CATALYTIC ACTIVITY OF VANADIUM OXIDE DOPED WITH PALLADIUM NANOPARTICLES ON OXIDATION OF 5-HYDROXYMETHYLFURFURAL

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Abstract

2,5-Furan dicarboxylic acid (FDCA) is a bio-based chemical used as a feedstock for a wide range of industrial applications - particularly the bioplastic industries. It is derived from 5-hydroxymethylfurfural (HMF) through a reaction of oxidation using either homogeneous or heterogeneous catalysts. According to the advantages of heterogeneous catalysts, this research aims to seek a novel catalyst type with high selectivity and high activity. We performed an investigation of the synergic effect of palladium nanoparticles and V₂O₅ catalysts on catalytic oxidation of HMF and physicochemical properties. A commercial vanadium oxide powder (V₂O₅) was doped with 1 wt.% palladium nanoparticles (Pd NPs). The Pd NPs were prepared by the colloid-chemical reduction method. Two different synthesis processes were performed based on the consequence of the combination of colloid-chemical reduction and immobilization steps, herein stepwise (ST) and simultaneous (SI) process. For the ST process, Pd NPs were reduced and then immobilized on V₂O₅ powder. During the SI process, the reduction and immobilization steps took place simultaneously. Physical and chemical properties of a prepared catalyst such as morphology, particle size distribution, and chemical structure and composition were characterized using various techniques, e.g. TEM, BET, X-ray diffraction, UV-vis spectrophotometer. It was distinctly found the synergic effect between Pd NPs and V₂O₅ catalysts on the surface catalytic activity of HMF oxidation and catalytic selectivity. The Pd NPs incorporated catalysts (ST and SI processes) gave catalytic activity at 63%, which are 2-fold in catalytic activity in comparison with bare V₂O₅ catalysts as well as they were selective to FDCA up to 19-24%. The step of catalyst preparation slightly influenced on catalytic activity and yield of FDCA; however, it did alter particle size distribution of Pd NPs and surface characteristics.

Keywords: FDCA derivatives, Heterogeneous catalyst, HMF, Oxidation, Pd/V₂O₅

Introduction

Sugar derivatives, for instance, glucose, sucrose, and fructose, can be converted into valuable chemicals, bioplastics monomers, fine chemicals, and medicines [1]. Regarding the U.S. Department of Energy (DOE) report [2] identified that 2,5-fural dicarboxylic acid (FDCA) is one of the bio-based chemicals included in the twelve essential building chemical blocks. The potential of FDCA biochemistry is the replacing terephthalic acid (TPA) feedstock-a petrochemical product used in the polymer industries, specifically for polyethylene terephthalate (PET) production. As an example, Avantium company uses FDCA to produce poly (ethylene
2,5-furandicarboxylate) (PEF), which is a facile degradable polymer as well as evading bioaccumulation [3], whereas thermal stabilities of PEF and PET are comparable. In the previous year, hence, the market margin for the FDCA reported approximately US$ 300 million, and its compound annual growth rate (CAGR) will enlarge of 8.2% in 2025 [4].

In the route of FDCA production, which derived from an oxidation process of 5-hydroxymethyl-2-furfural (HMF), there are other valuable bio-based chemicals such as 5-hydroxymethyl-2-furancarboxylic acid (HMFA), 2,5-diformylfuran (DFF), 5-formyl-2-furancarboxylic acid (FFCA) and consecutive reaction network is generally shown elsewhere [5]. The first step can undergo two routes, e.g. HMF to HMFA (oxidation) either or HMF to DFF (oxidation and dehydration). Subsequently, oxidation and consecutive dehydration or only oxidation can occur to change HMFA to FFCA or DFF to FFCA, respectively. The final series of the oxidation reaction is to transform FFCA to FDCA.

