

Research Article Alkaline Ionic Liquid Modified Pd/C Catalyst as an Efficient Catalyst for Oxidation of 5-Hydroxymethylfurfural

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Conversion of HMF into FDCA was carried out by a simple and green process based on alkaline ionic liquid (IL) modified Pd/C catalyst (Pd/C-OH⁻). Alkaline ionic liquids were chosen to optimize Pd/C catalyst for special hydrophilicity and hydrophobicity, redox stability, and unique dissolving abilities for polar compounds. The Pd/C-OH⁻ catalyst was successfully prepared and characterized by SEM, XRD, TG, FT-IR, and CO₂-TPD technologies. Loading of alkaline ionic liquid on the surface of Pd/C was 2.54 mmol·g⁻¹. The catalyst showed excellent catalytic activity in the HMF oxidation after optimization of reaction temperature, reaction time, catalyst amount, and solvent. Supported alkaline ionic liquid (IL) could be a substitute and promotion for homogeneous base (NaOH). Under optimal reaction conditions, high HMF conversion of 100% and FDCA yield of 82.39% were achieved over Pd/C-OH⁻ catalyst in water at 373 K for 24 h.

1. Introduction

Currently, fuel and chemicals needed in society are largely derived from fossil fuels. Rapid depletion of fossil resources has generated widespread interest in the utilization of renewable resources for the sustainable production of fuel and chemicals. Renewable energy, such as wind energy, solar energy, and geothermal energy, cannot be used to produce organic chemicals that are currently based on fossil fuels. In contrast, biomass resources with a large proportion of carbohydrates are extensive. Through selective dehydration or hydrogenation processes, biomass can produce liquid fuels and organic chemicals [1-3]. 5-Hydroxymethylfurfural (HMF) is one of the important biomass-based platform compounds [4, 5]. It can be obtained by catalyzing the dehydration of carbohydrates such as fructose, glucose, and cellulose [6-8]. HMF can be used to prepare important monomers of fine chemicals and polymers by oxidation, hydrogenation, ring opening, and polymerization [9]. Products can be used in medicine, plastics, fuel, and other fields. The study on the synthesis of important organic chemical intermediates or products from HMF as a platform has attracted immense attention [10-12]. 2,5-Furandicarboxylic acid (FDCA), one of the most important chemical building blocks from HMF via oxidation, can be used as a substitute for purified terephthalic acid (PTA) to produce bulk polyester materials, because it has a similar structure and properties with PTA [13, 14]; therefore, it is of great market potential to study the process of catalytic oxidation of HMF.

In the process of producing FDCA, first of all, Miura et al. used traditional oxidant KMnO₄ to synthesize FDCA [15]. The method has high cost and low catalytic selectivity. Also, homogeneous metal catalyst ($\text{Co}^{2+}/\text{Mn}^{2+}/\text{Br}^-$) was used for aqueous HMF oxidation [16]. But the catalyst could not be reused. Due to the difficulty of separation and poor reuse of the homogeneous catalysts, it is preferred to utilize heterogeneous catalysts over homogeneous catalysts for the oxidation of HMF into FDCA. Current literatures have reported using a variety of supported catalysts involving expensive precious metals with higher catalytic efficiency for the preparation of FDCA [17–19].

Among Pd, Pt, Ru, and Au-based catalysts, the catalytic efficiency of supported Pd nanoparticles is remarkable [20]. Active carbon materials have many excellent properties in support materials. They have good stability in high temperature, high pressure, acid, alkaline solution, and other reaction



SCHEME 1: Reaction of HMF oxidation to FDCA.

conditions. More importantly, their surface has abundant functional groups, which can be used to adsorb metal ions and immobilized metal nanoparticles [21, 22]. Therefore Pd loaded on activated carbon (Pd/C) has high catalytic activity in theory. Davis et al. have reported a 71% yield of FDCA over Pd/C under 690 kPa oxygen pressure and 295 K [23].

