Ethanol Dehydration over WO$_3$/TiO$_2$ Catalysts Using Titania Derived from Sol-Gel and Solvothermal Methods

Anchale Tresatayawed, Peangpit Glinrun, and Bunjerd Jongsomjit

1Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand
2Department of Petrochemicals and Environmental Management, Faculty of Engineering, Pathumwan Institute of Technology, Phathumwan, Bangkok 10330, Thailand

Correspondence should be addressed to Bunjerd Jongsomjit; bunjerd.j@chula.ac.th

Received 23 November 2018; Accepted 12 February 2019; Published 3 March 2019

Guest Editor: Masaru Watanabe

Copyright © 2019 Anchale Tresatayawed et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The present study aims to investigate the catalytic ethanol dehydration to higher value products including ethylene, diethyl ether (DEE), and acetaldehyde. The catalysts used for this reaction were WO$_3$/TiO$_2$ catalysts having W loading of 13.5 wt.%. For a comparative study, the TiO$_2$ supports employed were varied by two different preparation methods including the sol-gel and solvothermal-derived TiO$_2$ supports, denoted as TiO$_2$-SG and TiO$_2$-SV, respectively. It is obvious that the different preparation methods essentially altered the physicochemical properties of TiO$_2$ supports. It was found that the TiO$_2$-SV exhibited higher surface area and pore volume and larger amounts of acid sites than those of TiO$_2$-SG. As a consequence, different characteristics of support apparently affected the catalytic properties of WO$_3$/TiO$_2$ catalysts. As expected, both catalysts WO$_3$/TiO$_2$-SG and WO$_3$/TiO$_2$-SV exhibited increased ethanol conversion with increasing temperatures from 200 to 400°C. It appeared that the highest ethanol conversion (ca. 88%) at 400°C was achieved by the WO$_3$/TiO$_2$-SV catalysts due to its high acidity. It is worth noting that the presence of WO$_3$ onto TiO$_2$-SV yielded a remarkable increase in DEE selectivity (ca. 68%) at 250°C. In summary, WO$_3$/TiO$_2$-SV catalyst is promising to convert ethanol into ethylene and DEE, having the highest ethylene yield of ca. 77% at 400°C and highest DEE yield of ca. 26% at 250°C. These can be attributed to proper pore structure, acidity, and distribution of WO$_3$.

1. Introduction

Recently, catalytic ethanol dehydration to produce ethylene and diethyl ether (DEE) has been paid attention due to its cleaner technology and efficient utilization of ethanol, which is a renewable raw material obtained from fermentation of biomass. For instance, the production of ethylene from ethanol is considered as an alternative way to produce ethylene, which is currently produced by the catalytic thermal cracking of petroleum feed stocks such as naphtha and dehydrogenation of ethane from natural gas. In fact, dehydration of ethanol to ethylene is a cleaner technology due to lower operating temperature, uncomplicated process, and less impurity. It is well known that ethylene is one of the most important raw materials for petrochemical industry, which is used as a starting material for production of polyethylene, ethylene oxide, vinyl acetate, ethyl benzene, etc. Considering the production of commercialized DEE at present, although it is produced from dehydration of ethanol, the process is not benign since it uses mineral liquid acids such as H$_2$SO$_4$ to catalyze the reaction. Thus, further separation and purification are required. In this case, the solid acid catalysts are preferred since they are reusable and easy to separate from the product. Although the use of DEE is much lesser than ethylene, it is very important chemical. In particular, DEE is mainly employed as a solvent for fragrance and pharmaceutical industries. In transport fuel function, DEE is applied as an ignition-improving additive in engines according to its high volatility and cetane and octane number. The blending of DEE in diesel improves the
performance-emission characteristics with thermal efficiency and reduced emission of NOx, CO, and HC [1]. Hence, the production of ethylene and DEE from ethanol using suitable solid catalysts is very captivating.