The production of FDCA via oxidation of bio-based raw materials, e.g. HMF, employs either homogeneous or heterogeneous catalysts. Several researchers reported the potential of many homogeneous catalysts such as KMnO₄, K₂Cr₂O₇, Co(OAc)₂/Zn(OAc)₂/Br⁻ and metal/bromide salts. They were very active to 90% conversion and gave a high yield of FDCA production under different conditions. However, the methodology of homogeneous processes results in inorganic waste and a cumbersome process of separation. Recent development pays attention to the heterogeneous catalytic process. The standard heterogeneous catalysts generally used noble metals loaded over several supporting materials such as Au/TiO₂ [6], Pt/A₂O₃ [7], Pd/C [8], and Ru/C [9]. These noble metals are well-known since the catalysts were selective excellently to oxidation with molecular oxygen and gave an excellent yield of FDCA production. For example, Zou Bin and co-workers [8] transformed HMF directly into FDCA over Pd/base-modified Activated Carbon catalyst in the water at 373 K for 24 hours resulting in complete conversion of HMF and 82.4% FDCA yield. Tianqi Gao et al. [5] explored that mechanism oxidation reaction of HMF undergoes different pathways, which allows a competition of HMFA and DFF production. The HMF molecule was selectively oxidized either at the hydroxymethyl group (R-OH) or at aldehyde group (R=O), where located at the second and fifth position at the furan ring, respectively. In the attendance of a strong base, aldehyde groups in HMF and DFF molecules undergo Cannizzaro reaction readily [10], which changes two aldehyde groups to one carboxyl group and one hydroxyl group and lowers the production of FDCA. Several reports have studied selective oxidation of HMF, especially selectivity to DFF intermediate, using various heterogeneous catalytic systems include...
vanadium oxide (V₂O₅) [11, 12]. The HMF oxidation to DFF with the surface lattice oxygen atoms on the VOₓ domains, leading to the reduction of V⁵⁺ to V⁴⁺, such process is known as the Mars–van Krevelen redox mechanism. An amount of 85% DFF yield (93% selectivity at 91% conversion) was reported by Moreau and co-workers [12]. However, the catalytic activity of the synergism of vanadium oxide and a noble metal (i.e. palladium, gold, etc.) is rarely studied.

To address the above issue, we studied the potential of the HMF oxidation reaction using alternative Pd nanoparticles incorporated with V₂O₅ catalysts in this research. The Pd/V₂O₅ catalysts were prepared via two different routes: i) stepwise process (ST) and ii) simultaneous process (SI) and physicochemical properties of the synthetic catalysts were characterized by means of TEM, XRD, UV-Visible spectrophotometry and FT-IR spectroscopy. The effect of parameters of catalyst preparation toward catalytic property and efficiency is examined and discussed.

**Experimental**

**Pd/V₂O₅ Catalysts Preparation**

**Chemicals**

All chemicals used in catalysts development were analytical reagent (AR) grade and purchased from commercial suppliers. No further purification was done before using the chemicals.

**Pd Colloid Preparation**

Preparation of palladium nanoparticles via colloidal method has been described previously [13]. A typical protocol can be summarized as follows. The polyvinyl alcohol (PVA, average MW = 13000-23000, 87%-89% hydrolyzed) was dissolved in water at 70°C aging at least for 2 hours. [Note: the PVA used as a nanoparticle stabilizing agents - can block part of the active sites by covering the majority of the metal surface and can also manipulate adsorbed reactive species on the metal surface, influencing the activity and the selectivity of Pd catalysts] Then, the solution (2 wt.%) was cooled down to room temperature. A 50 ml of PdCl₂·2H₂O solution (0.2367 mmol Pd) and 5.83 ml of the prepared PVA solution were added into 250 ml DI water. The solution was well mixed for 3 minutes, and its color displayed homogeneity in a yellow-brown. A reducing agent of 0.03 mM NaBH₄ solution was slowly added under severe stirring. The reduction reaction of Pd²⁺ can be written in Equation 1; therefore, the brownish Pd colloid solution was formed. The final pH would be detected, typically between 4 to 5.

\[
4\text{PdCl}_2(\text{aq}) + \text{NaBH}_4(\text{aq}) + 2\text{H}_2\text{O(l)} \rightarrow 4\text{Pd(s)} + \text{NaBO}_2(\text{aq}) + 8\text{HCl(aq)}
\]  

**Colloid Immobilization**

To dope 1 wt.% Pd nanoparticles into V₂O₅, an amount of 3 g V₂O₅ was added to the Pd colloid solution immediately after the colloid preparation. Then, we slowly added a solution of hydrochloric acid (HCl) to modulate pH to ~2. The use of HCl solution during immobilization of Pd colloid on V₂O₅ particles is to destroy the polyvinyl alcohol stabilizing agent from the surface of the Pd nanoparticles (NPs). The slurry was stirred using an overhead stirrer (800 rpm) with a simple propeller placed at the center of liquid. This immobilization process exposed in the air and kept for 2 hours at room temperature. The slurry was then filtered and thoroughly
washed with water several times. In order to dry the obtained solids samples, we placed them in a vacuum oven at 40°C overnight.

