Pd Modification and Supporting Effects on Catalytic Dehydration of Ethanol to Ethylene and Diethyl Ether over W/TiO₂ Catalysts

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Abstract: In the present work, the palladium (Pd) modification and supporting effect of W/TiO₂ catalysts on catalytic ethanol dehydration to ethylene and diethyl ether were investigated. The Pd modification with different sequence of Pd and W impregnation on the catalysts was prepared by the incipient wetness impregnation technique. The catalyst characterization and activity testing revealed that the different sequence during impregnation influenced the physicochemical properties and ethanol conversion of catalyst. The differences in structure and surface properties were investigated by XRD, BET, SEM, EDX, XPS and NH₃-TPD. Upon the reaction temperature between 200 to 400°C, it was found that the conversion increased with increasing of temperature for all catalysts. The Pd incorporated into catalysts enhanced the ethanol conversion depending on the sequence of impregnation. At low temperature (ca. 200 to 300°C), diethyl ether is a major product and the Pd modification over W/TiO₂ catalyst resulted in increased diethyl ether yield. This is because an increase of ethanol conversion was obtained with Pd modification, while diethyl ether selectivity did not change. This can be attributed to the higher amount of weak acids sites present after Pd modification into catalyst. Among all catalysts, the Pd/W/TiO₂ catalyst (coimpregnation) achieved the highest diethyl ether yield of 41.4% at 300°C. At high temperature (ca. 350 to 400°C), ethylene is the major product. The W/Pd/TiO₂ catalyst (with sequential impregnation of Pd on TiO₂, followed by W) exhibited the highest ethylene yield of 68.1% at 400°C. It can be concluded that the modification of Pd onto W/TiO₂ upon different sequence of Pd and W impregnation can improve the diethyl ether and ethylene yield in catalytic ethanol dehydration.

Key words: ethanol dehydration, titania, tungsten, palladium, diethyl ether, ethylene

1 Introduction

Nowadays, the renewable energy resource such as solar, wind and biomass has become the most important energy sources due to its environmentally friendly, energy efficiency and reduction of harmful waste. Among energy resource, biomass has been recognized as one of the most utilization resources to provide the platform of chemical in various industries⁴⁻⁷. Besides, it has been interesting for many researches due to environmental concern about the emission of greenhouse gas from burning of fossil fuel (coal, oil and gas) and reducing of non-renewable feedstock supply in future. Recently, many researchers have played attention to convert the biomass-derived ethanol to the valued-added chemical compounds with a number of feasible process and technologies mostly applied with catalytic reactions⁴⁻⁷. Ethanol (bio-ethanol) is derived from fermentation of various types of agricultural products such as corn, sugarcane and cassava⁸. The bioethanol is the main potential source that becomes a sustainable fuel instead of fossil fuel. It can be potentially used to produce hydrogen and other value-added chemicals such as ethylene, diethyl ether, acetaldehyde, etc., which are widely consumed in many petroleum and petrochemical industries. Ethylene is widely used as a raw material fed to many petrochemical
industries to produce numerous polymer such as polyethylene, polyvinyl chloride and polystyrene. Diethyl ether is utilized as extraction solvent in fragrance and pharmaceutical industries. Moreover, diethyl ether can be consumed as a renewable fuel to improve the performance of diesel/biodiesel fuels and reduce an emission due to its high volatility and cetane/octane number. At the present time, the formation of ethylene and diethyl ether is derived from catalytic dehydration of ethanol as a renewable feedstock.

The ethanol dehydration reaction favors the lower temperature generally ranging from 180°C to 500°C compared to the thermal cracking in the range of 600°C to 1000°C, leading to saving of energy cost. Many researches have been examined how to optimize ethylene and diethyl ether yield over the ethanol dehydration reaction with various different catalysts in order to increase the catalytic activity and selectivity of product at lowest temperature. Mostly, many solid acid catalysts containing transition metal oxides such as zeolites, SiO₂, ZrO₂ and TiO₂ are used to catalyze this reaction. In fact, these oxides can act in many functions such as active phase, promoter, or support of solid catalysts. Each kind of catalyst has different characteristics, especially for its surface acidity, which determines the catalytic behaviors in dehydration reaction. Currently, there are some methods to increase the catalytic properties by adaptation the catalyst with adding other active metals. Among the active noble and transition metals, the addition of tungsten(W) over titania(TiO₂) support catalyst gave the higher catalytic activity at low temperature due to an increase of Brensted acid sites for catalyzing the reaction. Phung et al. claimed that among the transition metal oxide catalysts, WO₄/TiO₂ catalyst gave the highest catalyst activity for ethanol dehydration.