Theoretically, the catalytic ethanol dehydration to ethylene and DEE requires acid sites. This reaction essentially undergoes via thermodynamic and kinetic controls. The formation of ethylene is dominated by high reaction temperature since it is an endothermic reaction, whereas DEE mainly occurs at lower reaction temperature due to its exothermic reaction. However, during dehydration of ethanol, a side reaction such as dehydrogenation can occur resulting in the formation of acetaldehyde as a byproduct. From previous works, many solid acid catalysts have been investigated in ethanol dehydration reaction including the transition metal oxides [2–4], zeolites [5], silica-alumina [6, 7], and heteropolyacids [8]. Many researchers found that the transition metal oxides such as TiO2, ZrO2, SiO2, and Nb2O5 play an important role in heterogeneous catalysis acting as an active phase, promoter, or support of solid catalysts. Those solid catalysts have been developed on structure characteristics and acid properties to build up the product selectivity, catalytic activity, and stability. Among the transition metal oxides, TiO2 has been widely used as a support in heterogeneous catalysts due to its suitable surface areas, thermal stability and mechanical resistance [9, 10]. Furthermore, the modification by doping of the active noble and transition metals such as Cs [11], Au/Ag/Cu [12], Al [13], Ru [14], Pt, Pd [15], Mo [16], and W [17, 18] into catalyst supports apparently affected the catalyst selectivity and activity.

In addition, the presence of tungsten (W) metal was found to be very interesting since it contributes Bronsted acid site and increases the catalyst stability and activity [19–21]. It is reported that WO3/TiO2 catalyst is widely used in various reactions and processes including glycerol hydrogenation, reforming, oxidation of dibenzothiophene [22], selective catalytic reduction [23], dehydration [24], and photoelectrocatalytic degradation [25]. Phung et al. [26] also reported that WO3/TiO2 is promising for the catalytic dehydration of ethanol to ethylene and especially DEE at low temperature. They reported that the addition of tungsten on transition metal oxide provided the Bronsted acids sites that are active to the ethanol dehydration reaction to produce ethylene and DEE and also prevent the formation of byproducts such as acetaldehyde and higher hydrocarbons. In addition, with various tungsten loadings on TiO2, ZrO2 and SiO2 support, the WO3/TiO2 catalyst was found to be the most active in this reaction giving the highest yield of DEE. However, besides the active metals, one needs to consider on the properties of a wide variety of supports themselves. The variations of support characteristics mostly arise from different preparation methods. There are many reports focusing on using different methods to prepare various metal oxide supports including the sol-gel [27, 28] and solvothermal methods [29, 30]. In most cases, they found that different preparation methods can alter the properties of support and consequently, different catalytic properties were observed. Therefore, the effect of different preparation methods on the properties of support is crucial for better understanding.

Similarly to Phung et al. [26] study, the WO3/TiO2 catalyst was employed in ethanol dehydration reaction. They examined the difference in some support metal oxides such as ZrO2 and SiO2. However, the main goal of this present study is to develop a better understanding on different preparation methods including the sol-gel and solvothermal methods to synthesize the TiO2 supports for WO3 catalysts used in catalytic ethanol dehydration to ethylene and DEE. The different characteristics of TiO2 supports and WO3/TiO2 catalysts were determined using various characterization techniques. The change in catalytic properties was also investigated via the catalytic ethanol dehydration in a fixed-bed microreactor at the temperature range of 200 to 400°C. Ethanol conversion and product selectivity of different WO3/TiO2 catalysts were reported and discussed further.

2. Experimental

2.1. Materials. Chemicals used for preparation of the catalysts were titanium ethoxide (Ti~20%) purchased from Aldrich, ethanol (99.99%) from Merck Company Ltd., titanium (IV) n-butoxide (97%), 1,4-butadienol, and tungsten (VI) chloride (99.9+ % metals) from Aldrich. For the reaction study, ultrahigh purity nitrogen gas (99.99%) from Linde (Thailand) Public Company Ltd. was employed.

2.2. Preparation of TiO2 Supports and WO3/TiO2 Catalysts. In this study, TiO2 supports were synthesized using two different methods including the sol-gel and solvothermal methods as reported by Panpranot et al. [29] for a comparative study. For the sol-gel method, titanium ethoxide was used as the precursor. First, the precursor was dissolved in the excess ethanol before added to deionized water with the molar ratio of 165. The mixture solution was stirred under 20 rpm/min at room temperature at least for 2 h. The white precipitates of hydrous oxides formed instantly and separated by centrifugation. The product was dispersed in the ethanol at least 5 times following with centrifugation. The sample was dried and calcined at 450°C for 2 h at the heating rate of 10°C/min. Finally, the white powder of TiO2 prepared by the sol-gel method was obtained and denoted as TiO2-SG.