The influence of the catalyst preparation process was studied. There are two categories: i) stepwise process (ST) - Pd colloid was done before immobilizing Pd NPs on V2O5 ii) simultaneous process (SI) - Pd colloid and immobilization were done at the same time.

**Physical and Chemical Characterization**

Transmission electron micrographs of the as-synthesized Pd/V2O5, as well as V2O5 samples, were obtained using a transmission electron microscope (Phillip-Tecnai20 model). The potential magnitude was set at 100 kV with a resolution of 13,500x-13,000x. The powder samples were dissolved in 99% ethanol and sonicated for a few minutes to ensure the dispersion of particles on the Cu grid (carbon film 300 mesh).

The X-ray diffraction was performed by using the Bruker D8 Advance X-ray diffractometer with Ni-filtered CuKα radiation (λ = 1.54056 Å). The XRD patterns were recorded over an angular range (2θ) of 20-80 degree with 0.5 sec/step. Fourier transform infrared spectra of synthetic samples were obtained by an attenuated total reflectance Fourier Transform (ATR-FTIR) spectrometer (PerkinElmer-Frontier) with an accumulation of 250 scans at a wavenumber range of 4000-400 cm⁻¹ and a resolution of 4 cm⁻¹. UV-Visible spectra of the samples were recorded at 500-700 nm using a UV/visible spectrophotometer, Varian Carry 1E model. To prepare the UV-vis analyzed solution, an amount of ∼0.1 mg dried powder Pd/V2O5 sample was dissolved in pure ethanol using a sonicator.

**Oxidation of HMF into FDCA**

All the reaction experiments were carried out using a 100 ml batch reactor. The tube reactor was charged with 3 mmol of HMF, 9 mmol of Na2CO3, and 38 mmol of TBHP. The catalyst loading was 0.01 g/ml of which was made up to 30 ml by adding acetonitrile as a solvent. The mixed solution in the tube reactor was placed at a water bath, where was set the reaction temperature at 80°C. All the reactions were carried out for 24 hours without any agitation. The reaction samples were collected and kept at cold ambient.

The furan compounds contained in reaction samples were diluted with a hundredfold tetrahydrofuran (THF) and quantitatively analyzed by HPLC (High Prostar model) equipped with a UV detector. The samples were separated at the wavelength of 280 nm using a reverse-phase C18 column (125 x 4 mm). The carrier phase was composed of acetonitrile and 0.1 wt.% acetic aqueous acid solution at 1.0 ml/min flow rate. The calibration curves of standard materials, HMF and FDCA, was received. The specific calculation was as follows.

\[ \text{Conversion of HMF} = \frac{\text{initial moles of HMF} - \text{final moles of HMF}}{\text{initial moles of HMF}} \times 100\% \]  \quad (2)

\[ \text{Yield of FDCA} = \frac{\text{moles of FDCA}}{\text{initial moles of HMF}} \times 100\% \]  \quad (3)

\[ \text{Selectiviy of FDCA} = \frac{\text{moles of FDCA}}{\text{mole of total products}} \times 100\% \]  \quad (4)
Results and Discussion

