

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Bio-Ethanol

Bio-ethanol is a type of alcohol derived from agricultural feed stocks. It can be made from very common crops such as sugarcane, potato, manioc and corn by, mainly, hydrolysis and fermentation. Ethanol is colorless liquid, biodegradable, high octane, low in toxicity and low CO₂ emission. Due to the increase of energy demand and friendly environmental property of bio-ethanol, bio-ethanol is widely used as a petro substitute for transportation. Moreover, bio-ethanol can be used in chemical processes such as catalytic dehydration to obtain higher hydrocarbons or important compounds such as ethylene, propylene and p-xylene.

2.2 Catalytic Dehydration of Bio-Ethanol to Hydrocarbons

Excessive demand of fossil fuel leads to rapid depletion of oil reserve. Even though there is a discovery of new oil and natural gas reserves, it is unavoidable to confront with complete depletion of fossil fuel reserves. Catalytic dehydration of ethanol to hydrocarbon compounds such as light olefins, paraffins and BTX aromatics has been received much attention due to low production cost and energy consumption (Chen *et al.*, 2010). The catalytic dehydration of ethanol process consists two mainly competitive ways as shown in Figure 2.1

The first reaction is the intermolecular dehydration of ethanol to diethyl ether. The formation of diethyl ether is exothermic and favored between 150 C° and 300 C°. The second reaction is the intramolecular dehydration of ethanol to ethylene which its formation is favored above 300 C° up to 500 C°. Moreover, diethyl ether and ethylene could undergo further reaction to C₄ olefins, paraffins and aromatics (BTX) by oligomerization, cracking, cyclization, dehydrogenation and H-transfer (Inaba *et al.*, 2006). Oligomerization is the reaction that alkene is protonated over a metal cation by forming a carbenium ion and then reacts with another olefin to form

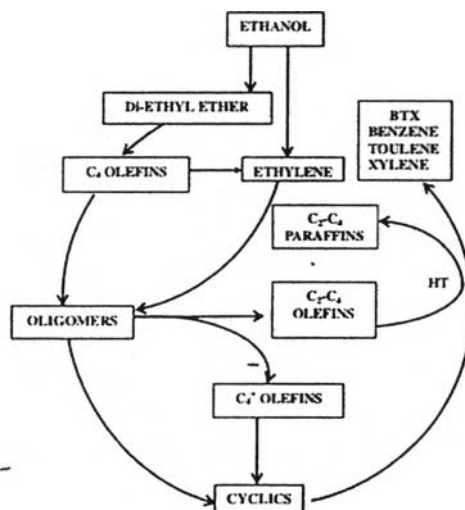


Figure 2.1 Reaction pathways to diethyl ether, ethylene and other higher hydrocarbons compounds (Viswanadham *et al.*, 2012).

higher molecular olefins. Other products, which are carbon dioxide, acetaldehyde, methane, ethyl acetate and hydrogen, can be formed by side reactions (Tsodikov *et al.*, 2008). The key factors that play an important role in determining the activity and selectivity of product are catalyst acidity, pore size, and the presence of heteroatom. The reaction parameters such as temperature, space velocity and feed composition also have the significant effect on activity and selectivity as well.

Generally, solid acid catalysts encourage the dehydration of ethanol because acid catalysts protonate the hydroxyl group of ethanol which later on leaves water molecule (Fan *et al.*, 2012). Hence, the catalyst properties as well as operating parameters play an important role in production of desired compounds. Many catalysts have been studied via ethanol dehydration. Earlier, γ - Al_2O_3 has been studied in this reaction as well as modified γ - Al_2O_3 . Chen *et al.* (2007) studied on catalytic ethanol dehydration over TiO_2/γ - Al_2O_3 . They found that loaded TiO_2 affected the acidity of catalyst. With 10wt% TiO_2 doped on catalyst, the ethanol conversion reached the maximum 99.96% at 500 C°, and the selectivity of ethylene was up to 99.4%. However, the temperature was still too high.

There are many studies on the catalytic dehydration of ethanol to light olefins and higher hydrocarbons, especially aromatics. HZSM-5 is well known as a

highly-shape selective solid acid catalyst due to well-defined zeolite structure as shown in Figure 2.2. The structure of HZSM-5 is three-dimensional 10-membered rings containing straight and zig-zag channels with approximately 5.5 Å pore diameter. Its framework Si/Al ratio plays an important role on determining product distribution.