For the solvothermal method, 25 g of titanium (IV) n-butoxide (TNB) was used as the precursor. TNB was suspended in 100 ml of 1,4-butadienol in a test tube and placed in the autoclave. The autoclave was completely purged with nitrogen at a pressure of 30 bars before increasing the temperature to 320°C at a heating rate of 2.5°C/min and further held at that temperature for 6 h. Autogenous pressure during the reaction gradually increased as the temperature increased. After the reaction, the autoclave was cooled down to room temperature. The white powder was collected and then washed with ethanol followed by centrifugation at least 5 times. The powder was dried overnight at 110°C, and finally the white powder of TiO2 prepared
by the solvothermal method was obtained and denoted as TiO$_2$-SV.

In order to prepare the WO$_3$/TiO$_2$ catalysts having W loading of 13.5 wt.%, the simple incipient wetness impregnation was used. The TiO$_2$-SG and TiO$_2$-SV supports obtained as mentioned above were used. It was accomplished using the tungsten (VI) chloride as a precursor, followed by drying the catalyst sample overnight at 110°C and calcined at 400°C with a heating rate of 10°C/min for 3 h. Consequently, the obtained WO$_3$/TiO$_2$ catalysts are denoted as WO$_3$/TiO$_2$-SG and WO$_3$/TiO$_2$-SV upon the TiO$_2$ supports employed.

2.3. Catalyst Characterization. The support and catalysts were characterized by several techniques, which are as follows.

2.3.1. Powder X-Ray Diffraction (XRD). The SIEMENS D-5000 X-ray diffractometer using CuK$_\alpha$ radiation ($\lambda = 1.54439\,\text{Å}$) was used to determine the crystalline phase structure of supports and catalysts. The crystalline domain sizes were calculated from the Scherrer equation. The supports and catalysts were scanned at a rate of 2.4 min$^{-1}$ in the range 2θ from 20 to 80 degrees with the resolution of 0.02°.

2.3.2. N$_2$ Physisorption. The adsorptiometer Micromeritics ASAP 2010 automated system instrument was used to determine surface area (BET method), pore volume/diameter, and pore size distribution (BJH method) by nitrogen gas adsorption-desorption at liquid nitrogen temperature at −196°C.

2.3.3. Temperature-Programmed Desorption of Ammonia (NH$_3$-TPD) and Carbon Dioxide (CO$_2$-TPD). The Micromeritics Chemisorb 2750 Pulse chemisorption system instrument was employed to identify the acidity and basicity on supports and catalysts. The 0.03 g quartz wool and 0.05 g of support were packed in a quartz tube and pretreated at 0.03 g quartz wool and 0.05 g of catalyst (or support) were packed in the middle of reactor. The catalyst was preheated by flowing N$_2$ with a flow rate of 60 ml/min at 200°C for 1 h under atmospheric pressure to remove the moisture and impurity on surface of catalyst prior reaction. Afterwards, the reaction was started by feeding vaporized ethanol and N$_2$ stream as carrier gas. The ethanol flow rate was maintained at 1.45 ml/h (weight hourly space velocity (WHSV) = 22.9 (g ethanol/g cat·h$^{-1}$)) controlled by a syringe pump injection. The reaction was operated at temperature varied from 200 to 400°C. After reaching steady-state condition, the reaction product compositions at reactor effluent were analyzed by a Shimadzu gas chromatography (GCBA) with flame ionization detector (FID) using DB-5 capillary column. Nitrogen with the pressure at 260 kPa was used as carrier gas in GC using the temperature of injector and detector at 150°C. The ethanol conversion was defined as follows:

$$X_{\text{EtOH}} = \frac{n_{\text{EtOH}\text{(in)}} - n_{\text{EtOH}\text{(out)}}}{n_{\text{EtOH}\text{(in)}}} \times 100. \tag{1}$$