Recently, researchers have developed new designed catalysts with adequate textual properties, controlled acidity and stability to enhance the catalytic properties. The bimetallic catalysts have been proven to be important for many catalyst applications. The presence of Pd oxides have been known to be an active for a wide range of reactions such as ethanol reforming, hydrogenolysis, oxidation, dehydration. Armenta et al. reported that the bimetallic (CuO-PdO)/(γ-χ-Al₂O₃) performed the highest catalytic activity when compared to monometallic catalysts (CuO/γ-χ-Al₂O₃ and PdO/γ-χ-Al₂O₃) in ethanol dehydration to dimethyl ether. Jinshuang et al. described that Pd/Al₂O₃–TiO₂ catalyst showed higher catalytic activity than Pd/TiO₂ in ethanol oxidation. Besides, Jing et al. found that the metal precursors affect the structure and catalyst performance. The catalyst prepared by first Co precursor impregnation(Ni/Co/MgO) resulted in the stronger catalytic activity and stability than those by the coimpregnation(Ni/Co/MgO) in steam reforming reaction. Roldan et al. studied on the mono- and bi-metallic (Pt and/or Pd) impregnated on beta-zeolite in hydroisomerization of alkanes. They claims that not only the presence of both metals, but also an adequate preparation method providing an improving the catalyst activity.

The objective in this study is to determine the effect of palladium(Pd) modification onto W/TiO₂ catalyst for enhancing the catalytic performance in ethanol dehydration to high value product (ethylene and diethyl ether). In addition, the effect of the different impregnation sequence of palladium(Pd) and tungsten(W) over TiO₂ support prepared by the incipient wetness impregnation method has been investigated on their characteristics and catalyst properties.

## 2 Experimental

### 2.1 Materials

Chemicals employed for synthesis of the catalysts were titanium(iv) n-butoxide (97%) (TNB), 1, 4-butanediol, tungsten(vi) chloride (99.9% metals) and tetraaminepalladium(ii) chloride monohydrate from Aldrich. For the reaction study, ethanol (99.99%) from Merck Company Ltd. as a reactant, ultrahigh purity nitrogen gas (99.99%) and air zero balance nitrogen from Linde(Thailand) Public Company Ltd. were employed.

### 2.2 Catalysts preparation

The TiO₂-supported catalysts were prepared by the solvothermal method according to the procedure reported from Panpranot et al. First, 25 g of TNB was used as the precursor. It was suspended in 100 ml of 1,4-butanediol in a test tube and set inside the autoclave. The autoclave was then fully purged with nitrogen at pressure of 30 bars and the temperature of 320°C for 6 h. Next, the white powder was collected, and then washed with ethanol followed by centrifugation at least 5 times. The powder was dried over night at 110°C and finally the white TiO₂ support was obtained.

In order to study the Pd modification on W/TiO₂ catalyst and the supporting effect, the W and Pd precursors were impregnated onto TiO₂ support obtained earlier. Tungsten(vi) chloride solution and tetraaminepalladium(ii) chloride monohydrate were used as W and Pd precursors, respectively. All catalysts in this study was prepared using the incipient wetness impregnation method. First, the W/TiO₂ catalyst having W loading of 13.5 wt% was prepared and used as reference. All Pd modification on W/TiO₂ catalysts contained 0.5 wt% of Pd. The different sequence of W and Pd impregnation was performed by introducing W on the support first followed by Pd(Pd/W/TiO₂) or introducing Pd on the support first followed by W(P/W/TiO₂). The coimpregnation of W and Pd was also prepared to obtain Pd/W/TiO₂ catalyst. All catalyst samples were dried overnight at 110°C and calcined in air at 500°C with a heating.
rate of 10°C/min for 3 h.