The oxidation of HMF requires addition of homogeneous base while utilizing noble metal-based catalysts. Without base, FDCA may not be produced in large quantities. It is now pointed out that the base can remove the HMF acidic oxidation product accumulated on the catalyst surface and allow the reaction to proceed continuously. For example, Nie et al. demonstrated a base-free process for no FDCA synthesis using activated carbon loaded Ru metal nanoparticles (Ru/C) catalyst in toluene with 95.8% 2,5-diformylfuran (DFF) yield [24]. But adding a large amount of base in the reaction system will increase the cost and pollute the environment. Therefore, some scholars consider the preparation of solid base as the catalyst carrier, For example, Wan et al. loaded bimetallic Au and Pd onto solid base carrier hydrotalcite (HT) to catalyze the oxidation of HMF. Without adding homogeneous base, finally, the reaction achieved a high yield of FDCA [25]. Although solid base HT can be used as a potential alternative to homogeneous base, it still has some problems. Zope et al. have investigated that the Mg2+ component leaching from the HT reacted with the product acid during reaction [26]. The interaction between solid base material and product must be considered.

In this work, we report a much more environmentally benign and safe process for aqueous HMF oxidation using solid base modified activated carbon-supported palladium nanoparticle catalyst (Pd/C-OH⁻). Conversion of HMF into FDCA could be carried out by a simple and green process based on a novel ionic liquid (IL) modified Pd/C catalyst and then exchanged Cl⁻ in ionic liquid with OH⁻ (Scheme 1). Alkaline ionic liquids were chosen to optimize Pd/C catalyst for their special hydrophilicity and hydrophobicity, redox stability, and unique dissolving abilities for polar compounds [27]. Finally, Pd/C-OH⁻ catalyst was found to exhibit remarkable activity for FDCA synthesis under the optimal conditions without addition of homogeneous base.

2. Experimental Section

2.1. Materials. 5-Hydroxymethyl-2-furancarboxylic acid (HFCA), 5-formyl-2-furancarboxylic acid (FFCA), HMF, and FDCA were purchased from the J&K Chemical Co., Ltd. (Shanghai, China). Palladium(II) chloride (PdCl₂, 59% Pd) was purchased from Aladdin Chemicals Co., Ltd. (Beijing, China). Activated carbon was purchased from Sigma-Aldrich (Beijing, China). 1-Methylimidazole, 3-(Chloropropyl)triethoxysilane, and all solvents were purchased from Sinopharm Chemical Reagents (Shanghai, China).

2.2. Preparation of Pd/C Catalyst. Pd/C was prepared by incipient wetness impregnation of activated carbon with aqueous solution of PdCl₂. 1 g PdCl₂ (5.64 mmol) was added to a 250 mL conical flask with 50 mL deionized water, and then the mixture was diluted to 100 mL with deionized water and shaken well. 3 g activated carbon was added to the PdCl₂ solution with 1000 rpm stirring condition for 10 h, followed by evaporation and drying at 383 K in air oven overnight. The obtained powder was reduced in a flow of 20% H₂ in N₂ at 623 K for 4 h to form final Pd/C catalyst.

2.3. Preparation of Ionic Liquid. 20 g 1-methylimidazole and 62 g 3-(chloropropyl)triethoxysilane (molar ratio 1:1.08) were added to a 250 mL round bottom flask; the mixture was sealed and heated in oil bath at 368 K with 1000 rpm magnetic stirring for 24 h to form ionic liquid. After that, the reaction mixture was cooled down to room temperature and the formed ionic liquid was reserved for further use.

2.4. Preparation of Ionic Liquid Modified Pd/C Catalyst. 2 g Pd/C catalyst and 6.46 g ionic liquid (20 mmol) prepared in 2.3 were added to a 250 mL round bottom flask with 50 mL toluene and were heated in oil bath at the reflux temperature with 1000 rpm magnetic stirring for 14 h and then the solid catalyst was filtered and washed with water and ethanol,



SCHEME 2: The schematic diagram of alkaline ionic liquid (IL) modified Pd/C catalyst (Pd/C-OH⁻) synthesis.

respectively. Finally, the crude product was dried in a vacuum oven at 323 K overnight (Scheme 2).