The selectivity to $i$ product was defined as follows:

$$S_{\text{ethylene}} = \frac{n_{\text{ethylene}}}{\sum n_i} \times 100,$$

$$S_{\text{DEE}} = \frac{n_{\text{DEE}}}{\sum n_i} \times 100,$$

$$S_{\text{acetaldehyde}} = \frac{n_{\text{acetaldehyde}}}{\sum n_i} \times 100. \tag{2}$$

The yield to $i$ product was defined as follows:

$$Y_{\text{ethylene}} = \frac{S_{\text{ethylene}} \times X_{\text{EtOH}}}{100},$$

$$Y_{\text{DEE}} = \frac{S_{\text{DEE}} \times X_{\text{EtOH}}}{100},$$

$$Y_{\text{acetaldehyde}} = \frac{S_{\text{acetaldehyde}} \times X_{\text{EtOH}}}{100}. \tag{3}$$

where $n_{\text{EtOH}\text{(in)}}$ and $n_{\text{EtOH}\text{(out)}}$ are defined as the molar flow rate (mmol/min) of ethanol in feed and product, respectively, $n_{\text{ethylene}}$, $n_{\text{DEE}}$, $n_{\text{acetaldehyde}}$, and $\sum n_i$ were defined as the molar flow rate of ethylene, DEE, acetaldehyde, and total products (mmol/min), respectively.

2.3.6. Catalytic Ethanol Dehydration Reaction. Essentially, the ethanol dehydration reaction system reported by Krutpijit and Jongsomjit was used [31]. It was performed in a fixed-bed continuous flow microreactor having an inside diameter of 0.7 cm and length of 33 cm length. First, 0.01 g of quartz wool and 0.05 g of catalyst (or support) were packed in the middle of reactor. The catalyst was preheated by flowing N$_2$ with a flow rate of 60 ml/min at 200°C for 1 h under atmospheric pressure to remove the moisture and impurity on surface of catalyst prior reaction. Afterwards, the reaction was started by feeding vaporized ethanol and N$_2$ stream as carrier gas. The ethanol flow rate was maintained at 1.45 ml/h (weight hourly space velocity (WHSV) = 22.9 (g ethanol/g cat·h$^{-1}$)) controlled by a syringe pump injection. The reaction was operated at temperature varied from 200 to 400°C. After reaching steady-state condition, the reaction product compositions at reactor effluent were analyzed by a Shimadzu gas chromatography (GCBA) with flame ionization detector (FID) using DB-5 capillary column. Nitrogen with the pressure at 260 kPa was used as carrier gas in GC using the temperature of injector and detector at 150°C. The ethanol conversion was defined as follows:

$$X_{\text{EtOH}} = \frac{n_{\text{EtOH}\text{(in)}} - n_{\text{EtOH}\text{(out)}}}{n_{\text{EtOH}\text{(in)}}} \times 100. \tag{1}$$

The selectivity to $i$ product was defined as follows:

$$S_{\text{ethylene}} = \frac{n_{\text{ethylene}}}{\sum n_i} \times 100,$$

$$S_{\text{DEE}} = \frac{n_{\text{DEE}}}{\sum n_i} \times 100,$$

$$S_{\text{acetaldehyde}} = \frac{n_{\text{acetaldehyde}}}{\sum n_i} \times 100. \tag{2}$$

The yield to $i$ product was defined as follows:

$$Y_{\text{ethylene}} = \frac{S_{\text{ethylene}} \times X_{\text{EtOH}}}{100},$$

$$Y_{\text{DEE}} = \frac{S_{\text{DEE}} \times X_{\text{EtOH}}}{100},$$

$$Y_{\text{acetaldehyde}} = \frac{S_{\text{acetaldehyde}} \times X_{\text{EtOH}}}{100}. \tag{3}$$

where $n_{\text{EtOH}\text{(in)}}$ and $n_{\text{EtOH}\text{(out)}}$ are defined as the molar flow rate (mmol/min) of ethanol in feed and product, respectively, $n_{\text{ethylene}}$, $n_{\text{DEE}}$, $n_{\text{acetaldehyde}}$, and $\sum n_i$ were defined as the molar flow rate of ethylene, DEE, acetaldehyde, and total products (mmol/min), respectively.