2.3 Catalyst characterization

All catalysts were characterized by several techniques. The crystalline structure for the synthesized catalysts was analyzed by X-ray diffraction (XRD) technique collected from Bruker D8 X-ray diffractometer using Cu Kα (α = 1.544398 Å). The intensities of the diffraction peaks were recorded in the 2θ range 20-80° with resolution 0.04° at rate of 2.4 min⁻¹. The crystalline domain sizes were calculated from the Scherrer equation.

The specific surface area and pore size of the catalysts were determined by N2 physisorption using Micromeritics model ASPS 2000 automated system. The measurement was conducted at −196°C and analysis by Brunauer-Emmet-Teller (BET) isotherm equation method. The average pore diameter and pore size distribution were derived by the desorption profiles of the isotherms using the Barrett-Joyner-Halenda (BJH) method.

The acid properties of the catalysts were analyzed by temperature-programmed desorption of ammonia (NH₃-TPD) using Micromeritics Chemisorb 2750 Pulse chemisorption system instrument. First, 0.03 g of quartz wool with 0.1 g of catalyst were packed in a quartz tube and pretreated at 500°C under He flowing for 1 h. Then, the catalyst was saturated with 15% of NH₃ in He at 40°C for 30 min. After that, the excess adsorbed gas (physorbed) NH₃ was purged with He until the base line was constant. Subsequently, the catalyst was heated from 40°C to 500°C with heating rate of 10°C/min to desorb NH₃. Finally, the amount of NH₃ in effluent was measured via the thermal conductivity detector (TCD) signal as a function of temperature.

The morphology, element composition (Ti, O, W, Pd), and distributions throughout the catalysts were explored by Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) model JEOL mode JSM-6400. Micrographs were taken at the accelerating voltage of 30 kV and magnification ranged between 1,000 to 10,000 of 3 nm. The SEM was operated using the secondary scattering electron mode. EDX was performed using Apollo X Silicon Drift Detector Series by EDAX.

The binding energy and chemical oxidation states of the catalysts were studied by X-ray photoelectron spectroscopy (XPS) using an AMICUS spectrometer with MgKα X-ray radiation at voltage 15 kV and current of 12 mA.

2.4 Ethanol dehydration reaction

The catalytic ethanol dehydration reaction was carried out in a fixed-bed continuous flow micro reactor in gas phase. The borosilicate glass reactor has an inside diameter of 1 cm and length of 49.5 cm. First, 0.01 g of quartz wool and 0.1 g of catalyst were packed in the middle of glass reactor. The catalyst was preheated by flowing N₂ with a flow rate of 50 ml/min at 200°C for 1 h under atmospheric pressure to remove the moisture on the surface of catalyst. Afterwards, the reaction was started by feeding vaporized ethanol and N₂ stream as carrier gas. The ethanol was vaporized and fed by a syringe pump injection at a flow rate retained at 0.397 ml/h [weight hourly space velocity (WHSV) = 3.13 (g_{catalyst} g_{cat}⁻¹ h⁻¹)]²⁰. The dehydration reaction was performed at temperature varied in stepwise from 200 to 400°C. Finally, the feed and product compositions at reactor effluent were detected by using Shimadzu gas chromatography (GC 8A) with flame ionization detector (FID) using DB-5 capillary column. The reaction testing system was also demonstrated by Kamsuwan and Jongsomjit²⁷.

