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# Metallic Sn- and $SnO_2$-doped SAPO-34 as Model Catalysts for Investigating the Effect of Oxidation States on Bio-Ethanol Dehydration Products

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Over the last decade, due to the increase of energy demand and lower cost of bio-ethanol production, the conversion of bio-ethanol to valuable products such as light olefins, paraffins and aromatics have been received considerable attention. From the previous result, it was found that tin oxide doped on SAPO-34 was discovered to have properties that enhance the formation of cooking gas and larger hydrocarbons. However, during the preparation, tin oxide doped on SAPO-34 cannot be made pure as a single oxide of tin; therefore, the outcomes from bio-ethanol were influenced by the oxidation states of tin. The aim of this work was therefore to examine the oxidation states of tin oxide doped on previously-tested SAPO-34 support, and study their effects on products. Metallic Sn- and $SnO_2$- doped on SAPO-34 were employed as model catalysts in order to investigate the influences of $Sn^0$ and $Sn^{+4}$ oxidation states on the products from bio-ethanol dehydration. The results were compared with those obtained from the tin-oxide-doped SAPO-34 catalyst previously tested. The loading percentage of tin oxides was fixed at 7 wt%, and the catalysts were characterized by using SAA, XRD, XRF and, mainly, XPS. The reaction was carried out in an isothermal fixed bed reactor at atmospheric pressure 400 °C and at WHSV of 0.5 $h^{-1}$. The product sampling was taken at 1 hour of time-on-stream. The gaseous products were analyzed by using an online-GC while the liquid products needed a SIMDIST-GC and a GC-TOFMS to identify petroleum fractions and hydrocarbon species, respectively. It was found that from XPS spectra, tin oxides on the previously-tested catalyst were found to be in the form of Sn–OH and $SnO_2$. After the catalytic test, tin oxide doped on SAPO-34 contained mixed valences of $Sn^0$ and $Sn^{+4}$, which affect the product distribution of both gas and liquid. The liquid product was distributed in gasoline range, and comprised, mainly, of benzene and oxygenate compounds. From the result, it was also observed that $Sn^{+4}$ seems to contribute in the production of oxygenate compounds; whereas, metallic tin contributes on benzene formation.

## 1. Introduction

Depleting oil resource and growing demands for fossil consumption combined with environmental concerns, such as the emission of green house gases have been the main driving forces for the development of alternative sustainable applications from renewable feedstocks. The bio-ethanol via fermentation process of biomass, such as corn stover, palm and sugar cane has been widely produced due to positive energy balance (Ko et al., 2013). Bio-ethanol is widely used as a fuel or additives for transportation (Chistyakov et al., 2011). Moreover, bio-ethanol has been received significant interest as a promising feedstock for catalytic dehydration to obtain light compounds or aromatic compounds such as ethylene, propylene and p-xylene.

The dehydration reaction of bio-ethanol is well known to be promoted by acid catalysts. Earlier, various catalysts, heteropolyacid catalysts (Varisli et al., 2007) as well as transition metal oxides (Zaki, 2005), have been tested for dehydration of ethanol. Other solid acid catalysts such as zeolites and silica-alumina

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were also studied for dehydration of ethanol, and it was observed that the number of Brønsted acid site played an important role on catalytic activity (Takahara et al., 2005). Moreover, many researchers have investigated HZSM-5 (Zaki, 2005) and modified HZSM-5 (Lu and Liu, 2011)on ethanol dehydration due to their high-shape selectivity. It was found that the product selectivity and activity were improved after the addition of metal oxides. However, HZSM-5 tends to accelerate oligomerization of ethylene, resulting in rapid formation of carboneous deposition on the zeolite. Silicoaluminophosphate molecular sieve-34 (SAPO-34) has been shown as a promising solid acid catalyst for converting bio-ethanol to light olefins and cracking of C4 (Zhou et al., 2008) due to its moderate acid strength and zeolite structure. The pore opening of SAPO-34 allows only small molecules such as light olefins and small paraffins to pass through. As a result, the formation of big hydrocarbons is restricted, leading to higher yield and selectivity of smaller olefins.