2.5. Synthesis of $Pd/C-OH^-$ Catalyst. The cation exchange of Cl^- in $Pd/C-Cl^-$ with OH^- was described as follows. 2 g catalyst prepared in 2.4 and 3.2 g NaOH were added to a 150 mL Erlenmeyer flask with 50 mL H₂O. The reaction system was sealed and stirred at room temperature for 24 h. Finally, the catalyst was filtered with water and dried in a vacuum oven at 323 K overnight.

2.6. Typical Procedure for the Aerobic Oxidation of HMF Over $Pd/C-OH^-$. The substrate HMF (0.08 mmol, 10 mg) was firstly dissolved in 4 g water. A certain amount of $Pd/C-OH^-$ catalyst (20 mg, 40 mg, 60 mg, and 80 mg) was added to the reaction mixture quickly and oxygen was passed into the reaction mixture for 5 min. At the end, the reaction mixture was sealed immediately. Finally, the reaction mixture was immersed in an oil bath at desired temperature (313 K, 333 K,

353 K, 373 K, and 393 K) with magnetic stirring at a constant rate of 500 rpm in high-pressure cylinders. After reacting for desired time (2 h, 4 h, 8 h, 12 h, and 24 h), 10 μ L aliquot was collected from the reaction mixture and analyzed by HPLC. In addition, the catalyst used in the experiment was recovered for reuse.

The furan compounds were analyzed by HPLC (Shimadzu Technology, model 20AB) equipped with a UV detector. The samples were separated at the wavelength of 280 nm using a reverse-phase C18 column (200 mm × 4.6 mm). The mobile phase was composed of acetonitrile and 0.1 wt.% acetic acid aqueous solution at the flow rate of 0.5 mL·min⁻¹. The contents of HMF, HFCA, FFCA, and FDCA were obtained by the calibration curves of the standard material. The specific calculation was as follows:

HMF conversion = moles of converted HMF/moles of starting HMF \times 100%.

HFCA yield = moles of HFCA/moles of starting HMF \times 100%.



FIGURE 1: SEM images of (a) Pd/C and (b) Pd/C-OH⁻.

FFCA yield = moles of FFCA/moles of starting HMF \times 100%.

FDCA yield = moles of FDCA/moles of starting HMF $\times 100\%$.

2.7. Catalyst Characterization. Scanning electron microscope (SEM) images were produced on a JSM-7500F instrument and obtained at 30 KV with 1.4 nm image resolution. Xray powder diffraction (XRD) patterns were measured on a Bruker D8 Advance powder diffractometer. XRD was collected in the 2θ range of 5°-80° with a scanning rate of 2° \cdot S⁻¹. FT-IR measurements were recorded using a Nicolet-460 FTIR spectrometer with a spectral resolution of 0.4 cm^{-1} in the wavenumber range of 400–4000 cm⁻¹. TG was obtained using a Rheometric Scientific STA1500 analyzer at the temperature from 323 K to 1073 K in nitrogen atmosphere to verify the property of catalyst under thermogravimetric analysis. CO₂-TPD was produced on a Micromeritics AutoChem II 2920 instrument. Typically, the sample was loaded and pretreated in a quartz reactor with high-purity Ar at 473 K for 2 h, followed by cooling down to 373 K. Then, the temperature was raised to 1073 K at a rate of 5 K \cdot min⁻¹.

3. Results and Discussion

3.1. Characterization of Catalysts. SEM images of Pd/C and Pd/C-OH⁻ catalysts were shown in Figure 1. It was interesting that there was no virtual difference in the SEM images of the Pd/C and Pd/C-OH⁻. Obviously, the structure of Pd/C has not been significantly damaged. In order to provide more information about the surface functional groups of the prepared Pd/C-OH⁻ catalyst, it was further characterized by FT-IR technology. As shown in Figure 2, peaks of 1100 cm⁻¹ and 1539 cm⁻¹ were the stretching vibration of C-O and - COO-, respectively, which were the characteristic peaks of activated carbon. It was pointed out that the functional groups on the surface of activated carbon surface [28]. The absorption peak at 1270 cm⁻¹ was assigned to the stretching



FIGURE 2: FTIR spectra of (a) Pd/C and (b) Pd/C-OH⁻.

vibration of C-N of imidazole ring and it verified the presence of the ionic liquid on the surface of activated carbon.