3 Results and Discussion

3.1 The catalyst characteristics

The XRD patterns of catalysts are shown in Fig. 1. All catalysts displayed the high intensity peak located at 20 degree of 25° (major), 38° and 48° corresponding to the crystal structure of (101), (004) and (200), respectively. The diffraction peak is identified to the formation of TiO₂ crystalline in tetragonal anatase phase²⁸. Besides, the low intensity peaks was occurred at 24° and 34° on Pd/W/TiO₂, W/Pd/TiO₂, PdW/TiO₂ and W/TiO₂ catalysts, which are assigned to the WO₃ formation of tetragonal phase¹¹. It is observed that the diffraction patterns of all catalysts were similar. However, the peak of Pd did not appeared due to the small loading of Pd metal and/or the very small size of crystallites being in the highly dispersed form on the TiO₂ support²⁹. According to the Scherrer equation, D = Kλ β COS θ, the crystalline sizes of bimetallic Pd/W/TiO₂, W/Pd/TiO₂ and PdW/TiO₂ are shown in Table 1. Considering the Pd-modified catalysts, the Pd/W/TiO₂ has the largest crys-
Table 1  Physical properties of catalysts.

| Sample        | \( S_{\text{BET}} \) \(^{a} \) (m\(^2\)/g) | Pore Volume \(^{b} \) (cm\(^3\)/g) | Pore Size \(^{c} \) (nm) | Crystalline size \(^{c} \) (nm) |
|--------------|-------------------|-----------------|----------------|-----------------|
| Pd/W/TiO\(_2\) | 54.5              | 0.23            | 14.6          | 15.9            |
| W/Pd/TiO\(_2\) | 44.3              | 0.26            | 15.7          | 15.4            |
| PdW/TiO\(_2\) | 30.4              | 0.13            | 13.9          | 11.8            |
| W/TiO\(_2\)   | 58.9              | 0.25            | 13.4          | 15.4            |

\(^{a}\) Measured by BET method, \(^{b}\) Measured by BJH desorption method, \(^{c}\) Measured by XRD using the Scherrer equation.

talline size (ca. 15.9 nm), whereas PdW/TiO\(_2\) exhibits the smallest crystalline size (ca. 11.8 nm). It is suggested that the different sequence of impregnation slightly affected the crystalline size of catalysts.

The morphology of the catalysts obtained by scanning electron microscopy (SEM) is shown in Fig. 2. It can be observed that the shape of the Pd incorporated into W/TiO\(_2\) displayed the small agglomerated spherical and porous particles, which is similar to the morphology of the unmodified one. It indicated that the Pd impregnation process and thermal treatment of catalysts resulted in a slight change of morphology. In order to investigate the dispersion of elements, the energy-dispersive X-ray spectroscopy (EDX) analysis was performed. The typical EDX mapping of catalysts is illustrated in Fig. 3. The results revealed good distribution of metals, which are elements of Ti, O, W and Pd on external surface of catalysts. The amounts of elements near the surface of catalysts are displayed in Table 2. It was found that the Pd particles were mostly located at outer surface of Pd/W/TiO\(_2\), W/Pd/TiO\(_2\) and PdW/TiO\(_2\) catalysts in the order of 1.97, 1.81, and 1.7 wt%, which are higher than the amounts of Pd loading (0.5 wt%) in bulk catalyst.

The Brunauer-Emmett-Teller surface area (\( S_{\text{BET}} \)), pore volume, and pore size diameter of catalysts examined by N\(_2\) physisorption technique are listed in Table 1. It indicated that the Pd modification onto W/TiO\(_2\) slightly decreased the \( S_{\text{BET}} \). The surface area of W/TiO\(_2\) apparently reduced from 58.9 m\(^2\)/g to 54.5 m\(^2\)/g, 44.3 m\(^2\)/g and 30.4 m\(^2\)/g for Pd/W/TiO\(_2\), W/Pd/TiO\(_2\) and PdW/TiO\(_2\), respectively due to some pore blockage from Pd particles in W/TiO\(_2\), especially for PdW/TiO\(_2\). The pore sizes of the samples calculated by Barrett–Joyner–Halenda (BJH) method are shown in Table 1. The pore sizes of all catalysts were ranged between 13-16 nm indicating their mesoporous porous structure. Considering the different sequence impregnation of Pd on W/TiO\(_2\), it revealed that the highest \( S_{\text{BET}} \) was found in Pd/W/TiO\(_2\) (54.5 m\(^2\)/g), while the lowest \( S_{\text{BET}} \) was found in PdW/TiO\(_2\) (30.4 m\(^2\)/g). In summary, the different sequence impregnation has an effect on the textual property of catalyst.

