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# Efficient Aerobic Oxidation of 5-Hydroxymethylfurfural in Aqueous Media with Au-Pd Supported on Zinc Hydroxycarbonate

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**Abstract:** Bimetallic catalysts with Au-Pd supported on zinc hydroxycarbonate (ZOC) were synthesized via a simple depositionprecipitation method and analyzed by transmission electron microscope (TEM) to have a narrow-size distribution of predominantly 1-2 nm. The prepared Au-Pd/ZOC catalysts exhibited excellent activity towards 5-hydoxymethyl furfural (HMF) oxidation in water in the presence of the base NaHCO<sub>3</sub> at benign conditions of 80 °C and 3 bar O<sub>2</sub>, resulting in quantitative yield of 2,5-furandicarboxylic acid (FDCA). The addition of base not only enhanced the yield of FDCA but also stabilized the support ZOC via preventing ZOC from the reaction with formed carboxylic acid intermediates/products, thus allowing Au-Pd/ZOC to be recycled for at least six times without significant loss of activity. It was speculated that the basicity of ZOC could play an important role in obtaining the improved yield of FDCA as compared to other supports.

### Introduction

Over the past few years, a great deal of attention has been devoted to the production of alternative sustainable energy and chemical feedstocks, mainly due to the rising cost, diminishing supply and environmental impact of fossil fuels.<sup>[1-4]</sup> Therefore, the chemical industry and academia are striving to produce fuels and chemicals from renewable resources which have potential to replace fossil-based chemicals and fuels. The biomass is one of the potential renewable and sustainable sources which can efficiently be transformed into high-value chemicals and fuels, such as 5-hydoxymethyl furfural (HMF), levulinic acid, lactic acid, and their derivatives, and thus reduce the heavy dependence on unsustainable petroleum-based resources.<sup>[5-7]</sup>

The catalytic oxidation of HMF - a dehydrated product of glucose/fructose - to 2,5-furandicarboxylic acid (FDCA) has been well studied among various routes of biomass transformation.<sup>[8-10]</sup> HMF is considered as an important biomass-based platform chemical, and the product FDCA is identified as one of 12 potentially useful building blocks by the U.S. Department of

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Energy.<sup>[11]</sup> Moreover, FDCA can potentially substitute petroleumderived terephthalic acid as a precursor for the production of PET (polyethylene terephthalate) plastic, due to the similar structural properties of the two compounds. It was recently reported that PEF (polyethylene furanoate), polymers of FDCA and ethylene glycol, showed many similar or improved properties compared to PET plastic.<sup>[13,45]</sup> Accordingly, the exploration of efficient and reusable catalytic systems for the oxidation of HMF into FDCA has recently spurred a great deal of interest in the field of biomass transformations.<sup>[14-18]</sup>

Noble metal-containing supported catalysts have been widely investigated for the oxidation of HMF into FDCA with molecular O<sub>2</sub> as the oxidant.<sup>[19-24]</sup> Particularly, Au-supported catalysts have shown high catalytic performances for HMF oxidation into FDCA in aqueous medium, as Au has relatively high resistance to water and O<sub>2</sub> compared to Pt and Pd.<sup>[25,26]</sup> However, Au can quite easily deactivate by sintering of Au nanoparticles and adsorption of formed products or intermediates during the oxidation process, especially in the absence of base, which hampers the lifetime of the catalyst and limits the industrial application.<sup>[27-29]</sup> Thus, stable and efficient supported Au catalysts have to be developed to lower costs for HMF oxidation in order to be industrially viable.

In general, Au catalysts showed high catalytic activities for many oxidation reactions and their catalytic activity and stability could be enhanced by alloying with other metals, such as Cu and Pd.<sup>[30-34]</sup> In connection to this, Hutchings and coworkers have discovered that Au-Pd alloy supported on TiO<sub>2</sub> catalysts showed higher catalytic activity and stability than corresponding Au or Pdbased catalysts for the selective oxidation of benzyl alcohol to benzyl aldehyde and toluene to benzyl benzoate.<sup>[33,34]</sup> However, understanding of the observed synergic effect between the two metals is still lacking.