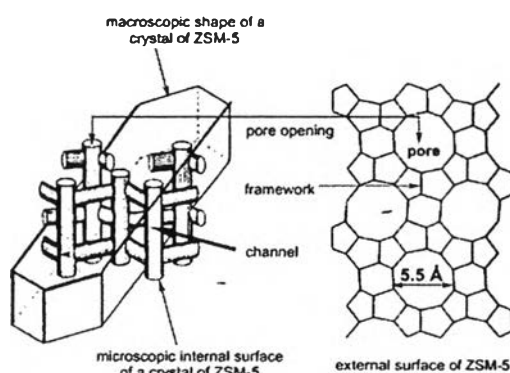


Figure 2.2 Structure of HZSM-5 zeolite (Lei *et al.*, 2003).

HZSM-5 is mostly used in petrochemical industries for many hydrocarbon productions. Due to its poor hydrothermal stability, Zhu *et al.* (2005) modified HZSM-5 with Ni by using impregnation method for the conversion of bioethanol to hydrocarbons. It was observed that Ni modified zeolite had less strong acid sites and more Lewis acid site than the parent zeolite. Ni caused a decrease of BET surface area and micro-pore volume due partial blockage of Ni content. Although the result showed that bio-ethanol conversion is complete at the temperature around 280 C° for referenced and modified catalysts, the hydrothermal stability of 1 wt% Ni/HZSM-5 catalyst was considerably improved. As the result, the Ni doped on HZSM-5 was effective in attenuating irreversible deactivation by dealumination. Other transition metals were studied. Van Niekerk *et al.* (1996) studied the effect of Co and Ni, and found that the number of strong acid sites depended strongly on the amount of metal loading and the type of metal. Lu and Liu (2011) studied on the effect of phosphorous content in HZSM-5 catalyst prepared by impregnation method on the conversion of ethanol to hydrocarbons. It was observed that the peaks of two types of acid in TPD-NH₃ profile shifted to lower temperature when P content increased. The peak representing strong acid started to disappear while the peak of weak acid site

increased. This indicates that the addition of P can reduce strong Bronsted acid sites by substituting into framework Al and extra framework of aluminum phosphate, resulting in the reduction of BET surface area, microporous volume and the change of zeolite structure. Due to the change of acidity of catalyst, the product selectivity has changed. The formation of aromatics and C1-C4 paraffins was suppressed, but the selectivity of C3-C4 olefins as well as resistant of coke formation was enhanced. The similar results were also observed in Takahashi *et al.* (2012) and Song *et al.* (2010). It was suggested that the added phosphorus suppressed the oligomerization of propylene and butane by decreasing of the acid sites of the zeolites and enhancing hydrothermal stability during ethanol conversion. Other types of oxide were also used to modify zeolite. Ouyang *et al.* (2009) investigated on the catalytic conversion of bio-ethanol over La -modified HZSM-5 catalysts. Lanthanum decreased acidity density and acid strength distribution, resulting in the decrease of coke formation during reaction and the increase in catalyst lifetime. With the effect of La, the ethanol conversion and selectivity of ethylene were favored for long run. Since both P and La can enhance the light olefins production and HZSM-5 properties, Zhan *et al.* (2012) studied on Lanthanum- and phosphorus- modified HZSM-5 catalysts in the dehydration of ethanol to ethylene. It was reported that 0.5 wt% La coimpregnated with 2 wt% P on HZSM-5 catalyst gave stronger strength of acid site than the other modified HZSM-5 zeolites. It was suggested that there was an interaction between lanthanum and phosphorus, which plays an important role in ethylene formation. Furthermore, the co-modification of La and P with Ga-HZSM-5 was studied by Furumoto *et al.* (2012). It was concluded that La and P helped to enhance the suppression of carbon deposition and catalyst stability as the same as previous study.

Alkaline earth metal over HZSM-5 zeolite was employed to study in conversion of ethanol by Goto *et al.* (2010). It was found that Sr-HZSM-5 zeolite with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 184 and a Sr/Al ratio of 0.1 gave the highest yield of propylene and high catalytic stability at 500 C°. This result indicated that the product yield and stability depended strongly on $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, M/Al ratio, and reaction conditions. Therefore, alkaline metal could be used to modify to the acidity of zeolite and other properties. The introduction of Ge was studied in the dehydration of 2-propanol and 2-butanol by Van de Water *et al.* (2004). Ge not only enhanced the

catalytic stability of HZSM-5 but also maintained the framework acidity of HZSM-5, unlike P and La.