As shown in Figure 3, there were two distinct peaks on the DTG curve, which had a corresponding weight loss in the TG curve. The first sharp peak appeared at 373 K. This peak belonged to the weightless peak of water. The second peak appeared between 473 K and 873 K and the tip temperature was 710 K, indicating that the ionic liquid on the carbon support began to decompose in this range. As the temperature continued to rise, the rate of weight loss slowed down, possibly corresponding to some residual ionic liquid for further decomposition. We could figure out the result from the graph; the loading of ionic liquid on the surface of Pd/C was 18.13 wt.%. In addition, the palladium loading in the Pd/C catalyst was quantitatively determined by ICP-AES. The Pd content was determined to be 10 wt.%.

XRD patterns of the Pd/C, Pd/C-Cl⁻, and Pd/C-OH⁻ catalysts were shown in Figure 4. The peak at 23° (2 θ) was



FIGURE 3: TG spectra of Pd/C-OH⁻.



FIGURE 4: XRD patterns of (a) Pd/C, (b) Pd/C-Cl⁻, and (c) Pd/C-OH⁻.

the characteristic diffraction peak of activated carbon. For the Pd nanoparticles, three peaks at 40°, 47°, and 68° (2 θ) were the characteristic diffraction peaks of the palladium nanoparticles. The intensity of the peak at 40° (2 θ) was significantly stronger than the other two peaks [29]. As shown in Figure 4, the decrease of intensity of peaks at 40° and 47° (2 θ) and the disappearance of the peaks at 68° (2 θ) were observed, which was attributed to the loading of ionic liquids and OH⁻ [30].

The CO₂-TPD profile for Pd/C-OH⁻ was shown in Figure 5. It was proven that Pd/C-OH⁻ was successfully synthesized and OH⁻ was successfully absorbed on the surface of the Pd/C catalyst. We can see from the graph that there was mainly one desorption peak in the CO₂-TPD around 798 K. The base amount of Pd/C-OH⁻ was in the range of our research and the base amount was 2.54 mmol·g⁻¹.

3.2. Effect of Catalyst Dosage on HMF Oxidation. In this experiment, different catalyst amounts were used to establish

TABLE 1: The effect of catalyst dosage on the HMF oxidation.^a

Entry	Catalyst dosage (mg)	HMF conversion (%)	HFCA yield (%)	FFCA yield (%)	FDCA yield (%)
1	0	8.10	_	_	_
2	20	80.78	66.52	8.36	5.54
3	40	100	26.61	11.13	61.52
4	60	100	35.48	4.73	59.54
5	80	100	30.64	_	45.89

 $^{\rm a} \rm Reaction$ conditions: Pd/C-OH $^-,$ HMF (10 mg), H_2O (4 g), 353 K, and 12 h.



FIGURE 5: CO₂-TPD profile for Pd/C-OH⁻.

the effect of catalyst dosage on the oxidation of HMF with keeping the other operation conditions constant. The effect of catalyst loading was varied over the range of 0-0.08 g/cm³ on the basis of total volume of the reaction mixture [31]. As HMF conversion and FDCA yield shown in Table 1, there was no FDCA produced by the HMF oxidation without catalyst. Initially, HMF conversion and FDCA yield were enhanced as the catalyst amount increased at the same reaction time point. For example, HMF conversions of 80.78% and 100% were obtained after 12 h with the catalyst amounts of 20 mg and 40 mg; the corresponding FDCA yields were 5.54% and 61.52%. This increase in HMF conversion and FDCA yield may be due to the increase of the availability and number of catalytically active sites as the catalyst amount increased [32]. With further increase of the catalyst amount to 60 mg or 80 mg, HMF conversion was almost the same and FDCA yield decreased to 59.54% and 45.89%. Unlike chemical reactions with homogeneous catalysts, reactions with heterogeneous catalysts were limited by mass transfer in the reaction system. A larger amount of catalyst made the mass transfer of substrate HMF from the liquid solution to the active sites slower. It may be also due to the side reaction caused by the base concentration and reaction temperature.