The N\(_2\) adsorption-desorption isotherms of the catalysts were obtained as shown in Fig. 4. All samples appeared to have the isotherm type IV with a hysteresis loop type H1 at high relative pressures (P/P\(_{0}\) = 0.7-0.9), which were represented to mesoporous structure according to the IUPAC (International Union of Pure and Applied Chemistry) classification. The pore size distribution (PSD) for the catalysts is shown in Fig. 5. All catalysts were in the average pore diameter range of 13-16 nm and broad distribution. These results were corresponding to the ones obtained from Barrett–Joyner–Halenda (BJH) method as seen in Table 1.

In Fig. 6, it shows the NH\(_3\) temperature - programmed desorption (NH\(_3\)-TPD)/profiles of the catalysts. It presents desorption of NH\(_3\) between 150°C and 300°C, which is attributed to weak acid sites. The desorption peaks between 300°C and 450°C are the moderate and strong acid sites, respectively. Table 3 is displayed the acid properties such as acid strength, acid site and acid density of catalysts. It is observed that Pd modification resulted in an increase of acidity on W/TiO\(_2\), especially for weak acid sites. The acidity tended to increase in the order of W/TiO\(_2\)<Pd/W/TiO\(_2\)<W/Pd/TiO\(_2\)<PdW/TiO\(_2\). Considering the effect of different sequence impregnation of Pd into catalysts, the
Fig. 3  The energy-dispersive X-ray spectroscopy (EDX) mapping analysis of a) Pd/W/TiO₂, b) W/Pd/TiO₂ and c) PdW/TiO₂ catalyst.

Table 2  Elemental distribution (wt%, %mol) on external surface of catalysts obtained from EDX.

| Catalyst      | O  | W (% weight) | Pd (%) | Ti (% weight) | O (% mol) | W (% mol) | Pd (% mol) | Ti (% mol) |
|---------------|----|--------------|--------|---------------|-----------|-----------|------------|------------|
| Pd/W/TiO₂     | 35.48 | 11.69 | 1.97 | 50.86 | 65.90 | 1.90 | 0.60 | 31.60 |
| W/Pd/TiO₂     | 39.55 | 12.32 | 1.81 | 46.32 | 70.10 | 1.90 | 0.50 | 27.50 |
| PdW/TiO₂      | 38.87 | 10.51 | 1.7 | 48.92 | 68.90 | 1.60 | 0.50 | 29.00 |
| W/TiO₂        | 35.1 | 8.29 | – | 56.61 | 64.10 | 1.30 | – | 34.60 |
Pd/W/TiO$_2$ catalyst showed the highest acidity of 2,884 µmol NH$_3$/g, while Pd/W/TiO$_2$ exhibited the lowest acidity of 1,926 µmol NH$_3$/g. It was suggested that different sequence impregnation of Pd apparently affected the acidity of W/TiO$_2$ catalysts. It is generally accepted that weak and/or medium acid sites play a major role in ethanol dehydration to diethyl ether and ethylene, whereas the formation of the higher hydrocarbon takes place in the strong acid sites$^{30, 31}$. The surface characterization of catalysts such as elemental composition on the catalysts was carried out using XPS. Table 4 summarizes the binding energy for all elements in catalysts. As expected, the binding energies for Ti, W, Pd and O were detected, which are in well agreement to those of EDX analysis. Considering the binding energy of Pd, it can be observed at 341.5, 334.8 and 336.1 eV for Pd/W/TiO$_2$, W/Pd/TiO$_2$ and PdW/TiO$_2$, respectively indicating the PdO$_2$ formation for Pd/W/TiO$_2$, metallic Pd for W/Pd/TiO$_2$ and PdO for PdW/TiO$_2$.$^{21, 32}$ However, the binding energy of metal can be shifted to the lower or higher by electron donate from or to neighboring atom. In addition, the spectral analysis of the XPS focused on O 1s core-level spectra providing the additional information for oxygen species on catalyst surface. The deconvolution of the O 1s spectra was fitted and separated into three kinds of oxygen species, which are displayed in Fig. 7. The binding energies were observed at 529.9, 531.6 and 533.2 eV corresponding to lactic oxygen (O), surface hydroxyl group (OH) and adsorbed water (H$_2$O), respectively.$^{33, 34}$ The atomic concentrations of each O 1s on surface catalysts were defined in Table 4. The results showed that the hydroxyl group area fraction decreased in the following order PdW/TiO$_2$ (41%) > W/Pd/TiO$_2$ (37%) > Pd/W/TiO$_2$ (29%) > W/TiO$_2$ (9%) corresponding to the acidity of catalysts analyzed by NH$_3$-TPD. The results showed that Pd modification essentially alters the acidity of catalysts due to the formation of Pd on support catalyst indicating that Pd/W/TiO$_2$ has the highest hydroxyl group (Brønsted acid) on the surface catalyst. It is reported that the Brønsted acid site is probably related to weak acidity, whereas the Lewis acid site is involved to strong acidity$^{35}$.