Typically, the support for noble metal nanoparticles is an important factor to determine the catalytic activity.[35-37] For example, Corma and coworkers have found that Au/CeO2 and Au/TiO<sub>2</sub> catalysts afforded over 99 % yield of FDCA after 8 h of reaction time, while only 44 and 15 % yield of FDCA were obtained with Au/C and Au/Fe<sub>2</sub>O<sub>3</sub> catalysts under the same reaction conditions, respectively.<sup>[24]</sup> However, the role of support on the catalytic activity is still unclear for noble metal catalysts. On the other hand, H-Y zeolite, hydrotalcite and Mg(OH)<sub>2</sub> have been employed as support for Au.[20,38] Although they showed significant catalytic activities towards HMF oxidation, the stability of these catalysts was poor as they were prone to deteriorate in water, leading to Au nanoparticle sintering and leaching of Au nanoparticles.<sup>[20,38,39]</sup> These previous studies indicate that choosing a suitable support for Au is important to enhance the catalytic activity and stability during the reaction. In accordance with this, Yang and coworkers have recently reported that water insoluble zinc hydroxycarbonate (Zn<sub>5</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>6</sub>, ZOC) as a good support for Au catalysts in the oxidation of benzyl alcohol to

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benzaldehyde. Interestingly, it was shown that the basicity of the support played an essential role to promote the oxidation of benzyl.<sup>[40]</sup> Moreover, the basicity of the support might influence the dispersion and average size of the Au nanoparticles.<sup>[41]</sup> These studies encouraged us to explore the catalytic activity and stability of Au and Pd on ZOC towards HMF oxidation in aqueous solution. To the best of our knowledge, the aerobic oxidation of HMF to FDCA in water with noble metal supported on ZOC has not been reported previously.

In the present work, we have synthesized Au-Pd/ZOC, catalysts using a simple deposition-precipitation method and characterized the materials with transmission electron microscope (TEM) and X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). Considering the superior catalytic performance of Au-Pd/ZOC catalyst, we have systematically investigated the effects of various supports on catalytic activity of Au-Pd alloy towards HMF oxidation to FDCA. Additionally, various reaction parameters correlated with the yield of FDCA such as influence of metal loading, reaction time, reaction temperature, and the addition amount of NaHCO<sub>3</sub> have been discussed detailedly in the study. The stability of Au-Pd/ZOC was also studied by performing recyclability test for seven runs.

### **Results and Discussion**

The XRD patterns were performed to investigate the crystal structure of Au-Pd/ZOC catalyst. As seen in Figure S1, all the major peaks corresponded to the reflections of  $Zn_5(CO_3)_2(OH)_6$  (ZOC) (JCPDS card No.19-1458). In addition, no characteristic

peak corresponding to Au or Pd was observed, mainly due to adequate small metallic particles on ZOC. The microstructures of the Au-Pd/ZOC catalyst was examined by TEM images, as shown in Figure 1. In Figure 1a, Au-Pd nanoparticles were homogeneously dispersed on the surface of the ZOC support. The metal particle size distribution of 2.0 wt% Au-Pd/ZOC was determined by measuring the mean diameter of over 400 particles from different areas and the results were illustrated in Figure 1b. The particle size distribution indicated that the diameter of the Au-Pd nanoparticles were predominantly in the range of 1-2 nm with an average particle size of 1.6 nm. As reported, possessing particle sizes smaller than 2 nm in noble metal-based catalysts would greatly improve the catalytic activity of HMF oxidation to FDCA.<sup>[44,45]</sup> Comparatively, the particle sizes of Au-Pd nanoparticles loaded on hydrotalcite (MG20), CeO2, TiO2 and activated carbon (AC) were also measured by TEM and found to be 2.1, 1.8, 1.7 and 2.2 nm, respectively (Figure S3).

The composition of the Au-Pd nanoparticles was determined by energy-dispersive X-ray spectroscopy (EDS) elemental mapping of randomly chosen nanoparticles and the images were given in Figure 1c-1f. The elemental maps of Au, Pd and Au-Pd overlay signals for the same nanoparticle were homogeneously distributed in each particle (Figure 1d-1f). The relative difference of atomic radii of Au (0.144 nm) and Pd (0.138 nm) was 4.17% based on the Hume-Rothery rule,<sup>[51]</sup> which revealed that Pd atoms might be incorporated into the Au lattice, and thus Au and Pd were alloyed in the lattice of the corresponding nanoparticle.<sup>[52]</sup> In addition, the EDS showed that the atomic ratio of Au to Pd is close to 1 (Figure S2), which was the exact molar ratio of Au:Pd used during the synthesis.



