.513$$

$$\phi_{21} = 0.513\left(\frac{0.0285}{0.015}\right)\left(\frac{60.09}{28.34}\right) = 2.067$$

$$\mu_m = \frac{0.05 \times 0.0150}{0.05 + 0.95 \times 0.513} + \frac{0.95 \times 0.0285}{0.95 + 0.05 \times 2.067} = 0.0271\text{cP} = 2.71 \times 10^{-5}\ \text{kg/m} - \text{sec}$$

<u>At 350°C</u>:

$$\phi_{12} = \frac{\left[1 + \left(\frac{0.0162}{0.030}\right)^{1/2}\left(\frac{28.34}{60.09}\right)^{1/4}\right]^2}{\left[8\left(1 + \frac{60.09}{28.34}\right)\right]^{1/2}} = 0.518$$

$$\phi_{21} = 0.518\left(\frac{0.030}{0.0162}\right)\left(\frac{60.09}{28.34}\right) = 2.034$$

$$\mu_m = \frac{0.05 \times 0.0162}{0.05 + 0.95 \times 0.518} + \frac{0.95 \times 0.0300}{0.95 + 0.05 \times 2.034} = 0.0286\text{cP} = 2.86 \times 10^{-5}\ \text{kg/m} - \text{sec}$$

Calculation of diffusion coefficients

Diffusion coefficients for binary gas system at low pressure calculated by empirical correlation are proposed by Reid (1988). Wilke and Lee method is chosen to estimate the value of D_{AB} due to the general and reliable method. The empirical correlation is

$$D_{AB} = \frac{\left(3.03 - \frac{0.98}{M_{AB}^{1/2}}\right)\left(10^{-3}\right)T^{3/2}}{PM_{AB}^{1/2}\sigma_{AB}^2\Omega_D}$$

Where, D_{AB} = binary diffusion coefficient, cm^2/s

T = temperature, K

M_A, M_B = molecular weights of A and B, g/mol

$$\mathrm{M}_{AB} = 2\left[\left(\frac{1}{\mathrm{M}_A}\right)+\left(\frac{1}{\mathrm{M}_B}\right)\right]^{-1}$$

Where, P = pressure, bar

σ = characteristic length, Å

Ω_D = diffusion collision integral, dimensionless

The characteristic Lennard-Jones energy and length, ε and σ , of air and 2-propanol are as follows: (Reid,1988)

For C_3H_7OH : σ (C_3H_7OH) = 4.549 Å, ε/k = 576.7

For air : σ (air) = 3.711 Å, ε/k = 78.6

The sample rules are usually employed.

$$\sigma_{AB} = \frac{\sigma_A+\sigma_B}{2} = \frac{4.549+3.711}{2} = 4.13$$

$$\varepsilon_{AB}/k = \left(\frac{\varepsilon_A\varepsilon_B}{k^2}\right)^{1/2} = (576.7\times78.6)^{1/2} = 212.9$$

Ω_D is tabulated as a function of kT/ε for the Lennard-Jones potential. The accurate relation is

$$\Omega_D = \frac{A}{(T^*)^B}+\frac{C}{\exp(DT^*)}+\frac{E}{\exp(FT^*)}+\frac{G}{\exp(HT^*)}$$

where $T^* = \frac{kT}{\varepsilon_{AB}}$, A = 1.06036 , B = 0.15610 , C = 0.19300 , D = 0.47635 , E = 1.03587 , F = 1.52996 , G = 1.76474 , H = 3.89411

Then, $T^* = \frac{473}{212.9} = 2.222$ at 200°C

$T^* = \frac{523}{212.9} = 2.456$ at 250°C

$$T^* = \frac{573}{212.9} = 2.691 \text{ at } 300^{\circ}\text{C}$$

$$T^* = \frac{623}{212.9} = 2.926 \text{ at } 350^{\circ}\text{C}$$

$$\Omega_D = \frac{1.06036}{(T^*)^{0.15610}} + \frac{0.19300}{\exp(0.47635T^*)} + \frac{1.03587}{\exp(1.52996T^*)} + \frac{1.76474}{\exp(3.89411T^*)}$$

Ω_D = 1.038 ; 200°C

Ω_D = 1.006 ; 250°C

Ω_D = 0.979 ; 300°C

Ω_D = 0.956 ; 350°C

With Equation of D_{AB},

At 200°C : D(C_3H_7OH-air) $$= \frac{\left(3.03 - \frac{0.98}{30.24^{0.5}}\right)(10^{-3})473^{3/2}}{1 \times 30.24^{0.5} \times 4.13^2 \times 1.038}$$

$$= 3.01\times10^{-5} \quad m^2/s$$

At 250°C : D(C_3H_7OH-air) $$= \frac{\left(3.03 - \frac{0.98}{30.24^{0.5}}\right)(10^{-3})523^{3/2}}{1 \times 30.24^{0.5} \times 4.13^2 \times 1.006}$$

$$= 3.62\times10^{-5} \quad m^2/s$$

At 300°C : D(C_3H_7OH-air) $$= \frac{\left(3.03 - \frac{0.98}{30.24^{0.5}}\right)(10^{-3})573^{3/2}}{1 \times 30.24^{0.5} \times 4.13^2 \times 0.979}$$

$$= 4.26\times10^{-5} \quad m^2/s$$

At 350°C : D(C_3H_7OH-air) $$= \frac{\left(3.03 - \frac{0.98}{30.24^{0.5}}\right)(10^{-3})623^{3/2}}{1 \times 30.24^{0.5} \times 4.13^2 \times 0.956}$$

$$= 5.04\times10^{-5} \quad m^2/s$$

Reactant gas mixture was supplied at 100 ml/min in tubular microreactor used in the 2-propanol oxidation system at 30°C

2-propanol flow rate through reactor = 100 ml/min. at 30°C

The density of 2-propanol , $\rho = \dfrac{1.0\times10^{5}\times29.928\times10^{-3}}{8.314(273+30)} = 1.188\ \text{kg/m}^3$

Mass flow rate = $1.188\left(\dfrac{100\times10^{-6}}{60}\right) = 1.98\times10^{-6}$ kg/s

Diameter of quartz tube reactor = 8 mm

Cross-sectional area of tube reactor = $\dfrac{\pi(8\times10^{-3})^2}{4} = 5.03\times10^{-5}$ m^2

Mass Velocity , $G = \dfrac{1.98\times10^{-6}}{5.03\times10^{-5}} = 0.039$ kg/m^2-s

Catalyst size = 40-60 mesh = 0.178-0.126 mm

Average catalyst size = (0.126+0.178)/2 = 0.152 mm

Find Reynolds number, Re_p, which is well known as follows:

$$Re_p = \frac{d_pG}{\mu}$$

We obtained,

At 200°C : $$Re_p = \frac{(0.152\times10^{-3}\times0.039)}{2.35\times10^{-5}} = 0.252$$

At 250°C : $$Re_p = \frac{(0.152\times10^{-3}\times0.039)}{2.51\times10^{-5}} = 0.236$$

At 300°C : $$Re_p = \frac{(0.152\times10^{-3}\times0.039)}{2.71\times10^{-5}} = 0.219$$

At 350°C : $$Re_p = \frac{(0.152\times10^{-3}\times0.039)}{2.86\times10^{-5}} = 0.207$$

Average transport coefficient between the bulk stream and particles surface could be correlated in terms of dimensionless groups, which characterize the flow conditions. For mass transfer the Sherwood number, kmρ/G, is an empirical function of the Reynolds number, d_pG/μ, and the Schmit number, $\mu/\rho D$. The j-factors are defined as the following functions of the Schmidt number and Sherwood numbers:

$$j_D = \frac{k_m \rho}{G}\left(\frac{a_m}{a_t}\right)\left(\frac{\mu}{\rho D}\right)^{2/3}$$