3. Results and Discussion

3.1. Characteristics. The XRD patterns of both TiO$_2$ supports and WO$_3$/TiO$_2$ catalysts are illustrated in Figure 1.
Considering the XRD patterns of the supports including TiO$_2$-SG and TiO$_2$-SV, they exhibited the similar XRD patterns having the strong diffraction peaks located at 2θ degree of 25° (major), 38°, and 48°, which are assigned to the tetragonal anatase phase of crystalline TiO$_2$ [32, 33]. When the support was impregnated with 13.5 wt.% of tungsten, the XRD patterns were also similar with those of titania supports. The intensities were lower indicating the smaller crystallite size of WO$_3$/TiO$_2$ catalysts than the TiO$_2$ supports. Besides, the low intensity peaks were observed at 24° and 34° for both WO$_3$/TiO$_2$-SG and WO$_3$/TiO$_2$-SV catalysts, which were assigned to the formation of the WO$_3$ crystals with tetragonal phase [34, 35]. When compared the intensity of XRD peaks between WO$_3$/TiO$_2$-SG and WO$_3$/TiO$_2$-SV, it appeared that WO$_3$/TiO$_2$-SG exhibited lower intensity than WO$_3$/TiO$_2$-SV suggesting that the crystalline size of the former was smaller than the latter. Based on the Scherrer equation, the average crystalline size of WO$_3$/TiO$_2$-SG was smaller than WO$_3$/TiO$_2$-SV as seen in Table 1, where the TiO$_2$ crystalline size was in the range of 10.7–14.3 nm.

The BET surface area ($S_{BET}$), pore volume, and pore size diameter of TiO$_2$ supports and WO$_3$/TiO$_2$ catalysts analyzed by N$_2$ physisorption are shown in Table 1. The results revealed that the TiO$_2$–SG exhibited smaller surface area (73 m$^2$/g) and pore volume (0.13 cm$^3$/g) than those of TiO$_2$–SV BET surface area (85 m$^2$/g) and pore volume (0.42 cm$^3$/g). The large surface area essentially enhances catalytic activity in ethanol dehydration by increasing possibility of ethanol to attach on the acid site [28]. In addition, the surface area, pore volume, and pore size diameter decreased with the presence of tungsten due to some pore blockage [36].

Figure 2 showed the N$_2$ adsorption-desorption isotherms at −196°C for the TiO$_2$ supports and WO$_3$/TiO$_2$ catalysts. The results displayed the Type IV adsorption isotherms with the H1 hysteresis loop indicating the mesoporous structure according to the IUPACs. After loading tungsten to obtain WO$_3$/TiO$_2$-SG and WO$_3$/TiO$_2$-SV, it was found that the Type IV isotherm was still observed. The hysteresis loop moved toward lower pressure for WO$_3$/TiO$_2$-SG and WO$_3$/TiO$_2$-SV suggesting that the addition of tungsten onto TiO$_2$ support catalyst resulted in decreased pore volume. The pore size distribution (PSD) for the TiO$_2$ support catalysts and catalysts are shown in Figure 3. All catalysts were in the average pore diameter range of 2–50 nm classified as mesoporous particles. The TiO$_2$-SG showed the narrower pore size distribution than that of TiO$_2$-SV. The average pore sizes for all samples calculated by Barrett–Joyner–Halenda (BJH) are shown in Table 1, which were corresponding to the results from N$_2$ adsorption-desorption isotherm as seen from Figure 2.

The morphology of supports and catalysts prepared by different methods showed the different morphologies. The TiO$_2$-SG formed irregular shape particles, while TiO$_2$-SV formed small agglomerated spherical and porous particles. When impregnated with tungsten on TiO$_2$-SG and TiO$_2$-SV supports, both samples exhibited more porous particles. This suggested that the presence of tungsten into TiO$_2$ resulted in an increase of porosity. The EDX mapping of WO$_3$/TiO$_2$-SG and WO$_3$/TiO$_2$-SV catalysts are illustrated in Figure 4. It shows the elemental distribution of Ti, O, and W dispersing on the external surface of catalysts.