3.2 Ethanol dehydration reaction study

Generally, the ethanol can be converted into value-added chemical products including ethylene and diethyl ether via catalytic dehydration over the solid acid catalysts. As shown in Scheme 1, the formation of the ethylene occurs by one ethanol molecule adsorption on catalyst, followed by water elimination to form an adsorbed ethoxide. Finally, the ethylene is formed. As presented in Scheme 2, the diethyl ether formation creates by either dissociative pathway or associative pathway. The dissociative pathway occurs by one ethanol adsorbed on catalyst and followed by water elimination to obtain the adsorbed ethoxide. Afterward, the ethoxide on surface catalyst reacts with the
second ethanol molecule to produce diethyl ether. The associative pathway arises from co-adsorption of two ethanol molecules reacted on catalyst, and then formed into diethyl ether as shown in Scheme 3. The ethylene formation is mainly produced at high temperature between 320°C and 500°C, while diethyl ether mainly favors at the low to moderate temperature between 150°C and 300°C. However, diethyl ether can decompose to ethylene at high temperature as shown in Scheme 3, resulting in the increased ethylene selectivity and decreased diethyl ether selectivity at high temperature. Moreover, acetaldehyde can be formed as a byproduct under the side reaction or dehydrogenation reaction. Acetaldehyde occurs by one ethanol adsorbed on the catalyst surface, followed by released H₂ to provide the adsorbed...
ethoxide group.

The catalytic behavior of the Pd modification on W/TiO$_2$ catalyst was investigated in the ethanol dehydration at temperature range of 200-400°C. The study focused on the catalytic activity, selectivity and yield of ethylene and diethyl ether. The ethanol conversion for all catalysts is demonstrated in Fig. 8. It was found that all catalysts displayed the similar behavior in which the ethanol conversion increased with increasing the reaction temperature. The obtained catalytic activity of all catalysts was the highest at 400°C without deactivation. The Pd modification on W/TiO$_2$ catalyst affected on the catalytic activity for W/Pd/TiO$_2$ and PdW/TiO$_2$ by a significant increase in ethanol conversion at low temperature (250-300°C). Likewise, the sequence of palladium impregnation into catalysts increased the catalytic activity when Pd was impregnated on the support before W(Pd/TiO$_2$) and Pd and W were co-impregnated on the support (PdW/TiO$_2$). The catalytic activity was found to increase in the order of PdW/TiO$_2$(90.2%) > W/Pd/TiO$_2$(89.6%) > Pd/W/TiO$_2$(81.5%) > W/TiO$_2$(80.2%) at 400°C. It should be noted that this result was related to acidity of catalysts obtained from NH$_3$-TPD as presented in Table 3. The acidity of the catalysts is a key factor to enhance the catalytic activity.

Furthermore, with higher acid density and shorter distance between two acid sites, it is benefit to increase the possibility of the reactant to be adsorbed and rapidly catalyzed to produce the chemical product, especially diethyl ether at low temperature as reported by Janlamool and Jongsomjit. As a result, it is summarized that the different sequence of impregnated Pd and W into TiO$_2$ catalyst can affect the interaction between Pd and W and promote the formation of an active site. Furthermore, it is observed that the catalytic activity and NH$_3$-TPD profile of Pd/W/TiO$_2$ catalyst is quite similar to those results for W/TiO$_2$ catalysts. This is probed that incorporat...
ed W into TiO₂ catalyst before Pd did not contribute the active site on the catalyst.