The ratio (a_m/a_t) allows for the possibility that the effective mass-transfer area a_m, may be less than the total external area, a_t, of the particles. For Reynolds number greater than 10, the following relationship between j_D and the Reynolds number well represents available data.

$$j_D = \frac{0.458}{\varepsilon_B}\left(\frac{d_p G}{\mu}\right)^{-0.407}$$

Where, G = mass velocity(superficial) based upon cross-sectional area of empty reactor (G = uρ)

d_p = diameter of catalyst particle for spheres

μ = viscosity of fluid

ρ = density of fluid

ε_B = void fraction of the interparticle space (void fraction of the bed)

D = molecular diffusivity of component being transferred

Assume $\varepsilon_B = 0.5$

<u>At 200°C</u> ; $$j_D = \frac{0.458}{0.5}(0.252)^{-0.407} = 1.605$$

<u>At 250°C</u> ; $$j_D = \frac{0.458}{0.5}(0.236)^{-0.407} = 1.649$$

At 300°C ; $$j_D = \frac{0.458}{0.5}(0.219)^{-0.407} = 1.699$$

At 350°C ; $$j_D = \frac{0.458}{0.5}(0.207)^{-0.407} = 1.739$$

A variation of the fixed bed reactor is an assembly of screens or gauze of catalytic solid over which the reacting fluid flows. Data on mass transfer from single screens has been reported by Gay and Maughan. Their correlation is of the form

$$j_D = \frac{\varepsilon k_m \rho}{G}\left(\frac{\mu}{\rho D}\right)^{2/3}$$

Where ε is the porosity of the single screen.

Hence, $$k_m = \left(\frac{j_D G}{\mu}\right)\left(\frac{\mu}{\rho D}\right)^{2/3}$$

$$k_m = \left(\frac{0.458G}{\varepsilon_B \rho}\right)\mathrm{Re}^{-0.407}\, Sc^{-2/3}$$

Find Schmidt number, Sc : $$Sc = \frac{\mu}{\rho D}$$

At 200°C : $$Sc = \frac{2.35 * 10^{-5}}{0.761 * 3.01 * 10^{-5}} = 1.026$$

At 250°C : $$Sc = \frac{2.51 * 10^{-5}}{0.688 * 3.62 * 10^{-5}} = 1.008$$

At 300°C : $$Sc = \frac{2.71 * 10^{-5}}{0.628 * 4.26 * 10^{-5}} = 1.013$$

At 350°C : $$Sc = \frac{2.86 * 10^{-5}}{0.578 * 5.04 * 10^{-5}} = 0.982$$

Find k_m : At 200°C, $k_m = \left(\frac{1.605\times 0.039}{0.761}\right)(1.026)^{-2/3} = 0.081\,\text{m/s}$

At 250°C, $k_m = \left(\frac{1.649\times 0.039}{0.688}\right)(1.008)^{-2/3} = 0.093\,\text{m/s}$

At 300°C, $k_m = \left(\frac{1.699\times 0.039}{0.628}\right)(1.013)^{-2/3} = 0.105\,\text{m/s}$

At 350°C, $k_m = \left(\frac{1.739\times 0.039}{0.578}\right)(0.982)^{-2/3} = 0.119\,\text{m/s}$

Properties of catalyst

Density = 12.102 g/ml catalyst

Diameter of 40-60 mesh catalyst particle = 0.152 mm

Weight per catalyst particle = $\frac{\pi(0.152\times 0^{-1})^3 \times 12.102}{6} = 2.225\times 10^{-5}$ g/particle

External surface area per particle = $\pi(0.152\times 10^{-3})^2 = 7.258\times 10^{-8}$ m^2/particle

$a_m = \frac{7.258\times 10^{-8}}{2.225\times 10^{-5}} = 3.262\times 10^{-3}$ m^2/gram catalyst

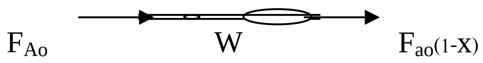
Volumetric flow rate of gaseous feed stream = 100 ml/min

Molar flow rate of gaseous feed stream = $\frac{(1\times 10^5)\left(\frac{100\times 10^{-6}}{60}\right)}{8.314(273+30)} = 6.616\times 10^{-5}\,\text{mol/s}$

2-propanol molar feed rate = $0.05\times 6.616\times 10^{-5} = 3.308\times 10^{-6}$ mol/s

2-propanol conversion (experimental data): 58.74 % at 200°C
99.54 % at 250°C
99.62 % at 300°C
99.74 % at 350°C

The estimated rate of 2-propanol oxidation reaction is based on the ideal plug flow reactor which there is no mixing in the direction of flow and complete mixing perpendicular to the direction of flow (i.e., in the radial direction). The rate of reaction will vary with reaction length. Plug flow reactors are normally operated at steady state so that properties at any position are constant with respect to time. The mass balance around plug flow reactor becomes



$$\{\text{rate of i into volume element}\} - \{\text{rate of i out of volume element}\}$$
$$+ \{\text{rate of production of i within the volume element}\}$$
$$= \{\text{rate of accumulation of i within the volume elecment}\}$$

$$F_{Ao} = F_{Ao}(1\text{-}x) + (r_W W)$$
$$(r_W W) = F_{Ao} - F_{Ao}(1\text{-}x) = F_{Ao} = F_{Ao}x$$

$$r_W = \frac{F_{Ao}x}{W} = \frac{3.308\times10^{-6}\times0.5871}{0.1} = 1.942\times10^{-5} \text{ mol/s-gram catalyst at } 200^{\circ}\text{C}$$

$$r_W = \frac{F_{Ao}x}{W} = \frac{3.308\times10^{-6}\times0.9954}{0.1} = 3.293\times10^{-5} \text{ mol/s-gram catalyst at } 250^{\circ}\text{C}$$

$$r_W = \frac{F_{Ao}x}{W} = \frac{3.308\times10^{-6}\times0.9962}{0.1} = 3.295\times10^{-5} \text{ mol/s-gram catalyst at } 300^{\circ}\text{C}$$

$$r_W = \frac{F_{Ao}x}{W} = \frac{3.308\times10^{-6}\times0.9974}{0.1} = 3.299\times10^{-5} \text{ mol/s-gram catalyst at } 350^{\circ}\text{C}$$

At steady state the external transport rate may be written in terms of the diffusion rate from the bulk gas to the surface. The expression is:

$$R_{obs} = k_m a_m (C_b\text{-}C_s)$$
$$= \frac{\text{2 - propanol converted (mole)}}{\text{(time)(gram of catalyst)}}$$

Where, C_b and C_s are the concentrations in the bulk gas and at the surface, respectively.

At 200°C, $$(C_b\text{-}C_s) = \frac{r_{obs}}{k_m a_m} = \frac{1.942\times10^{-5}}{0.081\times3.262\times10^{-3}} = 7.350\times10^{-2} \text{ mol/m}^3$$

<u>At 250°C</u>, $$(C_b\text{-}C_s) = \frac{r_{obs}}{k_m a_m} = \frac{3.293\times10^{-5}}{0.093\times3.262\times10^{-3}} = 1.085\times10^{-1} \quad \text{mol/m}^3$$

<u>At 300°C</u>, $$(C_b\text{-}C_s) = \frac{r_{obs}}{k_m a_m} = \frac{3.295\times10^{-5}}{0.105\times3.262\times10^{-3}} = 9.620\times10^{-2} \quad \text{mol/m}^3$$

<u>At 350°C</u>, $$(C_b\text{-}C_s) = \frac{r_{obs}}{k_m a_m} = \frac{3.299\times10^{-5}}{0.110\times3.262\times10^{-3}} = 9.194\times10^{-2} \quad \text{mol/m}^3$$

From C_b (2-propanol) = 2.25 mol/m^3

Consider the difference of the bulk and surface concentration is small. It means that the external mass transport has no effect on the 2-propanol oxidation reaction rate.