In 1982, SAPO-34 was synthesized by Union Carbide Laboratories. Its unique characteristics are three dimension framework, narrow pore size and mild acidity (Zhang *et al.*, 2008). SAPO-34 framework consists of tetrahedral Al, P and Si species. Its framework is similar naturally to zeolite chabazite (CHA) as shown in Figure 2.3.

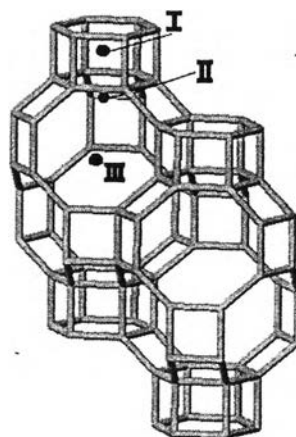


Figure 2.3 Schematic of the Chabazite(CHA) structure (Saxton *et al.*, 2010).

It consists of D6R units arranged in layers linked together by 4-membered rings. The pore structure comprises eight-member rings with 0.38×0.38 nm opening into large cavities of 0.67×1.0 nm. There are three different cation sites that have been determined from diffraction data for dehydrated crystals. Site I is in the centre of the D6R. Site II is at the centre of 6-rings and site III is at the 8-ring pore window. Due to effective pore openings (0.45 nm) of SAPO-34, it is well known as a solid acid catalyst for ethanol conversion to light olefins and for cracking of C4 (Zhou *et al.*, 2008). The pore opening of this material allows only small molecules such as primary alcohols, linear paraffins and olefins to diffuse through the pores. As a consequence, the large hydrocarbons or aromatic diffusion is restricted, leading to high yield and selectivity of lower olefins. In addition, other silicoaluminophosphate molecular sieve such as SAPO-17, SAPO-18, SAPO-35 and SAPO-44 gave good selectivity to light olefins (Dubois *et al.*, 2003).

In general, the incorporation of metal oxides into SAPO-34 could strongly influence on catalyst behavior in ethanol dehydration. Recently, there are many studies on catalytic dehydration of alcohol over metal-modified SAPO-34. Zhang *et al.* (2008) studied catalytic dehydration of ethanol over SAPO-34 and Ni modified SAPO-34. It was concluded that modified SAPO-34 possessed more of weak acid sites than SAPO-34 because nickel generated new acid sites, and NiAPO-34 sample exhibited higher desorption temperature of both weak and strong acid sites in the TPD-NH₃ profile. Other transition metals were used to modify SAPO-34. Chen *et al.* (2010) investigated the effect of Mn and Zn over SAPO synthesized by hydrothermal method and impregnation method. Mn⁺² and Zn⁺² made the ethylene selectivity higher than the original one because of smaller pore and higher acid density. From TPD-NH₃ profile, the result indicated that the insertion of Mn²⁺ and Zn²⁺ in the SAPO-34 framework could lead to the increment of weak acid strength and weak acid sites. The conversion of ethanol and selectivity of ethylene decreased in the following order: Mn-SAPO-34>Zn-SAPO-34>SAPO-11>Mn-SAPO-34>Zn-SAPO-34>SAPO-34. Wei *et al.* (2008) investigated the synthesis, characterization and catalytic performance of Me-SAPO-34 (Me=Co, Mn, Fe) for chloromethane transformation to light olefins by hydrothermal method and impregnation method. The TPR result showed that metals with different chemical environments gave different reduction properties. In this case, a metal introduced by hydrothermal method was much more difficult to be reduced than that prepared by impregnation method due to the incorporation into framework. Co prepared by impregnation method could be reduced at 400 C°, while Co sample prepared by hydrothermal method was reduced at 700-850 C°. Metal oxide has strong influence on catalytic activity. Co and Fe favored ethylene production, whereas Mn favored propylene production.