Figure 1. a) TEM images of 2.0 wt% Au-Pd/ZOC (Au:Pd = 1:1). b) Particle size distribution of 2.0 wt% Au-Pd/ZOC. c) High-angle annular dark-field (HAADF) image of 2.0 wt% Au-Pd/ZOC. d), e) and f) EDS mapping images corresponding to Au, Pd and Au-Pd overlay signals for the selected nanoparticle in the white square c) of 2.0 wt% Au-Pd/ZOC, respectively.

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Figure 2. XPS spectra of Au 4f<sub>7/2</sub> and Pd 3d<sub>5/2</sub> of 2.0 wt% Au-Pd/ZOC (Au:Pd = 1:1) and 2.0 wt% Au/ZOC or 2.0 wt% Pd/ZOC catalysts.

To further investigate the chemical state and composition of the sample surface, the Au-Pd/ZOC catalysts were subjected to XPS measurements and the results are shown in Figure 2. The binding energy (BE) of the Au  $4f_{7/2}$  for the Au-Pd/ZOC catalyst was found to be 83.6 eV, which was shifted slightly towards higher BE value of 84.0 eV for the Au/ZOC catalyst. Similarly, the BE of the Pd  $3d_{5/2}$  for Au-Pd/ZOC was 335.3 eV, which was slightly shifted towards lower BE value of 334.9 eV for the Pd/ZOC catalyst. The BE differences of Au and Pd further substantiated the formation of Au-Pd alloy nanoparticles and the electron transfer between Pd and Au. As in line with the previous report, the activity of Au-Pd alloy could be significantly enhanced via the electron transfer between Au and Pd.<sup>[46]</sup>

The HMF oxidation experiments were carried out with Au-Pd supported on various supports, such as MG20, CeO<sub>2</sub>, TiO<sub>2</sub>, AC and ZOC under identical reaction conditions and the results were summarized in Table 1. A full conversion of HMF with 77% and 55% selectivity to FDCA was obtained after 4 h, when Au-Pd supported on CeO<sub>2</sub> and TiO<sub>2</sub> were employed as catalysts, respectively. When the support was changed to AC, the conversion of HMF and selectivity to FDCA decreased to 75% and 35%, respectively. Interestingly, over 99% yield of FDCA was achieved when the support switched to ZOC. The order of activity

of Au-Pd on different supports was as follows: Au-Pd/ZOC > Au-Pd/MG20 > Au-Pd/CeO<sub>2</sub> > Au-Pd/TiO<sub>2</sub> > Au-Pd/AC.

As there was no significant difference in the particle sizes of Au-Pd regardless of the support, it was speculated that the high catalytic activity of Au-Pd/ZOC could also be in part from the surface property of the support. In order to understand the role of support, the basicity/acidity of the support was evaluated by measuring the pH of an equilibrated suspension of different supports in Milli-Q water. It was found that each support indeed exhibited differences in their acidic/basic properties. The pH value of the Milli-Q water (6.95) was taken into account to calculate the pH value of each support. The order of pH value of the support in water was:  $ZOC > MG20 > CeO_2 > TiO_2 > AC$ . Compared with corresponding support, the pH value of Au-Pd/ZOC, Au-Pd/MG20 Au-Pd/CeO<sub>2</sub>, Au-Pd/TiO<sub>2</sub> and Au-Pd/AC was about 8.16, 7.20, 6.25, 5.84 and 5.25, respectively. The slight differences indicated that Au-Pd alloys hardly had an effect on the pH of the supported catalysts due to their low loading (2.0 wt%). The activity order of Au-Pd with different support ascended gradually with the increased pH values of the supports/catalysts, which revealed that the basicity of the support (ZOC) could significantly improve the FDCA yield. This is in accordance with previous reports showing that the strongly basic supports can promote the

Table 1. Aerobic oxidation of HMF with Au-Pd supported on various supports. <sup>[a]</sup>								
Catalyst	Support pH in water	(Au+Pd) / wt%	Au/Pd molar ratio	Conv. / %	Selectivity / %			
					HMFCA <sup>[b]</sup>	FFCA <sup>[c]</sup>	FDCA	Others
Au-Pd/ZOC	8.05	2.01	1.00	>99	-	-	>99	-
Au-Pd/MG20	7.11	2.00	1.00	>99	1	8	90	1
Au-Pd/CeO <sub>2</sub>	6.13	1.98	0.99	>99	3	18	77	2
Au-Pd/TiO <sub>2</sub>	5.79	2.00	1.00	>99	14	35	50	1
Au-Pd/AC	5.20	1.96	0.98	75	17	44	35	4