The product selectivity for all catalysts is shown in Fig. 9. It revealed that the ethylene selectivity increased with increasing temperature, whereas the diethyl ether selectivity decreased with increasing temperature. Besides, the acetaldehyde selectivity was increased gradually at reaction temperature 250-400°C. From the experiment, all catalysts showed the highest ethylene selectivity at 400°C and diethyl ether selectivity at 300°C. It is noticed that the Pd modification on the catalysts affected the product selectivity by merely increasing the acetaldehyde selectivity. On the other words, the Pd modification resulted in an increase the ethanol conversion without significant change the main product selectivity. However, it should be noted that only PdW/TiO₂ catalysts exhibited high diethyl ether selectivity at high reaction temperature perhaps due to its weak acidity.

The ethylene and diethyl ether yields are shown in Table 5. Considering the Pd-Modified catalysts, it revealed that Pd modification on W/TiO₂ catalysts resulted an increasing of ethylene yield of 68.1% for W/Pd/TiO₂ at 400°C corresponding to the highest portion of weak to moderate/strong acid site. Wannaborworn et al. reported that the ethanol conversion to ethylene is mainly related to weak and moderate acid site. Furthermore, the Pd modification on W/TiO₂ catalyst enhanced the diethyl ether yield for both W/Pd/TiO₂ and PdW/TiO₂ catalysts at 15.9% and 41.4% respectively at 300°C. As a result, the Pd modification as a chemical promoter along with the metal sequence impregnation method enriched their catalyst activity and product yield in ethanol dehydration reaction. It is recognized that the dehydration of alcohol essentially takes place on Brønsted acid sites. The XPS results confirmed that the Pd modification increased amount of hydroxyl groups which is related to the Brønsted acid sites resulting in an increasing catalyst activity.

In Table 6, it summarized the catalytic performance for ethanol dehydration to ethylene and diethyl ether over various catalysts as reported so far. It was obvious that W/Pd/TiO₂ and PdW/TiO₂ are comparable to those of typical and modified catalysts. Thus, the W/Pd/TiO₂ and PdW/TiO₂ is an alternative route to obtain ethylene and diethyl ether in respectively via ethanol dehydration.

Fig. 8 Ethanol conversion of Pd/W/TiO₂, W/Pd/TiO₂, PdW/TiO₂, and W/TiO₂ catalysts.

Fig. 9 Product selectivity of Pd/W/TiO₂, W/Pd/TiO₂, PdW/TiO₂ and W/TiO₂ catalysts.
Table 5  Product yield (%) obtained from each catalyst as function of reaction temperature (the reaction condition at $T = 200 – 400 ^\circ C$, WHSV = 3.13 $g_{\text{ethanol}}/g_{\text{cat}} \cdot h^{-1}$, and catalyst weight = 0.1 g).

| Catalyst      | Temp (°C) | Conversion (%) | Product Yield (%)a |
|---------------|-----------|---------------|--------------------|
|               |           |       | Ethylene | Diethyl ether | Acetaldehyde |
| Pd/W/TiO2     | 200       | 2.3   | 0.0      | 0.0          | 2.3          |
|               | 250       | 12.3  | 2.6      | 6.0          | 3.7          |
|               | 300       | 28.7  | 15.3     | 6.3          | 7.1          |
|               | 350       | 76.3  | 56.6     | 6.0          | 13.7         |
|               | 400       | 81.5  | 60.5     | 5.3          | 15.7         |
| W/Pd/TiO2     | 200       | 1.2   | 0.0      | 0.0          | 1.2          |
|               | 250       | 23.5  | 7.3      | 9.1          | 7.0          |
|               | 300       | 54.2  | 28.1     | 15.9         | 10.3         |
|               | 350       | 79.8  | 59.1     | 4.8          | 16.0         |
|               | 400       | 89.6  | 68.1     | 2.7          | 18.7         |
| PdW/TiO2      | 200       | 2.0   | 0.0      | 0.0          | 2.0          |
|               | 250       | 33.1  | 3.7      | 24.9         | 4.5          |
| W/TiO2        | 200       | 0.3   | 0.0      | 0.0          | 0.3          |
|               | 250       | 11.3  | 3.3      | 7.4          | 0.6          |
| W/TiO2 (c)    | 300       | 31.5  | 22.4     | 7.4          | 1.7          |
|               | 350       | 76.5  | 67.0     | 3.2          | 6.4          |
|               | 400       | 80.2  | 67.8     | 3.1          | 9.3          |