2.3 Antimony and Tin

From the previous literature reviews, metal oxides could be used to enhance the catalyst activity and selectivity to light hydrocarbon compounds. Due to acidic property, tin oxide and antimony oxide are studied in the work. Oxides of

antimony exist in three phases, namely antimonytrioxide (Sb_2O_3), antimony tetroxide (Sb_2O_4), and antimony pentoxide (Sb_2O_5). These oxide forms have an oxidation state of +3, +4 and +5, respectively (Chin *et al.*, 2010). The change in Gibbs energy is the key parameter that affects the formation of the desired phase. For example, Sb_2O_5 does not exist above 525 C° at which only Sb_2O_3 and Sb_2O_4 are formed. Typically, Sb_2O_3 has two crystalline modifications, cubic polymorph (senarmontite stable phase) and orthorhombic polymorph (valentinite metastable phase). In addition, senarmontite exists as a low temperature a-phase and valentinite as a high temperature b-phase.

Properties	Sb_2O_3	Sb_2O_4	Sb_2O_5
Appearance	White solid	White or yellow solid	Yellow solid
Molecular weight (g/mol)	291.52	307.52	323.52
Density (g/cm ³)	5.2	6.64	3.78
Melting point (°C)	656	N/A	380
Boiling point (°C)	1425	N/A	N/A
Crystal structure	Cubic (<70 °C) Orthorhombic (>570 °C)	Orthorhombic Monoclinic	N/A
Solubility in water	Insoluble	Insoluble	Very slightly soluble

Figure 2.4 Properties of bulk antimony oxides (Chin *et al.*, 2010).

Antimony oxide is mainly used as an alloy material for lead and tin and for lead antimony plates which are used in solders, bullets and plain bearings as well as microelectronics. Antimony compounds are also used as additives for chlorine- and bromine-containing fire retardants found in many commercial and domestic products. Antimony oxide is amphoteric. The insertion of antimony oxide could modify physicochemical and catalytic properties. There are many reports that applied an antimony oxide in a catalytic reaction, for examples, in oxidation reaction, oxidative dehydrogenation and cracking either as a promoter or a catalyst itself.

Matsumura *et al.* (2006) studied on the selective oxidation of methane and ethane over antimony oxide-loaded catalysts prepared by usual impregnation method. SbCl_5 was used as initial precursor loaded on various supports and calcined at 500 C° in the presence of air. It was found that antimony oxide enhanced dehydrogenation, resulting in a high yield of ethylene. The same result is also shown in the study of Kubacka *et al.* (2000). Moreover, the selective oxidation of methane

to formaldehyde was performed under different phases of antimony oxide catalysts (Sb_2O_3 , Sb_6O_{13} , Sb_2O_5) in order to determine active site species as shown in Figure 2.5. Sb_2O_5 showed high selectivity to formaldehyde. The result indicated different oxidation states of antimony oxide that affected the product selectivity. Additionally, the results indicate that the antimony oxide species behaved differently on various supports.

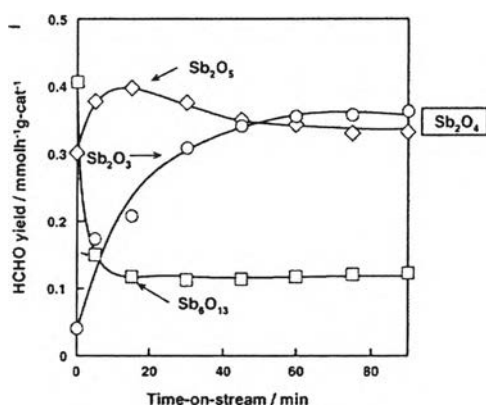


Figure 2.5 Correlation between phase transformation along time-on-stream and formaldehyde yield in the selective oxidation of methane (Matsumura *et al.*, 2006).

Antimony oxides are also used as a promoter in a mixed oxide catalyst in the ammoxidation of propane to acrylonitrile studied by Centi and Perathoner (1995), Nilsson *et al.* (1994), and Guerrero-Pérez and Bañares (2006). It is believed that antimony oxide could abstract hydrogen from hydrocarbons molecules.