APPENDIX C

CALCULATION OF ACID SITE

From Micromeritrics Chemisorb 2750, total peak area of TS-1 is 0.0818178

Calulation of total acid sites

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

1. Conversion of total peak area to peak volume

The conversion from Micromeritrics Chemisorb 2750 is equal to 77.57016 ml/area unit. Therefore, total peak volume is derived from

$$\begin{aligned}\text{Total peak volume} &= 77.57016 \times \text{total peak area}\\ &= 77.57016 \times 0.0818178\\ &= 6.34662 \text{ ml}\end{aligned}$$

2. Calculation for adsorbed volume of 15% NH_3

$$\begin{aligned}\text{adsorbed volume of 15\% NH}_3 &= 0.15 \times \text{total peak volume}\\ &= 0.15 \times 6.34662 \text{ ml}\\ &= 0.951993 \text{ ml}\end{aligned}$$

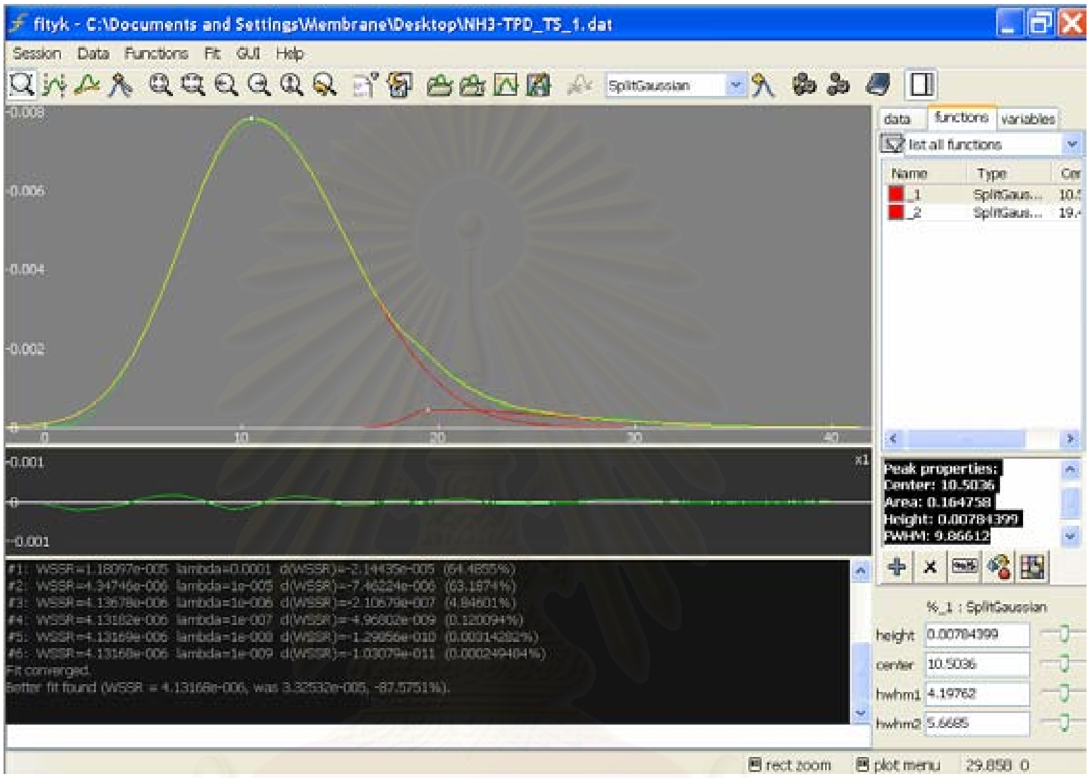
3. Total acid sties are calculated from the following equation

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

For TS-1, 0.1019 g of this sample was measured, therefore

$$\text{Total acid sites} = \frac{0.951993\,\text{ml} \times 101.325\,\text{Pa}}{\left(8.314 \times 10^{-3}\,\dfrac{\text{Pa}\cdot\text{ml}}{\text{K}\cdot\mu\text{mol}}\right) \times 298\,\text{K} \times (0.1019\,\text{g})}$$

$$= 382\ \mu\text{mol H}^{+}/\text{g}$$



```
#1: WSSR=1.18097e-005 lambda=0.0001 d(WSSR)=-2.14435e-005 (64.4855%)
#2: WSSR=4.34746e-006 lambda=1e-005 d(WSSR)=-7.46224e-006 (63.1874%)
#3: WSSR=4.13678e-006 lambda=1e-006 d(WSSR)=-2.10679e-007 (4.84601%)
#4: WSSR=4.13182e-006 lambda=1e-007 d(WSSR)=-4.96802e-009 (0.120094%)
#5: WSSR=4.13169e-006 lambda=1e-008 d(WSSR)=-1.29856e-010 (0.00314282%)
#6: WSSR=4.13168e-006 lambda=1e-009 d(WSSR)=-1.03079e-011 (0.000249484%)
Fit converged.
Better fit found (WSSR = 4.13168e-006, was 3.32532e-005, -87.5751%).
```

```
Peak properties:
Center: 10.5036
Area: 0.164758
Height: 0.00784399
FWHM: 9.86612
```

height: 0.00784399
center: 10.5036
hwhm1: 4.19762
hwhm2: 5.6685

Figure C1. Data for calculating of acid site ratio of TS-1 from peak fitting program

Calculation of acid site ratio

As known, the first peak of desorption process is indicated as weak acid, relative with another peak, and the second one is strong acid. Ratio of each acid site on catalyst surface is calculated from reported peak area of peak fitting program as shown above.

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

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

From peak fitting program, 1st peak area and 2nd peak area are equal to 0.164758 and 0.00926918, respectively.

$$\text{The ratio of weak acid} = \frac{0.164758}{0.164758 + 0.00926918} \times 100\ \%$$

$$= 94.67\ \%$$

$$\text{therefore, the ratio of strong acid} = 100 - 92.89\ \%$$

$$= 5.33\ \%$$

Note. Reported center values of both peaks from peak fitting program reveal times at the maximum of both peaks occur. Since, we have known for relation between time and temperature during desorption process from Micromeritrics Chemisorb 2750, hence, the temperature at the maximum of both peaks as we state as desorption temperature of both acid sites will be demonstrated

APPENDIX D

CALIBRATION CURVES

Flame ionization detector gas chromatograph, model 8A, was used to analyze the concentrations of oxygenated compounds. 2-propanol, propylene, isopropyl ether and acetone were analyzed by GC model 8A with using 15% Carbowax 1000, while ethanol, ethylene and acetaldehyde were analyzed by GC model 8A with using Carbopack B/3% SP-1500.

Gas chromatograph with the thermal conductivity detector, model 8A, was used to analyze the concentration of CO_2 by using Molecular Sieve 5A and Porapak-Q columns respectively.

The calibration curves of 2-propanol, propylene, isopropyl ether, acetone, and CO_2 are illustrated in the following figures.