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[a] Au:Pd=1:1, 0.5 mmol HMF, HMF/(Au+Pd)=100, 0.1679 g NaHCO<sub>3</sub>, 10 mL H<sub>2</sub>O, 353 K, 3 bar O<sub>2</sub>, 4 h. [b] 5-hydroxymethyl-2-furancarboxylic acid. [c] 5-formyl-2-furancarboxylic acid.

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Table 2. Catalytic performance of Au-Pd/ZOC catalysts with different Au:Pd molar ratios for the aerobic oxidation of HMF.<sup>[a]</sup>

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Catalyst	Au/Pd molar ratio	Conv. / %	Selectivity / %				
Calarysi			HMFCA	FFCA	FDCA	Others	
Au/ZOC	-	>99	19	7	73	2	
Au <sub>3</sub> -Pd <sub>1</sub> /ZOC	3.00	>99	13	8	79	0	
Au <sub>2</sub> -Pd <sub>1</sub> /ZOC	1.99	>99	2	6	90	2	
Au <sub>1</sub> -Pd <sub>1</sub> /ZOC	1.01	>99	0	0	>99	0	
Au <sub>1</sub> -Pd <sub>2</sub> /ZOC	0.50	>99	3	10	87	0	
Au <sub>1</sub> -Pd <sub>3</sub> /ZOC	0.33	>99	6	24	69	1	
Pd/ZOC	-	>99	14	35	50	1	

[a] 38 mg catalyst, 0.5 mmol HMF, 0.1679 g NaHCO<sub>3</sub>, 10 mL H<sub>2</sub>O, 353 K, 3 bar O<sub>2</sub>, 4 h. The molar ratios of the metals were adjusted to 2.0 wt% with respect to ZOC in all catalysts

oxidation of benzyl alcohol or aldehyde.[53,54]

It was reported that the addition of base, especially strong base (e.g. NaOH and KOH) could accelerate the HMF oxidation via the promotion of O-H and C-H bond activation from OH<sup>-</sup>.<sup>[27]</sup> The main role of weak base was to maintain the activity of catalyst by dissolving the formed products, especially FDCA, due to its low solubility in water. <sup>[18]</sup> The formed FDCA or other intermediates would block the active sites of the catalysts without addition of base, thus resulting in the decrease of the catalytic activity. In addition, the yields of FDCA increased dramatically with the increase of support acidity/basicity even under the optimal NaHCO<sub>3</sub>/HMF molar ratio of 4. These results indicated that the support basicity could be the predominant factor to improve the catalytic activity rather than the addition of NaHCO<sub>3</sub>.

To gain insights into the alloying effect between Au and Pd on the HMF oxidation, the influence of Au:Pd molar ratio in catalysts were examined. The inductively coupled plasma-atomic emission spectrometry (ICP-AES) measurements for all of these catalysts substantiated that the molar ratios between Au and Pd on the ZOC support were close to the actual molar ratio during the preparation and the catalytic results were summarized in Table 2. Au/ZOC and Pd/ZOC were also tested and the yields of FDCA were 73% and 50%, respectively. The yields of FDCA increased to > 99% when Pd was introduced to the Au-Pd/ZOC catalyst with an Au:Pd molar ratio of 1:1. These results evidently indicated a synergistic effect between Au and Pd on enhancing the HMF conversion and FDCA selectivity. However, the yield of FDCA significantly varied by changing the ratio between Au and Pd. Hence, lowering the Au/Pd ratio from 1 to 0.33, the yield of FDCA decreased from 99% to 69%, whereas the FFCA yield was increased from 0 to 24%, suggesting that Pd demoted the catalytic activity. A similar descending trend on the yield of FDCA was also observed when the Au content increased with respect to Pd in Au-Pd/ZOC catalysts. It clearly demonstrated the importance of having an appropriate Au:Pd molar ratio, especially 1:1 on ZOC, in order to achieve the desired catalytic activity.