Recently, the modification of tin oxide on SAPO-34 was studied by Wongwanichsin (2013). The result showed that the yield of propylene and cooking gas were promoted after adding tin oxide. This is because tin oxide could enhance the acid strength of catalysts. However, there is no evidence of how tin oxide could promote the formation of hydrocarbons. In this present study, the oxidation state of tin oxide doped on previously-tested SAPO-34 support was investigated for its impact. Metallic Sn- and $SnO_2$-SAPO-34 were applied as model catalysts in order to investigate the influences of $Sn^0$ and $Sn^{+4}$ oxidation states on the products from bio-ethanol dehydration. The modified SAPO-34, metallic tin, and tin(V) oxide were characterized using surface area analyzer (SAA), X-ray diffraction spectroscopy (XRD), X-ray fluorescence spectrometry (XRF) and X-ray photoelectron spectroscopy (XPS).

## 2. Experimental Section

### 2.1 Catalyst Preparation

SAPO-34 catalyst, supplied from Tainjin Chemist Scientific Limited, was dried at 110 ºC for 3 h and calcined with the heating rate of 10 ºC/min to 400 ºC. The catalyst was kept at this temperature for 2 h to remove the water and impurities. A calculated amount of $SnCl_2 \cdot 2H_2O$ was mixed with SAPO-34 by solid-solid interaction method to obtain elemental loading percentage of 7 %. After that, the catalysts were calcined in air at 400 ºC for 2 h. They were then pelletized using hydraulic pelletizer machine. The pellets were crushed and sieved in the range of 20-40 meshes.

### 2.2 Catalyst Characterization

The Brunauer-Emmett-Teller (BET) technique was performed to determine the specific surface area, the total pore volume, and the pore size of catalysts using a Thermo Finnigan/Sorptomatic 1990 surface area analyzer. The pore size distribution was calculated using the Horvath Kawazoe (HK) method. The oxide forms of catalyst were analyzed using a Bruker X-Ray diffractometer system (D8 Advance). The detector scanned as a function of 2θ by starting at the 5º to 80º (2θ) range with a scan speed of 10º (2θ)/min. The data from XRD were analyzed and recorded by an on-line computer. X-ray fluorescence spectrometry (AXIOS PW4400) was used to estimate the concentrations of elements present in the solid and powder samples. XPS spectra were carried out using a AXIS ULTRA$^{DLD}$. The system was equipped with a monochromatic Al X-ray source and a hemispherical analyzer. The spectrometer was operated with the pass energy of 160 eV and 40 eV when recording wide scan and core level spectra, respectively. All peaks were calibrated from referring C1s spectra located at 284.6 eV.

### 2.3 Catalytic Testing

The catalytic dehydration of bio-ethanol was performed in an isothermal fixed-bed stainless steel reactor under atmospheric pressure. The reaction temperature was controlled at a temperature of 400 ºC using temperature controllers. The bio-ethanol was fed by a syringe pump with helium gas, as carrier gas, through the catalyst bed. The products coming out from the U-tube reactor were condensed in a cooling condensing flask to collect the condensable products while the non-condensable products were kept in a gas bag. The gaseous products were then injected online to gas chromatograph equipped with in a flame ionization detector mode (FID).

### 2.4 Product Analysis

The non-condensable gaseous product was kept in the gas sampling bag, and then analyzed by a gas chromatograph (Agilent Technologies 6890 Network GC system) using an HP-PLOT Q column with a flame ionization detector (FID) for hydrocarbon gases; namely, $CH_4$, $C_2H_6$, $C_2H_4$, $C_3H_8$, $C_4H_{10}$, and $C_4H_8$. A DBWAX column, installed in parallel and also equipped with the FID, was employed to determine oxygenate components. In addition, a Gas Chromatograph equipped with a Mass Spectrometry of Time of Flight type (GC×GC-TOF) was used to identify the compositions of the oil products.