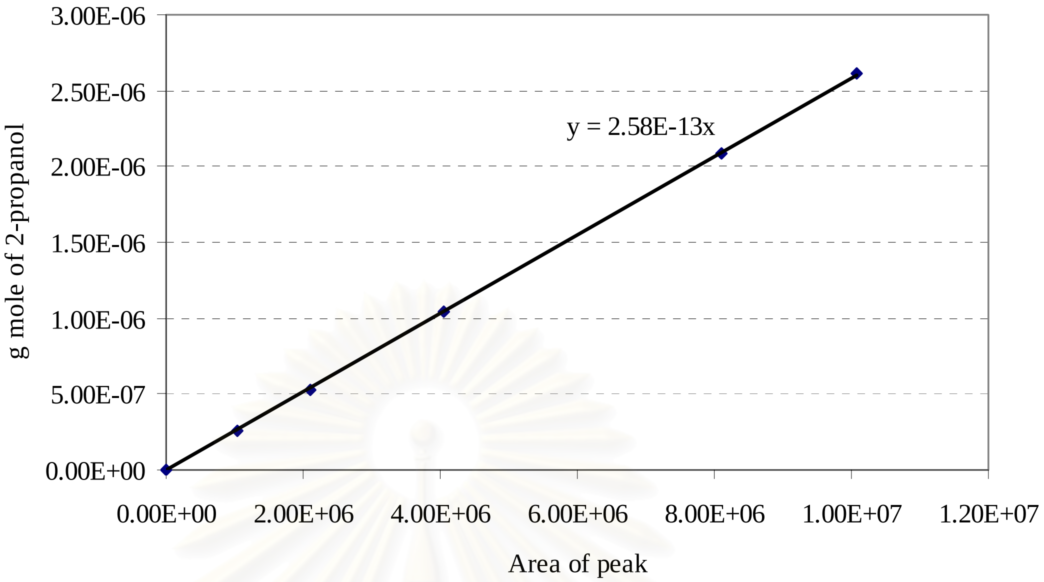


Figure D1 The calibration curve of 2-propanol

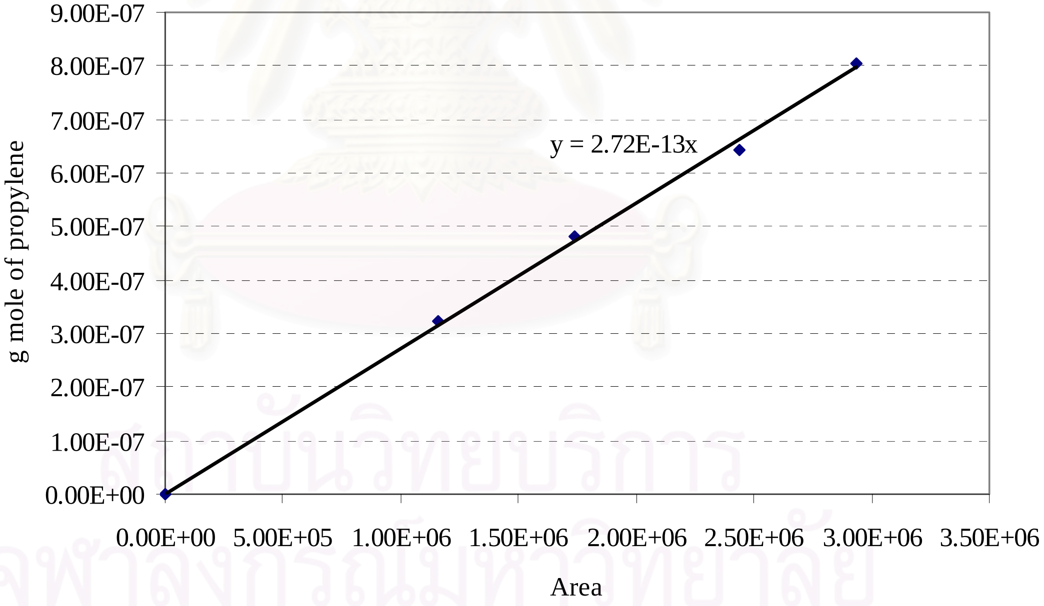


Figure D2 The calibration curve of propylene

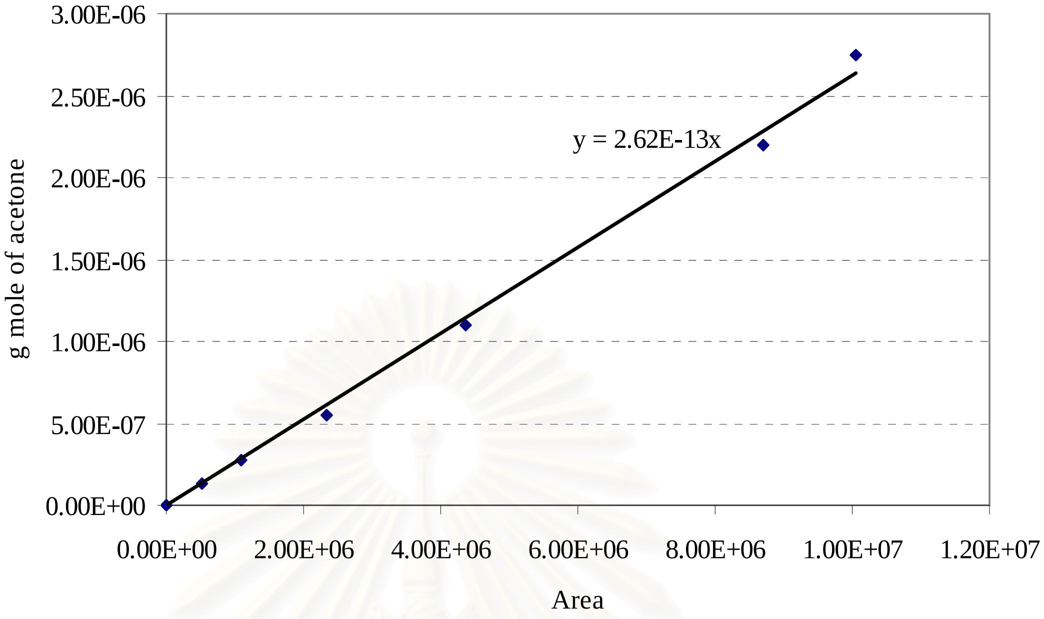


Figure D3 The calibration curve of acetone

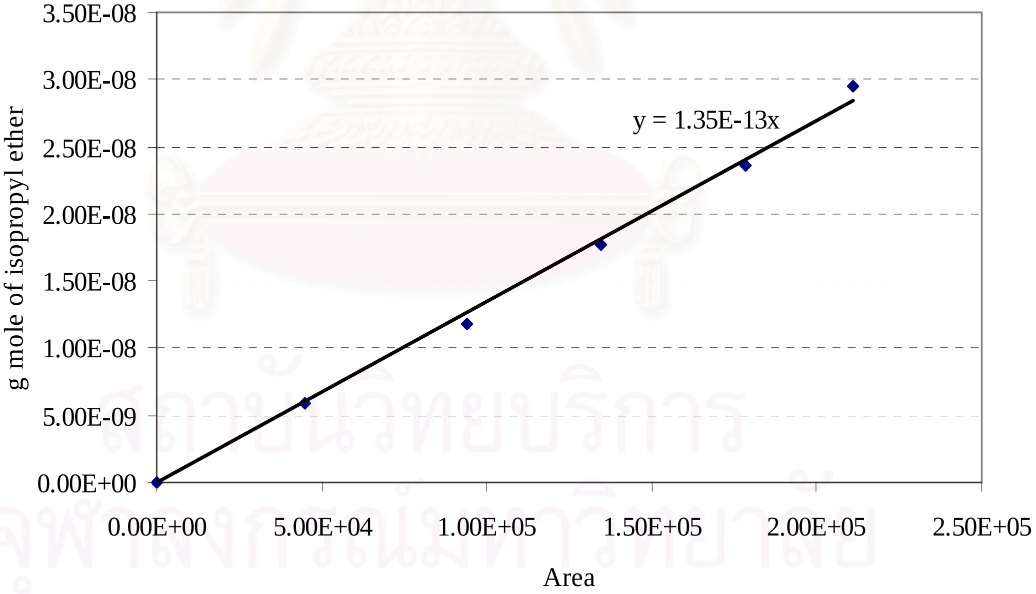


Figure D4 The calibration curve of isopropyl ether

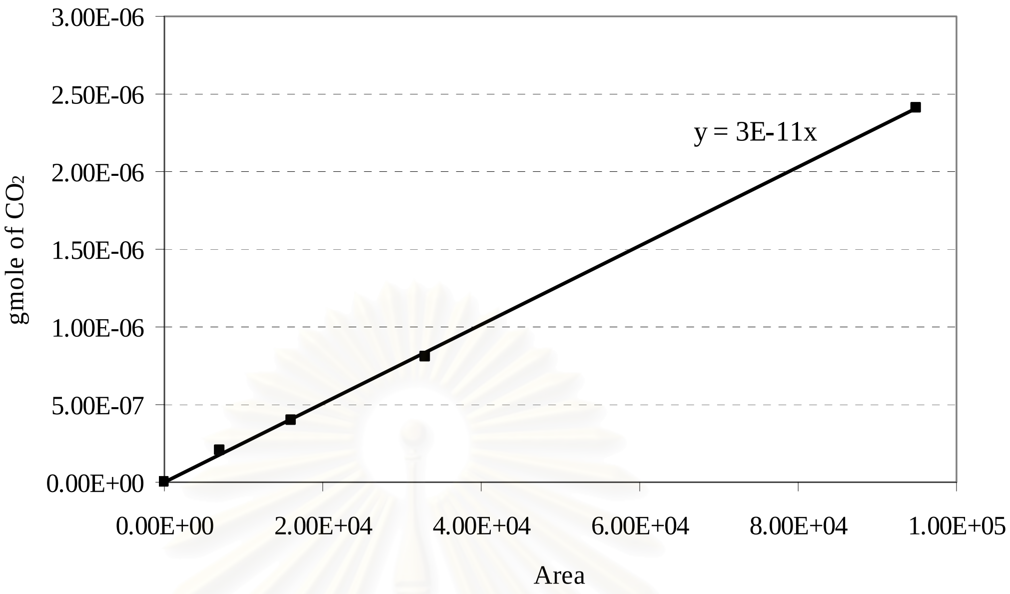


Figure D5 The calibration curve of carbon dioxide

APPENDIX E

DATA OF EXPERIMENTS

Table E1 Data of Figure 5.4a

Reaction temperature. (^{0}C)	Component			
	% 2-propanol (C)	% propylene (S)	% acetone (S)	% CO_2 (S)
100	0.00	0.00	0.00	0.00
150	2.79	98.61	0.00	0.00
200	31.52	99.64	0.36	0.00
250	85.94	95.88	3.99	0.13
300	97.73	89.70	10.15	0.16
350	99.20	70.35	29.00	0.65
400	99.10	68.37	30.41	1.23
450	99.43	61.71	36.81	1.48
500	99.59	55.97	42.15	1.88

Table E2 Data of Figure 5.4b

Reaction temperature. (^{0}C)	Component			
	% 2-propanol (C)	% propylene (S)	% acetone (S)	% CO_2 (S)
100	0.00	0.00	0.00	0.00
150	2.61	100.00	0.00	0.00
200	37.55	99.45	0.55	0.00
250	88.17	97.56	2.38	0.06
300	97.87	87.38	12.26	0.36
350	98.96	71.95	25.73	2.32
400	99.55	56.89	36.97	6.14
450	99.57	54.68	38.72	6.59
500	99.12	47.09	46.65	6.26

Table E3 Data of Figure 5.4c

Reaction temperature. (^{0}C)	Component			
	% 2-propanol (C)	% propylene (S)	% acetone (S)	% CO_2 (S)
100	0.00	0.00	0.00	0.00
150	3.67	99.99	0.00	0.00
200	58.71	99.59	0.41	0.00
250	97.46	96.65	3.26	0.09
300	99.34	86.66	12.83	0.51
350	99.88	64.51	31.25	4.24
400	99.84	41.80	45.71	12.50
450	99.06	43.65	45.34	11.01
500	99.55	37.06	51.38	11.56

Table E4 Data of Figure 5.4d

Reaction temperature. (^{0}C)	Component			
	% 2-propanol (C)	% propylene (S)	% acetone (S)	% CO_2 (S)
100	0.00	0.00	0.00	0.00
150	4.31	100.00	0.00	0.00
200	58.71	99.41	0.59	0.00
250	99.54	95.83	4.07	0.10
300	99.62	85.56	13.65	0.79
350	99.74	58.26	35.12	6.62
400	99.95	28.22	45.59	26.19
450	99.85	23.38	50.04	26.59