The catalytic performance of Au-Pd/ZOC catalysts with different metal loadings was also tested and the results were compiled in

Table 3. The ICP-AES results showed that almost all Au and Pd metals were immobilized onto ZOC and the molar ratios between Au and Pd in all the Au-Pd/ZOC catalysts were close to 1. As expected, no yield of FDCA was observed when using the ZOC support alone as catalyst. 28% conversion of HMF to the reaction intermediates, 5-hydroxymethyl-2-furancarboxylic acid (HMFCA) and 5-formyl-2-furancarboxylic acid (FFCA) were found as the major products, implying that only the oxidation of HMF to FFCA took place in the absence of Au-Pd alloy nanoparticles. As the loading of Au-Pd on ZOC increased from 0.5 to above 2.0 wt%, the FDCA selectivity increased from 37% to > 99%. Based on these results, one can expect that the incorporation of active metals into the suitable support would improve the oxidation further from FFCA to FDCA. These observations revealed that an appropriate amount of Au and Pd with a molar ratio of 1:1 was essential to achieve a quantitative yield of FDCA in water.

Table 3. The influence of metal contents (Au+Pd) on ZOC on the yield of FDCA.  $\ensuremath{^{[a]}}$ 

Catalyst	Conv.	Selectivity / %					
Calalysi	/ %	HMFCA	FFCA	FDCA	Others		
ZOC	28	62	28	0	0		
0.5% Au-Pd/ZOC	>99	25	37	37	1		
1.0% Au-Pd/ZOC	>99	12	27	61	0		
1.5% Au-Pd/ZOC	>99	0	13	82	2		
2.0% Au-Pd/ZOC	>99	0	0	>99	0		
3.0% Au-Pd/ZOC	>99	0	0	>99	0		

[a] 38 mg catalyst, Au:Pd=1:1, 0.5 mmol HMF, 0.1679 g NaHCO\_3, 10 mL H\_2O, 353 K, 3 bar O\_2, 4 h.

The influence of reaction temperature (60 to 90 °C) on the yield of FDCA was also been investigated with 2.0 wt% of Au-Pd/ZOC (Au:Pd = 1:1). As shown in Figure 3a, the obtained FDCA yields were 32% and 54% at 60 and 70°C, respectively.

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When the temperature further increased to 80 °C, the yield of FDCA was enhanced to over 99%. The yield of FDCA remained unchanged even if the temperature was raised further to 90 °C, implying that FDCA was quite stable under these conditions. This indicated that the reaction temperature had a positive influence on the catalytic activity of Au-Pd/ZOC catalyst. Based on the obtained results at various temperatures, the optimal reaction temperature for further studies was chosen to be 80 °C.

Catalytic experiments were also performed by varying the molar ratio of NaHCO<sub>3</sub>/HMF and the results were illustrated in Figure 3b. A significant influence of the NaHCO<sub>3</sub> to HMF ratio was observed on the conversion of HMF and product distribution. A poor yield of FDCA (20%) was observed at a HMF conversion of 73% with Au-Pd/ZOC when no NaHCO3 was added in the reaction system, leading to an unselective reaction pathway. Moreover, the catalyst was deactivated presumable due to adsorption of the formed carboxylic intermediates/products and/or humins on the surface of the noble metal particles. <sup>[14,17]</sup> When the NaHCO<sub>3</sub>/HMF molar ratio increased to 2. a total conversion of HMF with FDCA yield of 88% was obtained. As the NaHCO<sub>3</sub>/HMF molar ratio increased further to 4 or 6, a quantitative vield of FDCA (>99%) was attained. It was reported that the main role of weak base NaHCO<sub>3</sub> was to act as a promotor by reacting with the formed mono and/or dicarboxylic acid products/intermediates to make the corresponding salts, whereby the catalyst activity was retained.<sup>[18,19]</sup> Moreover, the pKa1 of FDCA was 2.60, which was much lower than the pK<sub>a1</sub> of carbonic acid (3.60).<sup>[50]</sup> Accordingly, it could be understood that the formed FDCA could react with the support if no base was added, thereby the role of NaHCO<sub>3</sub> in the oxidation process of HMF was not only to neutralize the formed products or intermediates, but also to stabilize the ZOC support.