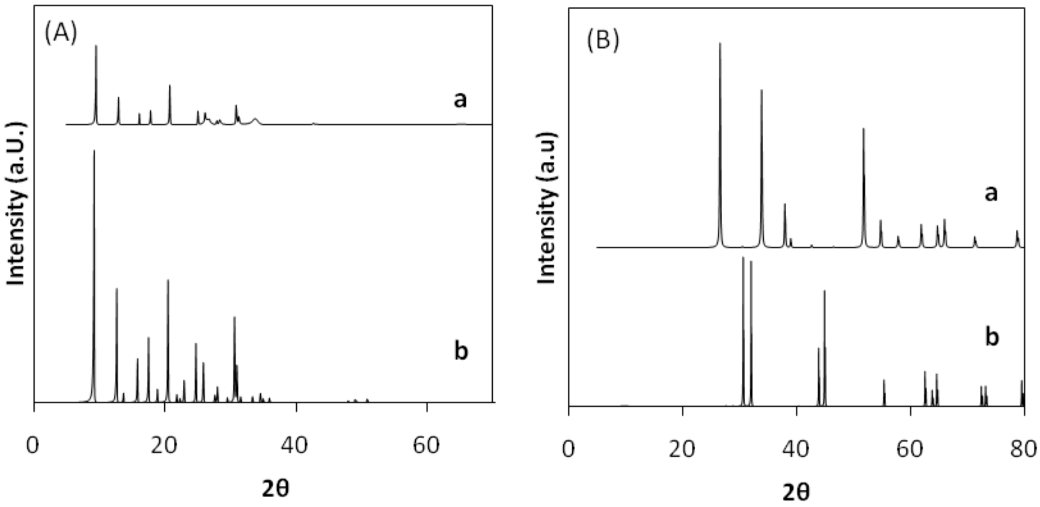

*Figure 1: (A) X-ray diffraction pattern of (a) SAPO-34 and (b) 7 wt% tin oxide-doped SAPO-34, and (B) X-ray diffraction spectra of (a) $SnO_2$ and (b) metallic tin*

## 3. Result and Discussion

The XRD patterns of fresh SAPO-34 and 7 wt% tin oxide-doped SAPO-34 are shown in Figure 1(A), whereas those of commercial metallic tin and $SnO_2$ are displayed in Figure 1(B). The rutile structure of $SnO_2$ can be mainly detected at 2θ=26.5°, 34° and 51.7° while the peaks of metallic tin can be detected at 2θ=30.6°, 32.0°, 43.9° and 44.9 °. The SAPO-34 and modified one exhibit similar pattern, but the peak intensity of the doped one is sharper. This indicates that the tin oxide may partially cover surface of the zeolite due to the solid-solid interaction method. Only small amount of tin oxide can disperse inside micropores of SAPO-34. The broad peak of $SnO_2$ can be seen at 2θ=26.5° and 34° in Figure 1(A), a, indicating that tin oxide can disperse well on the SAPO-34.

Table 1 displays the specific surface areas, pore volume, and Horvath Kawazoe (HK) pore diameter of SAPO-34 supported catalysts. The introduction of metal oxide via solid-solid interaction method leads to the reduction of specific surface area. This is because the metal oxide itself has much a lower surface area than that of the zeolite as can be seen in Table 1. Therefore, after doping with Sn or $SnO_2$ via solid-solid interaction method, the average surface area of the catalyst decreases significantly.

The XPS analysis of fresh and spent catalysts was done in order to observe the change of binding energy (BE) or oxidation state. After the binding energy calibration, the convolution of the Sn 3d was performed by based on the BE of metallic Sn (485 eV), SnO (486 eV), SnO2 (486.7-487.4 eV) and Sn-OH (488-488.5) (Krishnakumar et al., 2009). Figure 2(A) displays the fitting result of metallic tin before and after the dehydration of bio-ethanol. The peak of fresh metallic tin located at 485.0 eV is assigned to oxidation state of 0. After the catalytic test, the oxidation state of metallic tin changed to which could be assigned to the oxidation states of 0 and +4 with the relative peak area of 12.5 and 87.5 %, respectively. It is well known that tin tends to be oxidized when exposed to an oxidizing atmosphere. This indicates that metallic tin could be oxidized during dehydration reaction. Figure 3(B) displays the fitting peaks of fresh and spent tin oxide. It was found from the XPS result that the oxidation state of tin oxide did not significantly change. The relative peak area located at 488.0 eV and assigned to Sn-OH group increased from 3.2 to 9.4 %.

*Table 1: Physical characteristics of SAPO34, modified SAPO34, and metal oxides*

| Sample | $S_{bet}$ ($m^2/g$) | Pore Volume ($cm^3/g$) | Pore diameter (Å) |
|---|---|---|---|
| SAPO-34 | 364.4 | 0.22 | 0.49 |
| 7SnSAPO-34 | 315.2 | 0.17 | 0.47 |
| Sn | 3.7 | 0.003 | 19.2 |
| $SnO_2$ | 10.8 | 0.04 | 18.8 |

The sample containing –OH group was revealed that tin oxide is hygroscopic in nature (Krishnakumar et al., 2009), which may be able to act as bronsted acid, leading to bigger hydrocarbon formation. For the modified SAPO-34, the change of oxidation state of tin oxide doped on SAPO-34 is shown in Figure 3. The two different peaks of fresh 7 wt% tin oxide-doped SAPO-34 could be assigned to $SnO_2$ and Sn-OH. After the reaction, the peaks of the spent catalyst are assigned to tin oxides with the oxidation state of 0 and +4. It is suggested that tin oxide on SAPO-34 can be more easily reduced than the commercial tin oxide. The peaks of tin oxide on SAPO-34 are located at binding energies of 485.2 and 487.2 eV, which are higher than those of the commercial metallic tin and tin oxide, respectively. This suggests that there may be an interaction between tin oxide and support.