500	100.00	20.20	53.41	26.39

Table E5 Data of Figure 5.4e

Reaction temperature. (^{0}C)	Component			
	% 2-propanol (C)	% propylene (S)	% acetone (S)	% CO_2 (S)
100	0.00	0.00	0.00	0.00
150	7.46	100.00	0.00	0.00
200	60.47	98.43	1.57	0.00
250	97.55	90.75	9.12	0.13
300	98.48	79.93	19.35	0.72
350	99.09	23.65	58.71	17.64
400	99.28	21.00	42.04	36.96
450	98.73	22.70	27.32	49.98
500	98.96	20.74	28.21	51.05

Table E6 Data of Figure 5.4f

Reaction temperature. (^{0}C)	Component			
	% 2-propanol (C)	% propylene (S)	% acetone (S)	% CO_2 (S)
100	0.00	0.00	0.00	0.00
150	9.02	98.43	1.57	0.00
200	60.52	97.84	2.16	0.00
250	98.52	87.48	12.30	0.22
300	99.17	50.20	47.88	1.92
350	99.26	22.28	59.37	18.35
400	99.31	11.34	18.00	70.67
450	99.55	10.85	10.30	78.85
500	99.62	9.63	9.82	80.55

Table E7 Data of Figure 5.5

Reaction temperature. (^{0}C)	% propylene conversion	% selectivity to CO_2	% selectivity to undefined product
100	1.38	0.00	100.000
150	2.03	0.00	100.000
200	3.10	0.00	100.000
250	7.31	0.78	99.218
300	7.60	4.93	95.075
350	10.57	21.68	78.320
400	19.43	33.03	66.972
450	20.37	34.33	65.672
500	21.74	36.38	63.625

Table E8 Data of Figure 5.6

Reaction temperature. (^{0}C)	% Acetone conversion	% selectivity to CO_2	% selectiviy to undefined product
100	1.13	0.00	100.000
150	2.50	0.00	100.000
200	5.34	0.00	100.000
250	9.63	3.22	96.778
300	9.35	37.29	62.705
350	29.42	57.45	42.547
400	35.43	75.76	24.242
450	49.87	96.39	3.615
500	51.62	93.97	6.034

APPENDIX F

MATERIAL SAFETY DATA SHEET

Safety data for 2-Propanol

General

Synonyms: Isopropanol, Isopropyl alcohol
Molecular formula: C_3H_8O
Chemical formula: $CH_3CH(OH)CH_3$

Physical data

Melting point: -89.5°C
Boiling point: 82.4 °C
Ignition temperature: 425°C
Flash point: 12°C
Explosion limits: 2 % - 12.7 %
Vapor pressure: 31.68 mm (14.7°C)
Relative vapor density: 2.07
Density: 0.786 g/cm^3 (20°C)
Solubility in water: soluble (20°C)

Stability

Conditions to be avoided: Strong heating.