In order to get insight into the reaction pathway for the oxidation of HMF into FDCA over Au-Pd/ZOC, a time course study was also performed, and the results were shown in Figure 4a. The conversion of HMF gradually increased with the prolonged reaction time. The HMF conversion was about 73% after 30 min while nearly quantitative conversion of HMF (> 99%) was obtained after one hour. The yield of FDCA steadily increased at the expense of HMFCA and FFCA intermediates as the reaction time increased, and a FDCA yield of 99% was achieved within 4 h. As seen in Figure 4a, moderate yields of HMFCA (ca. 25%) and FFCA (55%) were obtained after 30 min and then the intermediates gradually transformed into FDCA. In contrast, the yield of 2.5-diformylfuran (DFF) remained below 2% during the entire reaction process. These results confirmed that HMFCA and FFCA were the main intermediates during the consecutive oxidation of HMF into FDCA. Moreover, the results revealed that the aldehyde functionality in HMF was preferentially oxidized compared to the hydroxyl group in HMF. Therefore, the oxidation of HMF to HMFCA, followed by oxidation to FFCA, and further to FDCA, rather than via DFF, was the fastest and thus predominant reaction pathway using Au-Pd/ZOC as catalyst (Scheme 1). The obtained reaction pathway was in good agreement with the pathway previous reported for the oxidation of HMF into FDCA with Au-Cu/CeO2 as catalyst.[24]

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Figure 3. Aerobic oxidation of HMF at a) different temperatures and b) with different NaHCO<sub>3</sub>/HMF molar ratios. Reaction conditions: 38 mg 2.0 wt% Au-Pd/ZOC catalyst, Au:Pd=1:1, 0.5 mmol HMF, 10 mL H<sub>2</sub>O, 3 bar O<sub>2</sub>, 4 h. For the different NaHCO<sub>3</sub>/HMF ratio experiments, the reaction temperature was 80 °C.

Thus, the catalytic activity of 2.0 wt% Au-Cu/ZOC catalyst was also tested under the same conditions. Unfortunately, only around 18% yield of FDCA along with 93% conversion of HMF were obtained after 4 h reaction time, which were much lower than those of 2.0 wt% Au-Pd/ZOC catalyst. The difference could be ascribed to the different role of Pd and Cu in the corresponding Au-based bimetallic catalysts. For Au-Pd alloys catalyst, Au as an efficient promoter of Pd prevented the overoxidation and poisoning of Pd by formed intermediates or products.[33] In contrast, Au was the active part in Au-Cu alloys while CuOx as a promotor would be formed in Au-Cu alloys by the oxidation of Cu, which could enhance oxidation performance via the activation of oxygen. [53,54] Generally, Pd was more active than Au, Cu or CuOx for oxidation reactions, which resulted in the high activity of Au-Pd/ZOC. In order to substantiate the influence of the formed HMFCA intermediate, it was also used as starting substrate. As shown in Figure 4b, > 99% conversion of HMFCA was achieved only after 4 h, establishing that the oxidaion of HMFCA to FFCA was slower than the oxidation of HMF to HMFCA. This was also in accordance with previous results obtained for aqueous HMF oxidation using Au catalysts.[25]

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Figure 4. Time course of the oxidative conversion of a) HMF and b) HMFCA. Reaction conditions: 38 mg 2.0 wt% Au-Pd/ZOC catalyst, Au:Pd=1:1, 0.5 mmol substrate, 0.1679 g NaHCO<sub>3</sub>, 10 mL H<sub>2</sub>O, 353 K, 3 bar O<sub>2</sub>.



**Scheme 1.** The possible reaction pathway in HMF oxidation to FDCA. The blue arrow is the predominant pathway.

The recyclability of Au-Pd/ZOC was also examined and the results were given in Figure 5. After each run, the catalyst was simply reused by centrifugation, washed with water and ethanol, and drying at 60 °C overnight. HMF was completely converted for each run, and the FDCA yield was generally stable at around 96%. Meanwhile, the turnover frequencies (TOF) for each run were all kept at around 24 h<sup>-1</sup>, indicating that no obvious deactivation occurred even after 7 runs. In addition, the filtrates of seven runs were subjected to ICP-AES analysis to detect possible leaching of metals. The amount of leached zinc for each run were less than 0.12% of total zinc amount in the corresponding used catalyst. Notably, no Au or Pd leaching was detected in the filtrates and it strongly demonstrated the good stability of the Au-Pd/ZOC catalyst. The 2.0 wt% Au-Pd/ZOC catalyst was further subjected to XRD and TEM analysis after being used for seven reaction runs (Figure S1, S4). No significant changes were observed in the major peaks of the XRD patterns before and after reaction,

thereby revealing that the crystalline structure of the ZOC support is quite stable under the chosen reaction conditions. The TEM image of the used 2.0 wt% Au-Pd/ZOC catalyst displayed that Au-Pd nanoparticles were still well dispersed on the surface of ZOC and the average diameter of Au-Pd nanoparticles was around 1.8 nm, indicating the good stability of Au-Pd alloys on the support ZOC. These results evidently demonstrated that Au-Pd/ZOC was a highly stable and efficient catalyst for the conversion of HMF to FDCA under the chosen reaction conditions.