The dehydration of bio-ethanol was studied at the reaction temperature of 400 ºC. The conversion of bio-ethanol was found not different with or without catalysts, indicating that bio-ethanol is able to convert to ethylene easily at 400 ºC. Table 3 presents the product distribution obtained from metallic tin, tin oxide, SAPO-34 and doped SAPO-34 in dehydration of bio-ethanol. All catalysts showed the decrease in ethylene selectivity and the increase of propylene, cooking gas and butylenes, compared to non-catalyst case (97.2 %). The selectivity of propylene slightly increases when metallic tin or tin oxide was added. This is because of large pore of metallic tin and tin oxide, unlike SAPO-34. The main products in oils using either metallic tin or tin oxide are oxygenates, non aromatics and benzene. The majority of oxygenate compounds are propanal, 2-butanone, and 1,1-diethoxyethane. In the non-aromatics obtained from metallic tin, hexane and cyclohexane are the main components. On the contrary, non-aromatics from tin oxide are mainly consisted of hexane and cyclohexane with and without branches. Because of no pore constraint, ethylene might undergo oligomerization and hydrogenation to form hexane, and cyclization and aromatization to form cyclohexane and benzene, respectively. It is noticed that metallic tin gives more hexane than tin oxide, indicating that metallic tin favours hydrogenation rather than cyclization. As seen from the XPS result, tin oxide is formed on the metallic tin surface, which may be caused by the adsorption of ethanol, leaving oxygen group in the surface. It was reported that tin oxide could produce both oxidation products and dehydration products (McCabe and MItchell, 1984). Therefore, the commercial tin oxide might enhance oxidation reaction since the oxidation state of tin 0 was observed after catalytic testing. As the result, the selectivity of oxygenate compounds increases as the oxidation state increases while the selectivity of benzene shows the opposite trend.

In addition, the parent SAPO-34 gives 10 wt% propylene due its small pore constrain and mild acidity. When tin oxide is doped with SAPO-34, the selectivity of propylene goes up remarkably. The trend also goes with the selectivity of cooking gas. From XPS result, the binding energy of tin oxide doped on SAPO-34 is higher than the commercial tin oxide, indicating that there is an interaction between tin oxide and zeolite and tin oxide is highly dispersed on the zeolite. This infers that highly-dispersed tin oxide is more active than tin oxide itself. It was previously reported that Sn doped on zeolite could act as Lewis acid (Corma et al., 2003). Therefore, tin oxide having oxidation state +4 on the support may enhance propylene and cooking gas formation.

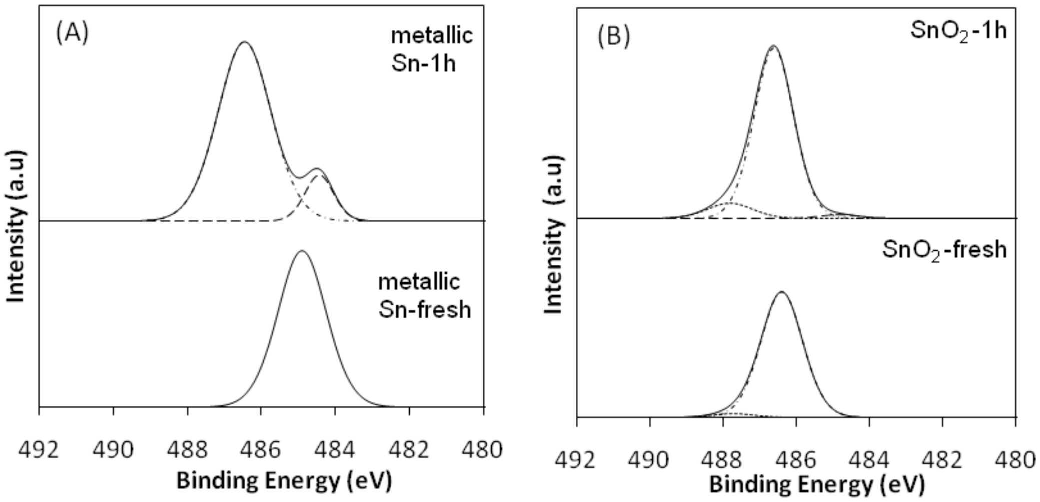

*Figure 2: (A) Sn 3d$_{5/2}$ XPS spectra of fresh and spent metallic tin, and (B) Sn 3d$_{5/2}$ XPS spectra of fresh and spent tin oxide*