3.3. Effect of Different Solvents on HMF Oxidation. It has been reported that solvents were very important in the chemical



FIGURE 6: Effect of the solvents on the HMF oxidation. Reaction conditions: $Pd/C-OH^-$ (40 mg), HMF (10 mg), 353 K, and 12 h.

reaction, because solvent has different properties, such as polarity, dielectric constant, steric hindrance, and acid base [33]. Thus, the oxidation of HMF was carried out in various solvents and the results were summarized in Figure 6. We can conclude that the solvent showed a remarkable effect on both HMF conversion and product yield. High HMF conversion and low FDCA yield were obtained in toluene. The catalyst showed high HMF conversion in aromatic solvents like toluene. The low FDCA yield may be because FDCA has a high dielectric constant and was insoluble in solvents of low polarity. Thus, FDCA yield was higher in polar solvents than those obtained in solvents with low polarity in theory. Interestingly, low HMF conversion and FDCA yield were obtained in protic ethanol and DMSO; high HMF conversion and FDCA yield were obtained in low boiling point aprotic acetonitrile. To our delight, water was proven to be the best solvent for the HMF oxidation. As expected, the Pd/C-OH⁻ catalyst showed the best catalytic performance in water. Full HMF conversion and FDCA yield of 61.52% were achieved in water at 353 K for 12 h. In addition, using water as a green solvent appears to be very appealing due to its low cost and the absence of toxic pollution.

3.4. Effects of Temperature on HMF Oxidation. As the results shown in Table 2, the reaction temperature had a remarkable effect on the HMF conversion and FDCA yield. Experiments were carried out at different reaction temperatures in the range of 313 K to 393 K. Generally speaking, we can conclude that HMF conversion and FDCA yield increased with increase of reaction temperature. When the temperature is 313 K, HMF conversion and FDCA yield were 83.32% and 35.5%, respectively. Increasing the reaction temperature to 333 K, 353 K, and 373 K greatly enhanced the reaction efficiency. HMF conversions were almost 100% and FDCA yields were 50.52%, 61.52%, and 76.79%. Significantly, more

TABLE 2: The effect of reaction temperature on the HMF oxidation.^a

Entry	Reaction temperature (K)	HMF conversion (%)	HFCA yield (%)	FFCA yield (%)	FDCA yield (%)
1	313	83.12	43.46	3.75	35.50
2	333	100	40.97	8.44	50.52
3	353	100	26.61	11.13	61.52
4	373	100	9.76	12.81	76.79
5	393	100	—	_	78.55

 aReaction conditions: Pd/C-OH $^-$ (40 mg), HMF (10 mg), H_2O (4 g), and 12 h.



FIGURE 7: Effect of the reaction time on the HMF oxidation. Reaction conditions: Pd/C-OH $^-$ (40 mg), HMF (10 mg), H $_2O$ (4 g), and 373 K.

substrate was in contact with catalyst active sites at higher reaction temperatures. However, increasing the reaction temperature to 393 K, FDCA was the only product and there was no other furan products produced. The possible reason could be that the degradation of HMF was serious at the higher reaction temperature of 393 K. HMF was not stable at high temperature and was degraded into byproducts [34].

3.5. Effect of Time Course on HMF Oxidation. In order to give more insights into the aerobic HMF oxidation over Pd/C-OH⁻ catalyst, the oxidation of HMF at different reaction time point was recorded, and the results were shown in Figure 7. HMF conversion and FDCA yield gradually increased during the reaction process [35]. Full HMF conversion was obtained within 2 h. The yield of FDCA also gradually increased with enhancement of the reaction time, and the maximum FDCA yield was obtained in 82.39% after 48 h. Besides FDCA, HFCA was also formed. Hence, we can know that the oxidation of HMF into HFCA and the further oxidation of HFCA into FDCA were the main reaction route for the HMF oxidation over Pd/C-OH⁻ catalyst.

TABLE 3: The effect of base on the HMF oxidation.