Figure 5. Recyclability tests for the Au-Pd/ZOC catalyst. Reaction conditions: 38 mg catalyst (2.0 wt% Au-Pd/ZOC), molar ratio of Au:Pd=1:1, HMF (63 mg),  $H_2O$  (10 mL), NaHCO<sub>3</sub> (0.1679 g), 3 bar O<sub>2</sub>, 353 K, 4 h, molar ratio of (Au + Pd)/HMF = 1:100).

### Conclusions

In summary, a series of Au-Pd bimetallic nanoclusters supported on ZOC, MG20, CeO<sub>2</sub>, TiO<sub>2</sub> and AC have been synthesized. TEM images showed that all of the Au-Pd supported catalysts contained particle size distributions of around 1.6 nm. Among the employed supports, ZOC was found to be the best support on improving the yield of FDCA because the basicity of ZOC support was an important factor on the enhancement of catalytic activity. In addition, Au-Pd/ZOC with an Au:Pd ratio of 1:1 showed the highest catalytic activity towards HMF oxidation in water at relative mild conditions, achieving > 99% yield of FDCA. A synergistic effect between Au and Pd played an important role on enhancing the catalytic activity towards the formation of FDCA. It was also found that the presence of NaHCO3 in the catalytic system could improve the yield of FDCA and stabilize the ZOC support, thus avoiding deterioration of ZOC by the formed carboxylic acid intermediates/products. Recyclability of Au-Pd/ZOC with respect to the catalytic conversion of HMF to FDCA revealed no significant change in seven consecutive runs. Moreover, XRD and TEM analysis of the Au-Pd/ZOC after the seven reaction runs indicated no change in the XRD patterns and nanoparticle size distributions compared to the parent catalyst, implying that Au-Pd/ZOC was a highly stable and efficient catalyst for the conversion of HMF to FDCA under the applied reaction conditions.

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### **Experimental Section**

#### **Catalyst preparation**

The ZOC support was prepared via a hydrothermal method previously reported.<sup>[42]</sup> Typically, 1.10 g zinc acetate dihydrate and 1.50 g urea were dissolved in 80 mL deionized water. After stirring for 10 min, the solution was transferred to a Teflon-lined stainless steel autoclave and treated at 120 °C for 5 h and then naturally cooled down to room temperature. The precipitate was separated by centrifugation, washed with copious amount of deionized water and ethanol, and finally dried at 60 °C for 6 h in static air to get the ZOC support.

The other supports (TiO<sub>2</sub>, CeO<sub>2</sub> and activated carbon) were purchased from Aladdin Industrial Corporation and used as received. The hydrotalcite PURALOX <sup>®</sup> MG 20 was purchased from Sasol Performance Chemicals. Prior to use, activated carbon (AC) was pretreated with 100 mL aqueous solution of 7 M HNO<sub>3</sub> at 80 °C for 48 h. AC was then separated by centrifugation, washed with deionized water and ethanol for several times and then dried at 80 °C overnight in static air.

The Au-Pd/ZOC bimetallic catalysts were prepared via a depositionprecipitation method.<sup>[43]</sup> Appropriate amounts of HAuCl<sub>4</sub> and K<sub>2</sub>PdCl<sub>4</sub> aqueous solution were added into the mixture containing 0.15 g of ZOC dispersed in 30 mL distilled water. For example, to prepare a catalyst containing a molar ratio of Au:Pd = 1:1, 198  $\mu L$  aqueous solution of 50 mmol/L HAuCl<sub>4</sub> and 85.5 µL aqueous solution of 115.7 mmol/L K<sub>2</sub>PdCl<sub>4</sub> were used for synthesis, corresponding to 2 wt% with respect to ZOC. The mixture was stirred for a short while and heated to 80 °C, and an appropriate amount of urea (molar ratio: urea:metal = 100:1) was then added to the mixture and stirred for 12 h. The final pH value of the mixture was around 8.50 due to the decomposition of the urea. The obtained precipitate was collected by centrifugation, washed with plenty of distilled water and ethanol, and dried at 60 °C overnight. The catalyst was then reduced at 100 °C under H<sub>2</sub> atmosphere (1 atm) with a flow rate of 60 mL/min for 6 h. Other catalysts were synthesized by adopting a similar procedure except Au-Cu/ZOC. The Au-Cu/ZOC catalyst was prepared via a similar procedure while the reduction temperature was increased to 200 °C since Cu could be reduced at high temperature.