Morphology Characteristics of Synthetic Pd/V_2O_5

Morphology analysis of V_2O_5 sample and reduced V_2O_5 using 0.1 M NaBH_4 in 50 ml was done to comprehend the background before incorporating the Pd NPs. The TEM images of both V_2O_5 and reduced V_2O_5 sample does not have a specific shape, a representative TEM image, as shown in Figure 1 at the right corner on top. The V_2O_5 particle size measured by the longest attitude show between 1,128 nm and 1,134 nm. Figure 1 shows the micrographs of Pd/V_2O_5 samples prepared by stepwise (Figure 1a) and the simultaneous process (Figure 1b). Furthermore, the histogram of its particle size distribution is illustrated in Figure 2. With the colloidal synthesis method, the Pd nanoparticles deposited on the surface layer of V_2O_5 for both samples enhanced a spherical shape. Table 1 indicates the summary of Pd particle size and particle distribution. The particle size of the sample prepared by the stepwise process (Figure 1a, 2a) revealed approximately 2-fold smaller than the one made by the simultaneous process (Figure 1b, 2b). However, the later process affected a high distribution of Pd particles over the V_2O_5 surface, probably due to the longer immobilizing time steps. On the one hand, the Pd nanoparticles received by the stepwise process appeared close to each other, leads to aggregate into larger particles.

Table 1. Measurement of Pd Particle Size and Distribution

| No. | Preparation Method | Pd Content (wt.%) | Particle Size (nm) | Particle Distribution (nm) |
|-----|--------------------|-------------------|--------------------|---------------------------|
| 1   | Stepwise (ST)      | 1                 | 5 ± 1.93           | 3.07 - 6.93               |
| 2   | Simultaneous (SI)  | 1                 | 11 ± 4.58          | 6.42 - 15.48              |

Figure 1. TEM micrographs of synthetic Pd/V_2O_5 sample obtained by A) stepwise and B) simultaneous [Note: pure V_2O_5 posed overlap on left-top TEM micrographs]
X-ray Diffraction

XRD patterns of V$_2$O$_5$ and reduced V$_2$O$_5$ sample are displayed in Figure 3. [Note: the reduced V$_2$O$_5$ as abbreviated as R-V$_2$O$_5$ is a powder sample of V$_2$O$_5$ reduced by 0.1 M NaBH$_4$ solution in order to make a comparison of the V$^{5+}$/V$^{4+}$ reduction effect using NaBH$_4$.] Six strongest peaks located at 20.32°, 21.74°, 26.14°, 31.05°, 32.38°, and 34.35° were observed, corresponding to the characteristic (001), (101), (110), (400), (011) and (310) planes of V$_2$O$_5$. These observed peaks are similar to the study of Lianyi Shao et al., which match with the JCDS Card no. 41-1426 [14]. It can be said that both V$_2$O$_5$ and reduced V$_2$O$_5$ samples exhibited an orthorhombic symmetry group with Pmmn space group (No. 59). The lattice parameters for the both samples were a = 1.5406 Å, b = 1.5444 Å, and c = 1.3902 Å. This observation confirms that the reduction step, which added an amount of 0.1 M NaBH$_4$ into V$_2$O$_5$ solution, does not impact on structural modification and chemical composition of V$_2$O$_5$ sample.
In the case of synthetic Pd/V$_2$O$_5$ samples received from SI and ST process, XRD patterns illustrate at the red and black spectra, respectively. The Bragg's peaks for both samples did not appear at 40°, 47° and 67°, which indicated a crystalline particle of zero-valent palladium [15] so that Pd$^0$ nanoparticles immobilized on Pd/V$_2$O$_5$ may occur in amorphous form or crystalline Pd$^0$ nanoparticles occurring is very small and it was undetectable. The traces of crystalline PdO structure were found instead in Pd/V$_2$O$_5$ samples received from ST process (Figure 3d). The diffractions peaks were observed at 2θ = 33.80°, 40.2°, 60.05° and 60.60° corresponding to the predominant formation of tetragonal phase of PdO, and indexed the characteristic of (100), (112), (103) and (200) planes as illustrated on the right side of Figure 3 [15, 16]. Hence, the stepwise process (ST) leads to an oxidation reaction of Pd$^0$ nanoparticles to form palladium oxide during the immobilization of Pd$^0$ nanoparticles to V$_2$O$_5$. The steps of palladium oxide formation are shown as the following equation:

\[
Pd^{2+} + BH_4^{-} \rightarrow Pd^0 \rightarrow V_2O_5(aq) \rightarrow PdO
\]

(5)