The tungsten was well dispersed at the outer surface of both TiO$_2$-SG and TiO$_2$-SV. The weight ratios of W/Ti are also listed in Table 2. The amount of tungsten present at outer surface of TiO$_2$-SG was larger than TiO$_2$-SV. Nevertheless, according to the XRF analysis the amount of tungsten in the bulk of TiO$_2$-SV catalyst was larger than TiO$_2$-SG indicating that the distribution of tungsten for TiO$_2$-SV catalyst was mostly located inside the pore of catalyst.

It is well known that acidity is the key factor relating to the activity of dehydration catalysts. The acidity of
supports and catalysts was evaluated by NH$_3$-temperature-programmed desorption as shown in Figure 5. As observed, the NH$_3$-TPD profiles for all samples exhibited the broad desorption peaks in range of 150–500 °C.

It is known that the NH$_3$-TPD desorption temperature of acidic sites are classified as 3 categories. The desorption of NH$_3$ between 150 and 300 °C is assigned as weak acidic sites, whereas the desorption between 300 and 450 °C is moderate acid sites and the desorption above 450 °C is strong acid sites [37]. As seen in Table 3, it indicated that the TiO$_2$-SG exhibited lower amount of acid site than the TiO$_2$-SV. However, with tungsten loading on both supports, it showed significant increase in weak and total acid sites for both WO$_3$/TiO$_2$-SG and WO$_3$/TiO$_2$-SV catalysts, which is necessary for enhancing the production of ethylene and DEE [38, 39]. In addition, it can be observed that the WO$_3$/TiO$_2$-SV catalyst exhibited the highest amount of total acid sites at 3645 µmol/g cat.

Considering the CO$_2$-TPD profiles as shown in Figure 6, the desorption peak displayed the narrow desorption in the temperature range of 50–200 °C. Both TiO$_2$ supports exhibited low temperature CO$_2$ desorption around 87 °C assigned to weak basic sites [40, 41]. The addition of tungsten into support catalysts resulted in a decrease of peak intensity around 80 °C. It also revealed that WO$_3$/TiO$_2$-SG had the higher amount of basicity site than WO$_3$/TiO$_2$-SV as seen in Table 4.

The amounts of carbon deposition after reaction obtained by EDX measurement are shown in Table 5. WO$_3$/TiO$_2$-SG and WO$_3$/TiO$_2$-SV exhibited higher amounts of carbon deposition than those of the TiO$_2$ supports due to their higher acidity. It is well known that high acidity yields high amount of carbon deposition.

### 3.2. Ethanol Dehydration Reaction

To investigate the catalytic activity and product distribution for all catalysts, the ethanol dehydration reaction in gas phase at atmospheric pressure and temperature ranging from 200 °C to 400 °C was performed. As seen in Table 6, the ethanol conversion for all samples increased with increasing reaction temperature indicating no deactivation of supports and catalysts. The highest ethanol conversion was achieved at 400 °C for all samples. The ethanol conversion was found in order of WO$_3$/TiO$_2$-SV (87.6%) > TiO$_2$-SV (56.3%) > WO$_3$/TiO$_2$-SG (45.4%) > TiO$_2$-SG (33.9%), which are related to total amount acid sites of catalysts. It should be noted that the conversion of TiO$_2$-SV was still higher than that of WO$_3$/TiO$_2$-SG, which is quite interesting.

The selectivity to ethylene, DEE, and acetaldehyde are presented in Table 6. It can be observed that the TiO$_2$ rendered acetaldehyde as a major product. However, with the introduction of tungsten into TiO$_2$ supports, ethylene and DEE are turned out to be the major products at different temperature. In general, ethanol dehydration reaction can produce ethylene and DEE in 2 competitive pathways:

\[
\text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O} + 44.9 \text{ kJ/mol (4)}
\]

\[
2\text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 + \text{H}_2\text{O} - 25.1 \text{ kJ/mol (5)}
\]

The reaction (4) is endothermic and favors the moderate to high temperature between 320°C and 500°C, while
Figure 4: Elemental distribution by EDX mapping for (a) WO$_3$/TiO$_2$-SG and (b) WO$_3$/TiO$_2$-SV catalyst.