Zheng *et al.* (2003) studied on the enhanced para-selectivity of HZSM-5 modified by antimony oxide. The modified HZSM-5 was prepared by solid state-reaction at 550 °C. From the IR and Al-NMR results, antimony was found to strongly interact with the hydroxyl group of HZSM-5 such as silanol, bridging hydroxyl group and extra framework alumina oxide. The antimony oxide was presented in the form of Sb_2O_3 . Modified HZSM-5 was found to improve on the para-selectivity from 33% (3.3 wt% Sb_2O_3) to 68% (10.2 wt% Sb_2O_3) in toluene disproportionation but lower catalytic activity. This is because antimony oxide reacted with acid sites, resulting in the decrease of Bronsted and Lewis acid sites. Moreover, antimony oxide loading affected the size of pore diameter by polymerizing and blocking the pore

mouths of HZSM-5. Narrowing of pore diameter would lower the diffusivity of o- and m- xylene, and then lead to highly p-xylene selectivity. Mao *et al.* (2010) studied on the synthesis of dimethyl ether from syngas over the admixed catalyst of CuO-ZnO-Al₂O₃ and antimony oxide modified HZSM-5 zeolite. The series of HZSM-5 were prepared by various loadings of antimony oxide by solid state ion exchange. They concluded that selectivity of DME was enhanced from 55% to 69% at the temperature of 260 C°. This is because the strong acid sites on HZSM-5 zeolite were reduced by the incorporation of antimony oxide, which inhibited further dehydration reaction to higher olefins and formation of carbon dioxide.

Zhang *et al.* (2006) studied on the antimony oxide species on SiO₂ catalyst within the loading range of 1-20 wt% prepared by incipient wetness impregnation of silica. The solutions of SbCl₅ and SbCl₃ were used as precursors. The samples were calcined at 650 C° for 6 hours. It was concluded that Sb₂O₃/SiO₂ and Sb₂O₅/SiO₂ were well dispersed in SiO₂. The SbOx species on Sb₂O₃/SiO₂ was Sb⁺³ with Sb₂O₃ loading lower than 5wt%. With a higher loading, the concentration of Sb⁺⁵ started to appear because the oxidation of highly dispersed Sb⁺³ occurred more difficultly than that of aggregated Sb⁺³. In addition, the result of catalytic activity indicated that different SbOx species provided a different oxidation activity and product selectivity.

There are two main oxides of tin: stannic oxide (SnO₂) and stannous oxide (SnO) (Batzill and Diebold, 2005). The existence of these two oxides reflects the dual valency of tin, with the oxidation states of 2+ and 4+. Figure 2.6 shows the Sn-O phase diagram at atmospheric pressure. This diagram also indicates the presence of an intermediate tin-oxide phase. These intermediate oxides of Sn are present as a mixture of Sn(II) and Sn(IV).

Tin oxide is an n-type semiconductor which is widely used as gas sensor, transitions. However, tin oxide is used as a catalyst due to acidic property. There were a few researchers that studied on tin oxide. Xu *et al.* (2005) studied on the nano-tin dioxide/ NaY zeolite prepared by impregnation of SnCl₂ solution and then calcined at temperature 350 C°- 700 C°. They concluded that SnO₂ was formed, but the structure of SnO₂ crystal strongly depended on the temperature of calcinations. Sokolovskii and Bulgakov (1977) investigated on the catalytic action of oxide catalyst on the allyl oxidation of propylene. They suggested that allyl group was

stabilized as a pi-bond complex; then, a high concentration of electrons on the surface which are n- semiconductor led to dimerization instead of oxidation. This could be implied that tin and antimony oxides could be able to produce larger hydrocarbons.

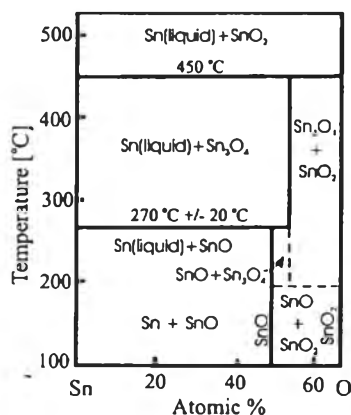


Figure 2.6 Sn-O phase diagram (Luxman and Dobner, 1980).

In addition, tin-modified HBeta was prepared by cation exchange as studied by Shah *et al.* (2012). The TPD-NH₃ result showed that tin oxide enhanced the acidity of HBeta zeolite. The zeolite exhibited higher acid strength but lower acid density because tin ion weakened OH bond which made them more acidic. The similar result was observed by Solsona *et al.* (2012) over SnO₂ promoted NiO catalyst. The result suggested that increasing Sn loading led to higher Lewis acid strength. This indicated that tin oxide could increase the acidic properties of zeolite.