a product yield is ethanol conversion (%) × product selectivity (%)

Table 6  Comparison of various catalysts for ethylene and diethyl ether yield and catalytic performance.

| Catalyst          | $S_{\text{BET}}$ (m$^2$/g) | Reaction temperature (°C) | Ethanol conversion (%) | Ethylene yield (%) | Diethyl ether yield (%) | Ref. |
|-------------------|----------------------------|--------------------------|------------------------|--------------------|------------------------|------|
| Pd/W/TiO2         | 55                         | 200–400                  | 2–90                   | 61                 | 6                      | This study |
| W/Pd/TiO2         | 44                         | 200–400                  | 1–90                   | 68                 | 16                     | This study |
| PdW/TiO2          | 30                         | 200–400                  | 2–82                   | 63                 | 41                     | This study |
| WO$_3$/ZrO$_2$    | 81                         | 150–500                  | 0–100                  | 99                 | 42                     | [12] |
| WO$_3$/TiO$_2$ (c)| 60                         | 150–500                  | 12–100                 | 98                 | 68                     | [12] |
| WO$_3$/MgO–Al$_2$O$_3$ | 168                  | 150–500                  | 0–100                  | 93                 | 17                     | [12] |
| WO$_3$/SiO$_2$    | 110                        | 150–500                  | 1–100                  | 42                 | 5                      | [12] |
| TiO$_2$           | 70                         | 150–500                  | 0–100                  | 65                 | 48                     | [12] |
| ZrO$_2$           | 94                         | 150–500                  | 0–100                  | 87                 | 1                      | [12] |
| Al$_2$O$_3$       | 199                        | 200–400                  | 14–89                  | 82                 | 27                     | [44] |
| 5P/Al$_2$O$_3$    | 151                        | 200–400                  | 9–86                   | 80                 | 34                     | [44] |
| Cr-Co/γ-Al$_2$O$_3$ | 134                     | 200                      | 93                     | –                  | 0.3                    | [45] |
| Fe$_2$O$_3$       | 40                         | 500                      | 97                     | 63                 | –                      | [46] |
Pd Modification and Supporting Effects on Catalytic Dehydration of Ethanol over W/TiO₂ Catalysts

4 Conclusion

In this research, the effect of Pd modification and the different sequence impregnation of Pd and W on W/TiO₂ catalysts were investigated and their catalytic properties for ethanol dehydration were evaluated. The introduction of 0.5 wt % of Pd into W/TiO₂ apparently affected the structure and surface acidity of the catalysts providing an increasing of catalytic activity for catalysts. The co-impregnated catalyst (Pd/W/TiO₂) exhibited higher ethanol conversion than those prepared by sequential impregnation method (W/Pd/TiO₂ and Pd/W/TiO₂). It is summarized that the Pd modification resulted in an increase of diethyl ether yield for PdW/TiO₂ and W/Pd/TiO₂, whereas that of Pd/W/TiO₂ catalyst was hardly affected. Besides, the Pd modification yielded a slight increase of ethylene yield for W/Pd/TiO₂ catalyst. From the experiment, PdW/TiO₂ was considered as the most effective catalyst for ethanol conversion to diethyl ether with diethyl ether yield of ca. 41 % at 300°C and W/Pd/TiO₂ was the most promising catalyst to convert ethanol into ethylene with ethylene yield of ca. 68% at 400°C. This is attributed to the increased amount of weak acid sites and total acidity with Pd modification onto W/TiO₂ catalyst.

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