Substances to be avoided: alkali metals, alkaline earth metals, aluminium in powder form, oxidizing agent, organic nitro compounds, aldehydes, amines, fuming sulfuric acid, phosgene.

Hazardous decomposition products: no information available.

Further information: highly inflammable; hygroscopic, explosive with air in a vapor/gas state.

Toxicology

Further toxicological information

After inhalation: Irritation symptoms in the respiratory tract Drowsiness

After skin contact: degreasing effect on the skin possibly followed by secondary inflammation.

After eye contact: Irritations.

After swallowing: after accidental swallowing the substance may pose a risk of aspiration. Passage into the lung can result in a condition resembling pneumonia

After absorption: headache, dizziness, inebriation

After uptake of large quantities: respiratory paralysis, coma.

Health effects

No adverse health effects expected if the product is handled in accordance with this Safety Data Sheet and the product label where applicable. Symptoms that may arise if the product is mishandled are:

Acute effects

Swallowed : May cause stomach pains, cramps, nausea and vomiting. Over 130 grams may be fatal.

Eye: Vapour is irritating to eyes above 400ppm. Eye contact with liquid causes severe irritation.

Skin : Brief contact is not irritating but repeated or prolonged contact may cause irritation.

Inhaled : Causes mild irritation of nose, throat and respiratory tract at concentration above 400ppm. Higher concentrations can cause drowsiness and unconsciousness.

Chronic effects

Repeated or prolonged contact with skin may produce dryness and cracking.

First aid

Swallowed : IF conscious give water to drink to dilute stomach contents. Seek immediate medical assistance.

Eye : Immediately irrigate with copious quantities of water for at least 15 minutes. Eyelids to be held open. Seek medical assistance.

Skin : Wash with soap & water. Remove contaminated clothing & wash before re-use. If irritation, occurs seek medical assistance.

Inhaled : Remove victim from exposure - avoid becoming a casualty. Remove contaminated clothing and loosen remaining clothing. Allow patient to assume most comfortable position and keep warm. Keep at rest until fully recovered. If breathing laboured ensure airways are clear. If breathing has stopped apply artificial respiration at once. Seek medical assistance.

Advice to doctor

Treat symptomatically.

Personal protection

Personal protective equipment: Protective clothing should be selected specifically for the working place, depending on concentration and quantity of the hazardous substances handled. The resistance of the protective clothing to chemicals should be ascertained with the respective supplier.

Industrial hygiene: Change contaminated clothing. Application of Skin-protective barrier cream recommended. Should be wash hands after working with substance.

Safety data for Propylene

General

Synonyms: methylethene, methylethylene, propylene, 1-propene, 1-propylene
Molecular formula: C_3H_6
Chemical formula: C_3H_6

Physical data

Appearance: colourless gas
Melting point: -185 C
Boiling point: -47.7 C
Vapour density: 1.48
Vapour pressure: 15.4 atm at 37.7 C
Density (g cm^{-3}):
Flash point: -108 C (closed cup)
Explosion limits: 2 - 11.1%
Autoignition temperature: 460 C
Water solubility:

Stability

Stable. **Highly flammable. Readily forms explosive mixtures with air.** Incompatible with strong oxidizing agents, strong acids, halogens.

Toxicology

Asphyxiant. May be harmful by inhalation.

Personal protection

Good ventilation, safety glasses. Remove sources of ignition from the working area.

Handling and Storage

Earth bond and ground all lines and equipment associated with the product system. Electrical equipment should be non-sparking and explosion proof.

Propylene is non-corrosive and may be used with any common structural material.

Use only in well-ventilated areas. Valve protection caps must remain in place unless container is secured with valve outlet piped to use point. Do not drag, slide or roll cylinders. Use a suitable hand truck for cylinder movement. Use a pressure regulator when connecting cylinder to lower pressure (<250 psig) piping or systems. Do not heat cylinder by any means to increase the discharge rate of product from the cylinder. Use a check valve or trap in the discharge line to prevent hazardous back flow into the cylinder.

Protect cylinders from physical damage. Store in cool, dry, well-ventilated area away from heavily trafficked areas and emergency exits. Do not allow the temperature where cylinders are stored to exceed 130oF (54oC). Cylinders should be stored upright and firmly secured to prevent falling or being knocked over. Full and empty cylinders should be segregated. Use a "first in-first out" inventory system to prevent full cylinders from being stored for excessive periods of time.

Post "No Smoking" signs in storage or use areas.

For additional recommendations consult Compressed Gas Association Pamphlet P-1.

Never carry a compressed gas cylinder or a container of a gas in cryogenic liquid form in an enclosed space such

Safety for Acetone

General

Synonyms: dimethyl ketone, methyl ketone, 2-propanone, acetone, dimethylketal, pyroacetic acid, dimethylformaldehyde
Molecular formula: $(CH_3)_2CO$
Chemical formula: CH_3COCH_3

Physical data

Appearance: colourless liquid with a fragrant, sweet odour
Melting point: -95 °C
Boiling point: 56 °C
Vapour density: 2.0
Vapour pressure: 181 mm Hg at 20 °C
Specific gravity: 0.79
Flash point: -18 °C
Explosion limits: 2.6% - 13.0%
Autoignition temperature: 538 °C

Stability

Stable. Incompatible with halogen acids and halogen compounds, strong bases, strong oxidizing agents, caustics, amines and ammonia, chlorine and chlorine compounds, strong acids, nitrosyl compounds. Highly flammable. Readily forms explosive mixtures with air.

Toxicology

May be harmful by inhalation, ingestion or skin absorption. Irritant. Liquid may cause permanent eye damage (corneal clouding). Contact with skin may cause defatting, leading to irritation. Long-term exposure may cause liver damage. Typical TLV 750 ppm.

Toxicity data

(The meaning of any abbreviations which appear in this section is given here.)
UNR-MAN LDLO 1159 mg kg^{-1}
ORL-RAT LD50 5800 mg kg^{-1}
UHL-RAT LC50 50 mg l^{-1}
IHL-RAT LC50 50100 mg m^{-3} / 8h
ORL-MUS LD50 3000 mg kg^{-1}
IHL-MUS LC50 44 g m^{-3} / 4h

Irritation data

(The meaning of any abbreviations which appear in this section is given here.)
EYE-HMN 500 ppm
SKN-RBT 395 mg open mld
EYE-RBT 20 mg sev

Risk phrases

(The meaning of any risk phrases which appear in this section is given here.) R11 R36 R66 R67. (Previously categorized as harmful by inhalation, ingestion or skin absorption, but Annex I does not include these risk phrases. Norway still categorizes acetone as harmful by inhalation. Possibility of corneal clouding suggests that R41 might also be specified.)

Environmental information

Biological degradability: good. Aquatic toxicity: low. Bioaccumulation potential: low. Fish toxicity LC50 (*L. macrochirus*) 8300 mg/l/96h.

Personal protection

Safety glasses. Good ventilation. Remove sources of ignition from the working area.

APPENDIX G

LIST OF PUBLICATION

Pichit Thitthaweerut, Kedsuda Chairat and Tharathorn Mongkhonsi, “Selective Oxidation of 1-propanol and 2-propanol in gas phase over TS-1”, Proceedings of Thai Institute of Chemical Engineering and Applied Chemical Conference 15th, Chonburi, Thailand, Oct, 2005, Ref. No.CA10

Selective Oxidation of 1-propanol and 2-propanol in gas phase over TS-1

Pichit Thitthaweerut*, Kedsuda Chairat and Tharathorn Mongkhonsi+
Center of Excellence on Catalysis and Catalytic Reaction Engineering,
Department of Chemical Engineering, Faculty of Engineering,
Chulalongkorn University, Bangkok 10330 Thailand.