**Infrared and UV-Vis Spectroscopy**

The structural information of samples is further presented by FTIR and UV-Vis spectra, as shown in Figure 4a and 4b, respectively. The FTIR spectra (Figure 4a) for all the samples observed in the wavenumber 500-2000 cm$^{-1}$. It is clear that there were three bands in low-frequency range: at $\sim$566 cm$^{-1}$ corresponding to the vibrational characteristic of V-O-V bond, at $\sim$761 cm$^{-1}$ due to the stretching mode of V-O and at $\sim$998 cm$^{-1}$ attributed to the stretching mode of V=O relationships [14, 17, 18]. It notices that the peak located at 1,426 cm$^{-1}$ observed for the reduced V$_2$O$_5$ sample can be assigned to symmetric COO$^{-}$ stretching [17], which represents the carboxyl group of PVA impurity remaining after the preparation process.

![Figure 4](image_url)

Figure 4. Spectroscopy results of the synthetic samples analyzed by (a) FT-IR (ATR mode) and (b) UV-Visible spectrophotometry

The UV-visible spectra of V$_2$O$_5$ and reduced V$_2$O$_5$ were shown in Figure 4b. A peak appeared at a wavelength of $\sim$321 nm for both samples regarding the characteristic absorption peak of V(V) ion [19], and it insists that reduction step after adding NaBH$_4$ as a reducing agent does not influence on V$_2$O$_5$ chemical structure. These results show in good accordance with the report of XRD that detected similar crystalline structures of an orthorhombic symmetry.
group in both V$_2$O$_5$ and reduced V$_2$O$_5$. In the case of Pd incorporated with V$_2$O$_5$ sample, especially the one received from ST process, broadband centered at wavelength 460 nm appeared, it corresponds to the central absorption peak of Pd(II) ion [20] which represents PdO compound in good agreement with PdO crystalline structure detected by XRD.

**Catalytic Activity**

To examine the catalytic activity for all the catalyst types - V$_2$O$_5$, R-V$_2$O$_5$, Pd/V$_2$O$_5$ (SI), and Pd/V$_2$O$_5$ (ST). The oxidation of HMF was performed using TBHP oxidant agent in 30 mL acetonitrile and 9 mmol Na$_2$CO$_3$ at 80°C for 24 hrs. The catalyst loading was 0.3 g. Figure 5 (left) illustrates HMF conversion (grey-sparse bar) and FDCA yield (red-filled bar).

Regarding similar physical and chemical characteristics of R-V$_2$O$_5$ and V$_2$O$_5$ catalysts, discussed in the above section, HMF conversion was approximately 35-39%. Both R-V$_2$O$_5$ and V$_2$O$_5$ catalyst gave selectivity toward FDCA products 8-9%, and the yield of FDCA production was 5-7%. Catalytic oxidation performances of vanadium oxide doped on activated carbon were reported by Antonyraj and co-workers [21]. The V$_2$O$_5$/AC catalysts were tested under 100°C, methyl isobutyl ketone solvent (MIBK) 20 ml and with oxygen pressure 2.8 bar with catalyst loading 200 mg, the catalyst gave the highest conversion at 95.2%, and it was selective to DFF 96.4%, partly selective to FFCA only 3.6% and other by-products were absence. Vanadium oxide coated on hydrotalcite or alumina exhibited low HMF conversion 2.4-6.5% [21]. Vanadium oxide supported on acidic supports such as H-beta was tested under atmospheric pressure at 100°C with oxygen, and HMF conversion was 50%, and it gave DFF selectivity 45% [22] and testing condition was reported in Table 2. The oxidation of HMF was selective to DFF 50% over vanadyl phosphate [23]. The comparison of catalysts composed of vanadium with palladium doped on vanadium oxide was shown in Table 1. Unfortunately, all previous researches and our catalysts were carried out at different conditions. The present work exhibits the influence of noble metal palladium that can facilitate oxidation of HMF to FDCA, while vanadium oxide dominates oxidation of HMF to DFF. It was notable that the catalysts consisting of vanadium were remarkable on HMF oxidation to DFF. The influence of the redox mechanism discovered by Junfang Nie and co-authors [11]. The reduction of V$^{5+}$ to V$^{4+}$ could facilitate oxidation and dehydration of HMF convert to DFF at hydroxymethyl (R-OH) site, but the step of further oxidation is plausibly prolonged so that the reaction was rarely selective to FDCA.
Table 2. Selective Oxidation of HMF in the Catalysts Composed of Vanadium Oxide Compared to Present Work