Entry	Base (mmol)	HMF conversion (%)	HFCA yield (%)	FFCA yield (%)	FDCA yield (%)
1 ^a	0	36.79	_	10.08	21.75
2 ^b	0.10 (solid base)	100	26.61	11.13	61.52
3 ^c	0.10 (solid base)	100	9.76	12.81	76.79
4^d	0.10 (homogeneous base)	99.90	62.09	18.70	18.62
5 ^e	0.10 (homogeneous base)	100	49.67	11.42	37.64

^aReaction conditions: Pd/C (10 mg), HMF (10 mg), H₂O (4 g), 353 K, and 12 h. ^bReaction conditions: Pd/C-OH⁻ (40 mg including 10 mg Pd/C), HMF (10 mg), H₂O (4 g), 353 K, and 12 h. ^cReaction conditions: Pd/C-OH⁻ (40 mg including 10 mg Pd/C), HMF (10 mg), H₂O (4 g), 373 K, and 12 h. ^dReaction conditions: Pd/C (10 mg), 4 mg NaOH, HMF (10 mg), H₂O (4 g), 353 K, and 8 h. ^eReaction conditions: Pd/C (10 mg), 4 mg NaOH, HMF (10 mg), H₂O (4 g), 353 K, and 8 h. ^eReaction conditions: Pd/C (10 mg), 4 mg NaOH, HMF (10 mg), H₂O (4 g), 353 K, and 12 h.

3.6. Effect of Base on HMF Oxidation. Base played an important role in the oxidation of HMF into FDCA. One important reason for the use of base was that base can be used to neutralize the FDCA, avoiding FDCA adsorbed on the surface of catalyst. The salt of FDCA was dissolved in the reaction solution and kept the catalyst activity stable [36]. The results were shown in Table 3. Under the same reaction condition, HMF oxidation was carried out over Pd/C, Pd/C with homogeneous base, and Pd/C-OH⁻, respectively, with the corresponding FDCA yields of 21.75%, 37.64%, and 61.52%. Hence, we can conclude that base was helpful to achieve rapid conversion of HMF to the FDCA and Pd/C-OH⁻ catalyst showed a remarkable effect on HMF oxidation.

3.7. Catalyst Recycling Experiments. To verify the recyclability and stability of heterogeneous catalysts, the recycling experiments of the Pd/C-OH⁻ were carried out at 373 K with 40 mg catalyst for 12 h. After the reaction, the supernatant was removed. The catalyst was washed with water and ethanol twice. Finally, the catalyst was dried in a vacuum oven at 323 K. Then the spent catalyst was reused for the next cycle under the same reaction conditions. The results were shown in Figure 8. HMF conversions and FDCA yields decreased with the cycle of the catalyst. This may be due to the loss of OH⁻ on the surface of the catalyst, which belonged to physical adsorption rather than covalent binding. On the other hand, it may be also due to the reduction of catalyst activity. There was a small decrease in the FDCA yield of the first and second run. However, HMF conversion and FDCA yield were observed to show a significant decrease from 100% and 61.96% in the second run to 60.46% and 26.27% in the third run. Then, there was a small decrease in the HMF conversion and FDCA yield of the next runs.

4. Conclusion

In summary, the Pd/C-OH⁻ catalyst was successfully prepared and characterized by SEM, XRD, TG, FT-IR, and CO₂-TPD technologies. The catalyst showed high catalytic activity in the HMF oxidation and reaction temperature, reaction time, catalyst amount, and solvent greatly affected the oxidation of HMF. Under optimal reaction conditions, high HMF conversion of 100% and FDCA yield of 82.39% were achieved over Pd/C-OH⁻ catalyst in water at 373 K for 24 h. A much more environmentally benign and green



FIGURE 8: Recycle experiments of the catalyst. Reaction conditions: $Pd/C-OH^-$ (40 mg), HMF (10 mg), 373 K, H_2O (4 g), and 12 h.

process for aqueous HMF oxidation was reported using solid base modified activated carbon-supported palladium nanoparticle catalyst (Pd/C-OH⁻).

Conflicts of Interest

The authors declare that the received funding did not lead to any conflicts of interest regarding the publication of this manuscript.

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