#### **Catalysts characterization**

The crystal phase of the catalyst was examined by powder X-ray diffraction (XRD, Bruker D8 Advance diffractometer) with Cu-Ka radiation ( $\lambda = 1.5406$ Å ) in the range of  $2\theta = 10 - 80^\circ$ . Transmission electron microscopy (TEM) coupled with energy-dispersive X-ray spectroscopy (EDS) were recorded by a FEI Tecnai G2 F20 S-Twin (operated at 200 kV) to determine the particle sizes and metal compositions of the obtained materials. X-ray photoelectron spectroscopy (XPS) measurements were recorded on a Thermo Scientific ESCALAB 250Xi X-ray photoelectron spectrometer with Al-Ka X-ray as the excitation source. All binding energies were referred to the C 1s peak at 284.8 eV of the surface adventitious carbon. The metal contents in the prepared catalysts and the leaching of metals to the solution during the reaction were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) on an Agilent 725ES instrument. The basicity of the ZOC support was measured by using Mettler Toledo FE-20 pH meter. To measure pH, 0.05 g of ZOC was suspended in 5 mL Milli-Q water and stirred for 30 min prior to the measurement.

### HMF oxidation

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HMF ( $\geq$  97% purity) was purchased from Adamas Reagent Co., Ltd. The aerobic oxidation of HMF was performed in a batch stainless-steel autoclave (20 mL). Typically, 63 mg HMF and an appropriate amount of catalyst corresponding to a HMF:(Au + Pd) molar ratio = 100:1) were added into the reactor precharged with 10 mL of an alkaline aqueous solution containing 0.1679 g NaHCO<sub>3</sub> (molar ratio NaHCO<sub>3</sub>:HMF = 4:1). The reactor was then sealed and purged with O<sub>2</sub> for four times. The mixture was heated to the reaction temperature of 80 °C. Once the system reached the desired temperature, the reactor was pressurized with 3 bar O<sub>2</sub> and stirred vigorously with a magnetic stirrer at a speed of 600 rpm. The autoclave was cooled down to room temperature by quenching with cold water after a specific reaction time, and the catalyst was filtered off prior to the analysis.

#### Analysis of the reaction mixture

The reaction mixtures were analyzed by high-performance liquid chromatography (HPLC, Shimazu LC-20A) equipped with a UV/vis detector (206 nm) and an ODS-SP column (8 mm × 250 mm) thermostatted at 50 °C. An aqueous buffer solution of KH<sub>2</sub>PO<sub>4</sub>/K<sub>2</sub>HPO<sub>4</sub> (pH = 3.50) was used as a mobile phase at a flow rate of 0.5 mL/min. To analyse the amount of 2.5-diformylfuran (DFF), a HPLC (Agilent Technologies 1200) equipped with an Aminex HPX-87H column (7.8 mm × 300 mm) thermostated at 60 °C was employed. Here a 0.005 M aqueous solution of H<sub>2</sub>SO<sub>4</sub> was used as the mobile phase. The conversion of HMF, the yield of FDCA and other intermediates were quantified by making series of individual standards with propandioic acid as the internal standard. All the samples were neutralized with 1% H<sub>3</sub>PO<sub>4</sub> solution prior to the analysis.

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Au-Pd supported on zinc hydroxycarbonate (ZOC) catalysts showed high activity for HMF oxidation. The basicity of ZOC could play a crucial role for enhancing the yield of FDCA. Moreover, Au-Pd/ZOC was prone to recycling for at least six times without significant loss of its activity.



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Efficient Aerobic Oxidation of 5-Hydroxymethylfurfural in Aqueous Media with Au-Pd Supported on Zinc Hydroxycarbonate