*Presenting author, +Corresponding author (Tel: +66-02-2186867, Fax: +66-02-2186877,
Email:tharathon.m@chula.ac.th)

ABSTRACT

1-Propanol and 2-propanol are oxidized by O_2 in the presence of titanium sillicalite-1 (TS-1) to oxygenate compounds. The research found that the catalyst activity and product selectivity depend on reactant, temperature and oxygen concentration. The conversions of 1-propanol and 2-propanol increased up to 100 % at 400°C. Acetone selectivity of 2-propanol oxidation was fairly constant at about 100 % in the reaction temperature range 200°C and 350°C. For 1-propanol oxidation, the selectivity of acetone increased in the temperature range 200-350°C. In the reaction temperature above 400°C, CO_2, a product of over oxidation, became a significant product of both reaction leading to a decrease in the selectivity of acetone

Keyword: 1-propanol, 2-propanol, oxidation, TS-1

1. INTRODUCTION

Selective oxidation is an important reaction that is widely used in several processes to produce chemical intermediates of use in many downstream industries. Oxidation of alcohols into carbonyl compounds is one of the most important functional group transformations in organic synthesis. In recent years, selective oxidation of alcohols using different catalysts is interested [1-3]. In particular, researches have been carried out to develop suitable heterogeneous catalysts that can be used. Most attention has been given to noble metal [2] and to transition metal oxide catalysts [3], which are effective for the oxidation of alcohols.

The discovery of titanium silicalite-1 (TS-1), which is a zeolite of the pentasil family [3], opened a new route for organic synthesis. Owing to its excellent shape selective as well as its environmentally benign character, TS-1 plays an outstanding role in the partial oxidation for many organic compounds such as hydroxylation of aromatic compounds, olefin epoxidation, dehydrogenation of paraffin and alcohol oxidation using aqueous H_2O_2 and O_2 as an oxidant [4-7].

Reaction of alcohol can involve the breaking of either of two bonds: the C-OH bond, with removal of the -OH group; or the O-H bond, with removal of -H bond. The oxidation of an alcohol involves the loss of one or more hydrogens (α-hydrogens) from the carbon bearing the -OH group. The kind of oxidation product that is formed carbonyl compound. The another way of reaction of alcohol is dehydration that an alcohol is converted into an alkene by elimination of a molecule of water. To the best of our knowledge, the gas phase oxidation of alcohol using O_2 as an oxidant over TS-1 has never been investigated before. Therefore, in this study the gas phase oxidation of 1-propanol and 2-propanol over TS-1 catalyst was performed to explore a new route for oxygenate synthesis.

2. EXPERIMENTAL

2.1 The preparation of the TS-1 catalyst

The TS-1 catalyst was prepared by hydrothermal process using tetraethyl orthotitanate as Ti source, tetraethyl orthosilicate as silicon source and tetrapropylammoniumhydroxide as template. The crystallization was carried out in a stainless steel autoclave from room temperature to 175°C with a heating rate of 2°C/min and held at this temperature while being stirred for 4 days. After washing by de-ionized water, the product crystals were dried over night and calcined in air at 550°C for 6 hrs.

2.2 The characterization of the TS-1 catalyst

The crystallization products were characterized by a number of different techniques. The crystallinity was characterized using X-ray powder diffraction technique (Siemens D-5000 diffractometer). Fourier transform infrared spectroscopy (Nicolet) was used to quantify the characteristic peak at 960 cm^{-1}. The surface area of the catalyst was characterized using BET technique. The catalyst surface area was found to be 212 m^2g^{-1}. Atomic absorption spectroscopy (AAS) was used to determine the Si/Ti mole ratio of the synthesized catalyst. The Si/Ti mole ratio was found to be 34.

2.3 The catalytic reaction

The catalytic performance tests were performed in a stainless steel tubular fixed-bed reactor packed with 0.1 gram of the TS-1 catalyst. Alcohol reactants were fed via a saturator. Pure dry air was used as oxygen source and argon was used as balancing gas. The feed contained 5 mol% alcohol while the concentration of oxygen was varied between 0 to 16 vol% with total flow rate of 100 ml min^{-1}. The reaction was studied in the temperature range 200-500°C. GC TCD 8A using He as carrier gas with two columns, a molecular sieve 5A and Porapak-Q, was used to analyze CO and CO_2 respectively. GC FID 8A using N_2 as carrier gas with 15% Carbowax 100 was used to analyze hydrocarbons and oxygenate compounds.

3. RESULTS AND DISCUSSION

3.1 2-propanol oxidation

The 2-propanol conversion and product selectivities over the TS-1 catalyst without oxygen are shown in Figure 1. Only dehydration and oxidation products were produced. No combustion product was observed. The selectivity of the products depends significantly on the reaction temperature. Between 200-350°C, the conversion of 2-propanol rapidly increased up to 100% around 400°C. Because of no using oxygen as oxidant, the major product became propylene with the maximum selectivity about 99% and the minor product was acetone with the maximum selectivity about 27%.

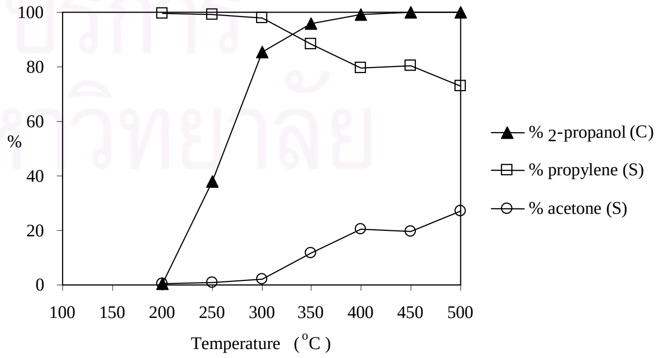


Figure 1. Selective oxidation of 2-propanol without oxygen, C – conversion, S – selectivity.

The catalytic activity and product selectivities of 2-propanol oxidation over TS-1 catalyst for 8 and 16 vol% O_2 are showed in Figures 2 and 3, respectively. Both figures showed similar behavior. When oxygen was introduced into the system, the main reaction became the selective oxidation of 2-propanol to acetone. Between 200-400°C, the conversion of 2-propanol rapidly increased to reach a value around 100% and maintained at this level. In the temperature range 200-400°C, the selectivity of acetone was fairly constant nearly 100%. When the reaction temperature was further increased beyond 350°C, the selectivity of acetone rapidly dropped while CO_2 became a new major product with traces of propylene and isopropyl ether were observed in the product stream. This behavior indicated that CO_2 was the secondary product produced via the further oxidation of acetone.