| Catalyst   | Condition                                                                 | % HMF Conversion | % Selectivity | Ref.          |
|------------|----------------------------------------------------------------------------|-------------------|---------------|---------------|
| V$_2$O$_5$/AC | 100°C, 2.8 bar, O$_2$, 240 min (200 mg HMF, V/HMF molar ratio = 10, 20 ml MIBK) | 95.2 %           | -             | 96.4 %        | [21]          |
| V$_2$O$_5$/H-beta | 125°C, 10 bar, O$_2$, 180 min (100 mg HMF, 100 mg cat., 5 ml DMSO)           | 84.0 %           | -             | -             | 98 % 2        | [22]          |
| VOPO$_4$.2H$_2$O | 80°C, 1 bar,O$_2$, 360 min, 12 mmol HMF, 600 mg, 30 ml MIBK                  | 98.0 %           | -             | -             | 50 % 50       | [23]          |
| Pd/V$_2$O$_5$(ST) | 80°C, 1 bar, TBHP:HMF = 9:1, 24 h, 3 mmol HMF, 300 mg, 30 ml Acetonitrile | 65.0 %           | 18 %          | -             | 82 %          | Present work  |
| Pd/V$_2$O$_5$(SI) | 80°C, 1 bar, TBHP:HMF = 9:1, 24 h, 3 mmol HMF, 300 mg, 30 ml Acetonitrile | 65.0 %           | 23 %          | -             | 77 %          | Present work  |

Others: such as AMF: 5- acetoxymethyl-2-furaldehyde, OBMF: 5,5'-[oxybis(- methylene)]-bis-2-furaldehyde LA: Levulinic acid

The incorporation of 1 wt.% Pd NPs into V$_2$O$_5$ can increase HMF conversion from 20% to 65% as well as FDCA yields were approximately twofold increased. The Pd nanoparticles incorporated in V$_2$O$_5$ were more active than the bare V$_2$O$_5$ and reduced V$_2$O$_5$. It is because of the synergetic effect between Pd nanoparticles and V$_2$O$_5$. Noble metals play an essential role in the high oxidation activity of HMF [5]. The FDCA yield percentage over Pd/V$_2$O$_5$ prepared from two different processes slightly differed; it is possible due to PdO impurity that exists in Pd/V$_2$O$_5$ derived by ST process. The PdO impurity can suppress the activity of the oxidation, and it is not comparable to palladium metal. FDCA yield was 12-15%. Besides FDCA, DFF intermediate was found. Figure 5 (right) exhibited product selectivity to FDCA, DFF, and decomposition of HMF. Most of HMF were decomposed, possibly due to the drastic oxidizing agent used (TBHP) and operating temperature. The HMF conversion was generally improved when increasing the reaction
temperature [21]; however, most of them were decomposed, leading to low product selectivity. Catalysts differed in chemical compositions, and surface chemistry needs appropriate conditions for selective oxidation such as temperature, base content, and solvents.

Conclusions

To summarize, Pd NPs incorporated in V$_2$O$_5$ catalysts were prepared by facile colloid-chemical reduction and immobilization methods. The sequence of reduction using NaBH$_4$ solution does not impact on physical and chemical characteristics of V$_2$O$_5$, but it does on Pd NPs. Palladium oxide was formed during ST process, namely as PdO impurity, while the Pd$^0$ NPs were completely immobilized to V$_2$O$_5$ during SI process because of no trace of Pd$^{2+}$ signal in UV-visible spectrophotometry. The Pd/V$_2$O$_5$ catalysts prepared from these two different processes differed slightly in HMF conversion and FDCA yield because of the PdO impurity. The absolute Pd NPs loaded on V$_2$O$_5$ catalysts gave slightly superior FDCA yield for the oxidation. Besides that, the synergic effect of Pd NPs and V$_2$O$_5$ on the oxidation to FDCA and DFF should be noted.

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