Recently, Wongwanichsin (2013) studied the dehydration of bio-ethanol to light olefins over SAPO-34 modified with Ga₂O₃, GeO₂, SnO₂ and Sb₂O₃. The catalysts were prepared by solid-solid interaction and calcined at the temperature 400 °C. The product distribution indicated that tin oxide and antimony oxide can increase acidity of SAPO-34. 3 wt% of Sb₂O₃/SAPO-34 gave the highest concentration of ethane and 5 wt% of Sb₂O₃/SAPO-34 gave a considerable amount of C10+ aromatics. Moreover, 5 wt% SnO₂/SAPO-34 gives a high yield of propylene and cooking gas. Pasomsub (2013) also studied the catalytic activity of modified HZSM-5 with P₂O₅, Sb₂O₅ and Bi₂O₅. It was observed that the oxides doped on the zeolite could lead to difference in product distribution because of different acid strength.

Moreover, it was found that Sb_2O_5 could enhance the aromatic formation like p-xylene and heavier aromatics because Sb_2O_5 doped on HZSM-5 showed higher acid strength than the unmodified HZSM-5 that could protonate hydrocarbon molecule to form carbenium ions. These ions then could react with small molecules to form larger molecules.

The interaction between two oxide components deposited on the support has a significant influence on the structure definition and the catalytic activity. Saad and Riad (2008) studied on the dehydration-dehydrogenation of isobutanol over mono and bifunctional of zinc oxide catalyst prepared by precipitation method. It was found that the binary oxide catalyst was selective to isobutene rather than isobutylaldehyde. This indicated that binary oxide catalyst favored dehydration reaction more than dehydrogenation because of the presence of high electronegativity cation of Ti^{+4} and Cr^{+3} . A higher Lewis acid density and acid strength on the surface led to the faster formation of olefins. Talehilo and Lurt (1989) investigated on the oxidation of propene to acrolein over antimony-tin mixed catalysts. The result showed that, on Sb-Sn-O catalyst, tin ions interacted more readily with propylene than antimony ions to abstract first hydrogen, while Sb^{+3} and Sb^{+5} were responsible for the conversion of π -allyl species to acrolein. This indicates that the mixed catalyst of antimony and tin oxide participate in oxidation by providing a favorable surface structure. Cross and Pyke (1978) studied on the surface composition of mixed tin and antimony oxide catalyst prepared by the coprecipitation of anhydrous SnCl_4 and SbCl_5 in ammonium hydroxide solution. The catalyst sample was calcined in the range of 100 to 1,000 $^\circ\text{C}$. They concluded that antimony oxide formed was composed of +3 and +5 oxidation states while tin oxide maintained in the form of Sn^{+4} . At a calcination temperature of higher than 400 $^\circ\text{C}$, antimony oxide started to segregate to form larger size resulting in a higher concentration of Sb^{+3} . The similar result was also observed by Herrmann and Portraix (1979) using an electrical conductivity technique as well as reported in Figueras *et al.* (1982). It was suggested that calcinations temperature affected the structural properties of Sn-Sb-O catalyst. This could lead to the difference in the selective oxidation of xylene.

Both tin oxide and antimony oxide have dual stable valences. Tin oxide has 2 stable oxidation states, which are +2 and +4. Antimony has 2 stable oxidation

states as well, which are +3 and +5. Tin oxide is amphoteric oxide which reacts with both acid and base. However, for antimony oxide, the one with +3 oxidation state is amphoteric, while the +5 oxidation state is acidic. Acid strength increases with the amount of oxygen substitution on the central atom. More oxygen atoms weaken the O-H bond, leading to easier loss of proton. For two acids with the same number of oxygen or in the same group on the periodic table, the one with the larger principal quantum number has the more weakly bound proton. Therefore, it is the stronger acid. In this work, difference of oxidation state of metal oxide doped on SAPO-34 zeolite was studied in order to observe the effect of oxidation state of oxide to catalytic dehydration reaction.