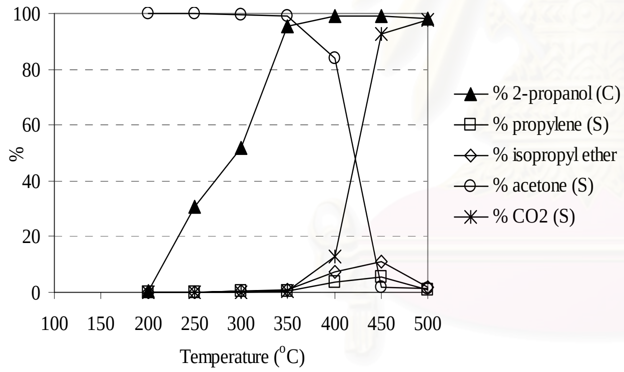


Figure 2. Selective oxidation of 2-propanol for 8 vol% O_2, C – conversion, S – selectivity

The results showed that the oxygen concentration in the feed gas did not strongly affect the conversion of 2-propanol but strongly affected the product selectivities, especially the formation of propylene. It was hypothesized that the absence of propylene at low reaction temperature region might be due to the fast oxidation of propylene to acetone. Therefore, the oxidation of propylene (5 vol% in feed gas) over the TS-1 was performed and the result is showed in Figure 4. Despite the fact that the catalyst could convert propylene to acetone, the activity was not high enough to support the fast oxidation of propylene hypothesis. The fast oxidation of propylene hypothesis, therefore, was rejected. The appearance of water in the product stream of 2-propanol oxidation indicated that acetone was most likely originated from the direct oxidation of 2-propanol. In other words, the acetone produced mostly came from the direct oxidation of 2-propanol rather than the oxidation of propylene.

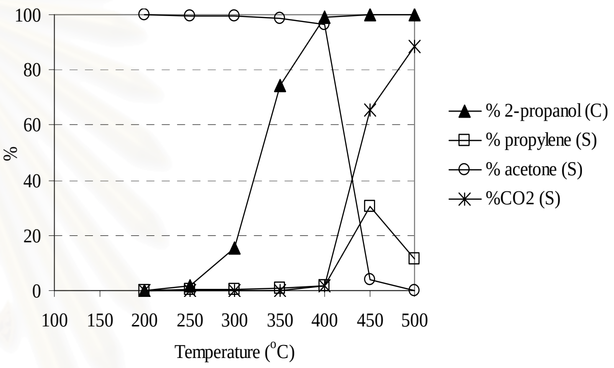


Figure 3. Selective oxidation of 2-propanol for 16 vol% O_2 ,C – conversion, S – selectivity

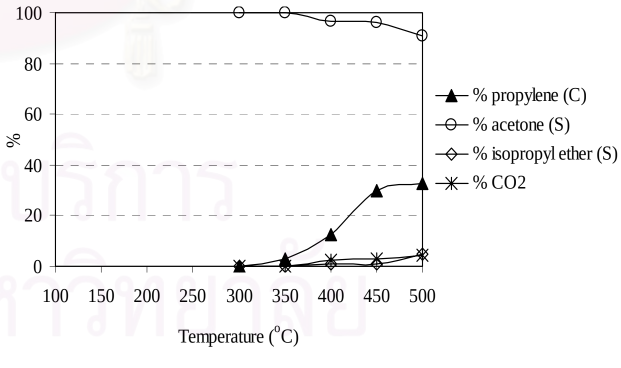


Figure 4. Selective oxidation of propylene for 8 vol% O_2, C – conversion, S – selectivity

3.2 1-propanol oxidation

The 1-propanol oxidation over TS-1 catalyst without oxygen in the feed gas is presented on Figure 5. When the reaction temperature was higher than 300 °C, the catalyst activity of TS-1 catalyst rose from 0.54 % to 14.9% and dramatically increased up to approximately 100 % at 400 °C. The main product was propylene with selectivity 86.4 % and small amount of acetone was observed with selectivity up to 13.6 %

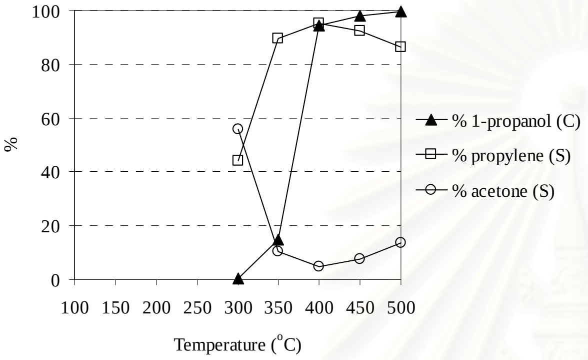


Figure 5. Selective oxidation of 1-propanol without oxygen, C – conversion, S – selectivity

The behavior of TS-1 catalyst for 1-propanol oxidation for 8 and 16 vol% O_2 are illustrated in Figures 6 and 7, consecutively. Both figures showed similar 1-propanol conversion and product selectivity pattern. The conversion was observed firstly at 200 °C and rapidly increased to nearly 100 % at about 400 °C. At low reaction temperature range 250-350 °C, the main product was acetone with selectivity higher than 70 %. Furthermore, there was some formation of propylene, isopropyl ether and trace of CO_2. When the reaction temperature is further increased, the main product became CO_2.

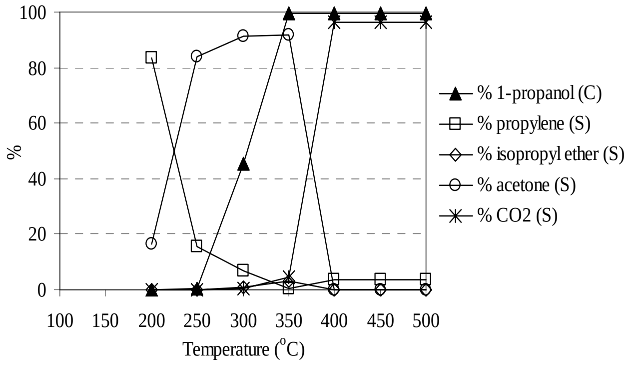


Figure 6. Selective oxidation of 1-propanol for 8 vol% O_2 , C – conversion, S – selectivity

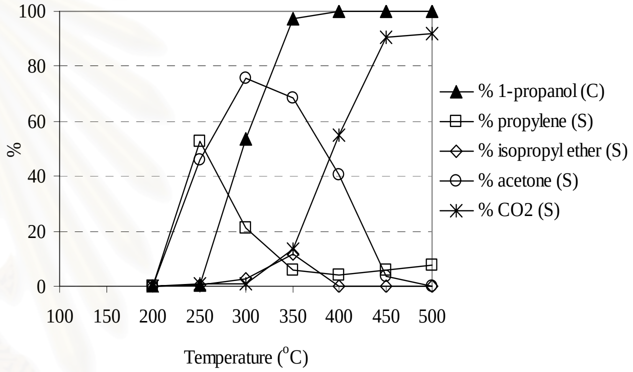


Figure 7. Selective oxidation of 1-propanol for 16 vol% O_2, C – conversion, S – selectivity

4. CONCLUSION

Form all of the results presented, the product formation pathway of 1-propanol and 2-propanol oxidation reaction over TS-1 catalyst can be summarized in Figure 8 below.

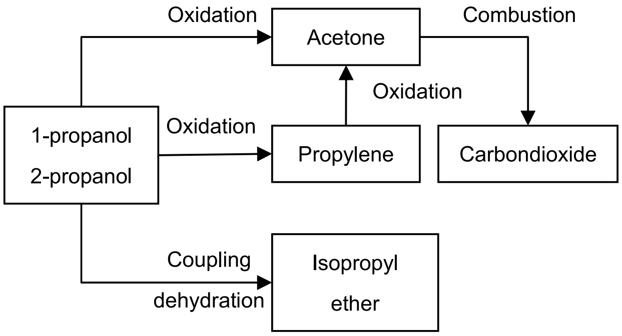


Figure 8. Schematic pathway of the product formation in 1-propanol oxidation and 2-propanol oxidation

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VITAE

Mr. Pichit Thitthaweerut was born on July 23th, 1982 in Bangkok, Thailand. He finished high school from Suankularbwittayalai, Bangkok in 2000, and received the bachelor’s degree of Chemical Engineering from Faculty of Engineer, Chulalongkorn University in 2004. He continued his master’s study at Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University in June, 2004.