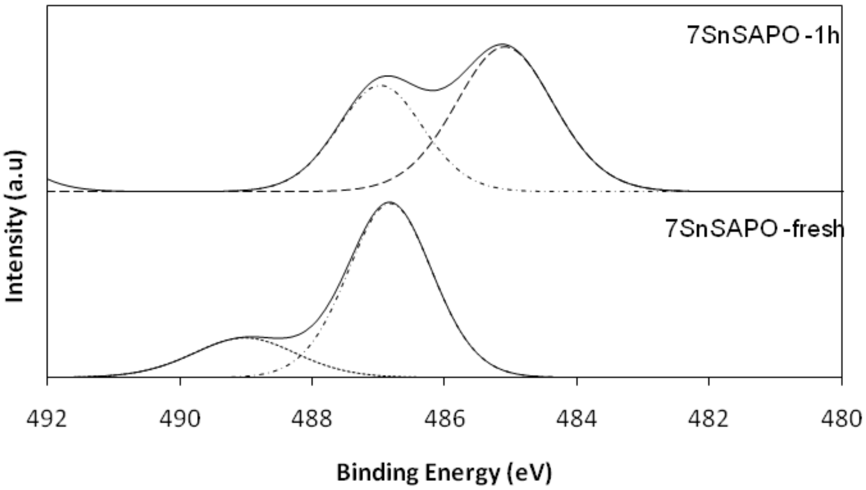

*Figure 3: Sn 3d$_{5/2}$ XPS spectra of fresh and spent 7 wt% tin oxide doped on SAPO-34*

*Table 1: Product distribution in gas and oil from dehydration of bio-ethanol*

| Sample | Concentration (wt %) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | C2H4 | C3H6 | nC3-C4 | C4H8 | Oxygenates | Non-aromatic | Benzene | Aromatics (C10+) |
| Sn | 90.9 | 0.5 | 1.1 | 6.8 | 20.9 | 15.0 | 64.1 | 0.0 |
| $SnO_2$ | 86.2 | 0.4 | 0.5 | 7.0 | 25.9 | 27.0 | 47.1 | 0.0 |
| SAPO-34 | 70.1 | 10.0 | 8.0 | 2.7 | 45.4 | 0.0 | 53.5 | 2.0 |
| 7SnSAPO-34 | 47.5 | 18.6 | 16.7 | 5.2 | 13.4 | 0.0 | 72.0 | 14.5 |

The oils from SAPO-34 and the modified SAPO-34 contain only oxygenates and benzene. The major oxygenate components obtained from SAPO-34 are branched pentanone and cyclopentanone. The number of carbon atom is limited to five carbons, whereas the oxygenates from using 7 wt% of tin oxide-doped SAPO-34 consist of branched phthalic acid group, which contain carbon atom more than five. In addition, Naphthalene is formed with using SAPO-34, indicating that naphthalene is formed through carbenium ion pathways. The addition of tin oxide increases naphthalene significantly. It was reported that aromatics are usually formed from acidic zeolites. In this case, naphthalene is formed outside the pore of SAPO-34 since the kinematic diameters of aromatics, such as benzene and bigger aromatics, are much larger than the pore diameter of SAPO-34. Therefore, the formation of aromatics depends on the acidity of zeolites. From the XPS studies, highly-dispersed tin oxide on SAPO-34 shows the reducibility, leading to the formation of metallic tin on the support surface. This metallic tin together with cyclization and dehydrogenation abilities of acidic support zeolite may increase the selectivity of aromatics as can be seen from Table 2.

## 4. Conclusions

Different oxidation states of commercial tin oxide were investigated to observe the effect on the product distribution on bio-ethanol dehydration. From our study, it was revealed that different oxidation states of tin were selective to different products. Metallic tin favors more benzene formation through cyclization and dehydrogenation while tin oxide with oxidation state +4 is selective to oxygenate compounds and non-aromatics. When tin oxide was doped on SAPO-34, there is a synergistic effect between metal oxide and acidic support, which enhanced the formation of propylene, cooking gas, benzene and naphthalene. Its reducibility of highly-dispersed tin oxide on SAPO-34 is the reason for high selectivity to aromatics naphthalene.

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