Not only metal oxide but also metal could affect the catalytic activity. De Lima *et al.* (2009) studied on ethanol decomposition over CeZrO_2 and Pt/CeZrO_2 , and suggested that Pt favored the acetaldehyde formation via the dehydrogenation of ethanol. The significant amount of hydrogen was also observed. The similar result was observed by Yee *et al.* (2000). The TPD and FT-IR results showed that ethanol adsorbed dissociatively and formed ethoxide and adsorbed hydrogen. Later on, ethoxide were further dehydrogenated to acetaldehyde. This could be implied that the incorporation of metal on the support might convert ethanol to oxygenate compounds instead of olefins, resulting in different reaction pathway. In order to prepare the catalysts doped by metallic tin and antimony, the oxides of tin and antimony must be reduced. Chernogorenko *et al.* (1977) studied on the reaction of antimony oxide by hydrogen. The result showed three grams of chemically pure grade Sb_2O_3 was fully reduced in a flow-type quartz reactor at 550 C° and 600 C° for 25 and 5 hours, respectively. Furthermore, Kim *et al.* (2011) investigated the reduction of SnO_2 with hydrogen. The effect of reaction temperature on the reducibility of SnO_2 powder was performed by varying the reaction temperatures between 500 and 750 C° at a fixed hydrogen partial pressure of 101.3 kPa as shown in Figure 2.7.

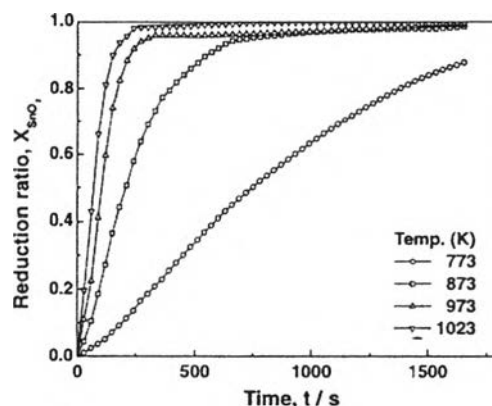


Figure 2.7 Effect of reduction temperature vs. time of reaction (Kim *et al.*, 2011).

In this work, the effects of tin and antimony metals from the reduction of tin oxide- and antimony oxide- doped on SAPO-34 on the product distribution were studied.

In summary, the objectives of this research were to study the effect of oxidation state of acidic oxides of SnO_x - and Sb_2O_x - on SAPO-34 catalyst. The catalysts with different oxidation states were prepared by varying loading amounts and at various calcination temperatures in order to study the effect of metallic tin and antimony on SAPO-34. The scope of research therefore covers the following items:

Scope 1: Studies of zeolite stability and the interaction between oxides and zeolite

The stability test of SAPO-34 was done by using TGA and XRD to observe the temperature which SAPO-34 can maintain its structure. Three grams of SnO , SnO_2 , Sb_2O_3 and Sb_2O_5 powder was loaded individually into the reactor to observe the effect of each oxide on the dehydration of bio-ethanol.

Scope 2: Studies of oxides loading and calcinations temperature on oxidation state and catalytic activity

An amount of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and SbCl_3 was individually mixed with SAPO-34 by solid-solid interaction to obtain the elemental loading percentages of 5% and 7%. Then, the catalysts were calcined at different temperatures to get various oxidation states of metal oxide. The reactor used in this research was an isothermal fixed bed reactor. The amount of a catalyst loaded into the reactor tube was 3 g. The bio-ethanol concentration was 99.5% in the feed. The reaction temperature was 300-

600 C°. The reaction time was performed for 8 hours, whereas the gaseous product was analyzed at every 45 minutes.

Table 2.1 The number of experiments for the second scope

Temperature of Calcination	%Loading	5%Sn	7%Sn	5%Sb	7%Sb
400		(1)	(3)	(5)	(7)
700		(2)	(4)	(6)	(8)

Scope 3: Effect of tin and antimony metals

Metallic Tin and antimony supported on SAPO-34 catalyst were treated under hydrogen atmosphere. Then, the catalysts were loaded into an isothermal fixed bed reactor. The amount of catalyst loaded into the reactor tube was 3 g. The bio-ethanol concentration was 99.5% in the feed. The reaction temperature was 300-600 C°. The reaction time was performed for 8 hours, whereas gaseous product was analyzed at every 45 minutes.

Table 2.2 The number of experiments for the third scope

Catalyst	%Loading	5%Sn	5%Sb
SAPO-34		(9)	(10)