Table 2: Elemental compositions (wt.%) on external surface of catalysts obtained from EDX.

<table>
<thead>
<tr>
<th>Sample</th>
<th>O</th>
<th>Ti</th>
<th>W</th>
<th>Cl</th>
<th>W/Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$-SG</td>
<td>44.67</td>
<td>55.33</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>TiO$_2$-SV</td>
<td>44.37</td>
<td>55.63</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>WO$_3$/TiO$_2$-SG</td>
<td>30.71</td>
<td>35.17</td>
<td>33.84</td>
<td>0.28</td>
<td>0.96</td>
</tr>
<tr>
<td>WO$_3$/TiO$_2$-SV</td>
<td>39.00</td>
<td>48.25</td>
<td>12.36</td>
<td>0.39</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Figure 5: NH$_3$-TPD profiles of TiO$_2$ supports and WO$_3$/TiO$_2$ catalysts.
reaction (5) is exothermic and favors the low to moderate temperature between 150 °C and 300 °C [42]. The formation of the ethylene occurs by acid catalyst protonating to hydroxyl group of ethanol molecule (proton transfers from acid to O atom to form alkylloxonium ion), and then the water molecules is generated. Subsequently, an ethoxide surface group forms and deprotonates its methyl group to produce the ethylene. The DEE formation proceeds via either dissociative pathway or associative pathway [43]. The dissociative pathway is happened by one ethanol adsorption on catalyst and water elimination providing an adsorbed ethyl group. After that, the ethyl group reacts with the second ethanol and finally the DEE is formed. The associative pathway takes place from coadsorption of two ethanol reacted and formed into DEE. It is recognized that the dehydration of alcohol essentially takes place on Brønsted acid sites [39, 44], while Lewis acid sites rarely contribute for this reaction [45, 46]. The mechanism of ethanol dehydration to ethylene and DEE over the WO 3 /TiO 2 catalysts is illustrated in Schemes 1 and 2, respectively. Besides, acetaldehyde is produced under the side reaction or dehydrogenation reaction in reaction (6), which is favored on the basic sites:

\[
\text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_4\text{O} + \text{H}_2 + 52.4 \text{ kJ/mol} \quad (6)
\]

According to the experiment, it was observed that TiO 2 -SG and TiO 2 -SV support catalysts still showed high acetaldehyde selectivity at ca. 81 °C and ca. 71 °C, respectively. This is perhaps due to the high reaction temperature or the heat treatment effect to an oxidation of Lewis oxygen in pure TiO 2 structure with the basic site is more dominant than acid as seen from the pure SBA-15 catalyst used in ethanol dehydration reported by Autthanit and Jongsomjit in 2018 [47]. The mechanism of ethanol dehydrogenation to acetaldehyde over TiO 2 support is illustrated in Scheme 3. Acetaldehyde occurs by ethanol molecule firstly adsorbed on the catalyst surface. An
The ethoxy group is further generated and converted into acetaldehyde. When impregnated the tungsten on the TiO₂ supports, it revealed increased ethylene selectivity at high temperature and increased DEE selectivity at low temperature. The ethylene and DEE selectivities over WO₃/TiO₂-SV catalyst were higher than those of WO₃/TiO₂-SG catalyst. It was found that the highest ethylene selectivity of ca. 88% under the reaction temperature at 400 °C and the highest DEE selectivity of ca. 68% under the reaction temperature at 250 °C for WO₃/TiO₂-SV. The factor to increase the ethylene and DEE selectivity is the high amount of weak acid or Bronsted acid, which is the active site for ethanol dehydration after adding the tungsten on TiO₂ supports. As shown in Table 3, the weak acid sites for WO₃/TiO₂ catalyst were significantly higher than TiO₂ support catalyst, whereas the strong acid sites for TiO₂ were higher than the WO₃/TiO₂ catalyst. It is familiar that amount of weak acid site is probably correlated to Bronsted acid site, while the Lewis acid site may correlate to the strong acid site [47].

Besides two products, the acetaldehyde was formed as byproduct over WO₃/TiO₂-SG and WO₃/TiO₂-SV catalysts.

### Table 6: Ethanol conversion, product selectivity, and product yield as a function of reaction temperature (the reaction condition: \( T = 200–400 \text{ °C}, \text{ WHSV} = 22.9 \text{g ethanol} \cdot \text{g cat}^{-1} \cdot \text{h}^{-1} \), and catalyst weight = 0.05 (g)).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temp (°C)</th>
<th>Ethanol conversion (%)</th>
<th>Product selectivity (%)</th>
<th>Product yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ethylene</td>
<td>DEE</td>
</tr>
<tr>
<td>TiO₂-SG</td>
<td>200</td>
<td>4.5</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>8.6</td>
<td>1.8</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>13.2</td>
<td>4.0</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>32.3</td>
<td>11.4</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>33.9</td>
<td>17.7</td>
<td>0.9</td>
</tr>
<tr>
<td>TiO₂-SV</td>
<td>200</td>
<td>21.1</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>23.2</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>35.7</td>
<td>2.5</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>54.3</td>
<td>9.7</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>56.3</td>
<td>25.5</td>
<td>3.4</td>
</tr>
<tr>
<td>WO₃/TiO₂-SG</td>
<td>200</td>
<td>12.4</td>
<td>4.7</td>
<td>37.4</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>16.4</td>
<td>17.1</td>
<td>40.9</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>25.0</td>
<td>39.5</td>
<td>10.4</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>33.4</td>
<td>54.5</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>45.4</td>
<td>64.6</td>
<td>1.3</td>
</tr>
<tr>
<td>WO₃/TiO₂-SV</td>
<td>200</td>
<td>33.2</td>
<td>5.2</td>
<td>42.6</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>37.7</td>
<td>22.4</td>
<td>67.7</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>51.8</td>
<td>52.6</td>
<td>42.4</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>71.7</td>
<td>76.4</td>
<td>17.8</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>87.6</td>
<td>88.2</td>
<td>3.5</td>
</tr>
</tbody>
</table>

[Scheme 1: Ethanol dehydration to ethylene over WO₃/TiO₂ catalyst.]
The acetaldehyde selectivity over WO$_3$/TiO$_2$-SG was higher than that of WO$_3$/TiO$_2$-SV relating to higher amounts of basic site present in WO$_3$/TiO$_2$-SG catalyst. The mass balance (carbon balance) in the reaction test typically closed to 90%. Such a deviation may occur due to mainly from coke formation.

The comparison of product yield for each temperature over supports and catalysts is reported in Table 6. It showed that presence of tungsten essentially improved the ethylene and DEE yield. The highest ethylene yield was found to be ca. 77% at 400°C over WO$_3$/TiO$_2$-SV. Moreover, it was observed that the highest DEE yield of ca. 26% at 250°C was obtained with WO$_3$/TiO$_2$-SV. However, DEE yield was rather small due to the low conversion at low temperature. It should be mentioned that the highest acetaldehyde yield of ca. 48% at 350°C obtained from TiO$_2$-SV was observed, which is quite interesting.

### 4. Conclusion

The WO$_3$/TiO$_2$-SV catalyst is promising for dehydration of ethanol to ethylene and DEE having the highest ethylene of 77% at 400°C and the highest yield of 26% at 250°C. It showed that the more efficient method to synthesize TiO$_2$
support was the solvothermal method due to high acidity and surface area. It is worth noting that the TiO$_2$-SV itself also rendered the highest yield of acetaldehyde at 48% at 350°C. This support can be potentially used as support for a catalyst in dehydrogenation of ethanol to acetaldehyde.

**Data Availability**

The data used to support the findings of this study are included within the article.

**Conflicts of Interest**

The authors declare that there are no conflicts of interest regarding the publication of this paper.

**Acknowledgments**

The authors thank the Grant for International Research Integration: Chula Research Scholar, Ratcadaphiseksomphot Endowment Fund, Endowment Fund, Grant for Research: Government Budget, Chulalongkorn University (2018), and the National Research Council of Thailand (NRCT) for their financial support of this project.

**References**


