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Basic anion-exchange resin (AER)-supported Au-Pd alloy nanoparticles for the oxidation of 5hydroxymethyl-2-furfural (HMF) into 2,5-furan dicarboxylic acid (FDCA)

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Graphical Abstract

Basic anion-exchange resin (AER)-supported Au-Pd alloy nanoparticles were readily prepared and successfully applied to the oxidation of 5-hydroxymethylfurfural (HMF) into 2,5-furan dicarboxylic acid (FDCA).

Highlights

- Au-Pd alloy nanoparticles were simply supported on basic anion-exchange resin.
- The nanoparticles were dispersed both on the resin surface and inside resin sphere
- HMF was oxidized to FDCA with 93.2% yield using this catalyst.
- This catalyst could be used 6 times without any significant loss of activity.
- With this catalyst, FDCA was obtained from HMF with an 82.9% in air.

Abstract

Au-Pd alloy nanoparticles supported on basic anion-exchange resin (AER) have exceptional catalytic activity for the oxidation of 5-hydroxymethyl-2-furfural (HMF) into 2,5-furan dicarboxylic acid (FDCA) with an equimolar amount of base. SEM-EDX and TEM analyses show that 5-20 nm Au-Pd alloy nanoparticles are well dispersed both on the resin surface and inside resin spheres by a simple procedure without any assistance of additives. XPS analysis reveals that Au- and Pd metals exist in an alloy form on the AER support, which is confirmed by a comparison study with a mixture of AER-supported monometallic nanoparticles (AER-supported Au and AER-supported Pd). In the presence of a 1:1 ratio of Au-Pd alloy nanoparticles over Amberlite IRA-743 resin with O₂ (10 bar) at 373 K in an equimolar Na₂CO₃ aqueous solution, HMF is oxidized to FDCA with a 93.2% yield. On the other hand, mixture of AER-supported Au and AER-supported Pd affords only a 52% FDCA yield under identical conditions. This catalyst can be used 6 times without any significant loss of activity. FDCA is also obtained from HMF with an 82.9% yield in air (40 bar).

Keywords: Anion-exchange resin (AER);Au-Pd alloynanoparticles; oxidation; 5-hydroxymethyl-2furfural (HMF); 2,5-furan dicarboxylic acid (FDCA)

1. Introduction

Polyethylene terephthalate (PET) is a well-known fossil-derived polymer obtained by the condensation polymerization of ethylene glycol and terephthalic acid that has a market size approaching 4 billion lb/yr [1]. Purified terephthalic acid was also used to make resins, fibers and films and was a versatile plastic precursor; however, as of today, it has harmful effects because of its bioaccumulation in living organisms [2]. 2,5-Furan dicarboxylic acid (FDCA) is a renewable

chemical obtained by the oxidation of biomass derived 5-hydroxymethyl-2-furfural (HMF) that can replace terephthalic acid in PET [3,4]. The synthesis of p-xylene from HMF which can further be converted to terephthalic acid is another multi-step approach towards renewable PET [5,6]. Poly(ethylene furanoate) (PEF), which is obtained from the polymerization of ethylene glycol and FDCA is an easily degradable polymer that also evades bioaccumulation. Furthermore, PEF has better physical properties than PET, such as a higher gas impermeability, and higher glass transition temperature [7,8]. Multiple reports are available on the successful oxidation of HMF to FDCA over Au or Pt supported on metal oxides [9-16]. However, Au catalysts are found to be deactivated by the byproducts or intermediates in some cases [17]. To overcome the weakness, bimetallic catalysts containing Au have been developed to have catalytic activities towards HMF oxidation that are superior to those of the monometallic catalysts because of the alloying effect [18-22]. Oxidation is a complex multi-step reaction and recent reports claim that no commercial process is available for the production of FDCA [23]. Another important issue with the existing powder catalysts is the need to overcome mass transfer limitations when used in continuous reactors. Polymer materials could be ideal catalyst supports to meet the specific demands of catalysts for different chemical reactions because of their various structures, excellent processability, recyclability and surface properties. More importantly, the acidity or basicity of polymer materials can be adjusted at the molecular level by means of chemical functionalization, so that the desired reaction could be promoted and/or side reactions could be minimized [24]. In addition, swollen polymeric resins can provide reactants and reaction intermediates easy access to catalysts in the aqueous phase, which is a crucial role of the support [18].

Herein we report the use of Au-Pd alloy nanoparticles supported on basic anion-exchange resins (AERs) as a catalyst for the oxidation of HMF. Using this catalyst, a mild and efficient conversion of HMF to FDCA can be performed with oxygen and an equimolar amount of base in the aqueous phase. AER-supported Au-Pd alloy nanoparticles are simple to synthesize in the absence of a stabilizer via two step procedure: (i) Entrapment of Au³⁺ and Pd²⁺ by the interaction between the metal cations and the phenyl rings of polystyrene backbone, when metal species can be dispersed all around resin sphere, then (ii) reduction of metal cations to Au-Pd alloy nanoparticles (Fig 1) [25-27]. Moreover, these bead-shaped resin supports are commercially available and readily packed in column, which can easily be extended to the larger scale production of the catalyst for industrial purposes.



Fig. 1. Schematic view of preparing procedure onanion-exchange resin (AER)-supported Au-Pd alloy nanoparticles (AER: Amberlite IRA-743).

2. Experimental

2.1. Materials

Gold (III) chloride trihydrate (AuCl₃·3H₂O 99.9%); palladium (II) chloride (PdCl₂, 99.9+%); 5hydroxymethyl-2-furfural (HMF, 99%); 2,5-furandicarboxylic acid (FDCA, 97%); sodium carbonate

(99.995%);methanol (99.8%); ethanol (99.5%); sodium boro hydride (98%); and anion-exchange resins including Amberlite IRA-743 free base (IRA-743), Amberlite IRA-400 chloride form (IRA-400), and Amberlite IRA-900 chloride form (IRA-900) were purchased from Sigma-Aldrich (USA). All reagents were directly used without further purification unless otherwise mentioned.

2.2. Methods

SEM-EDX analysis was performed using a JEOL-JSM-6701F field-emission scanning electron microscope and elemental analysis was performed using an energy dispersive X-ray detector.Transmission electron microscope (TEM) images were taken with a Maker FEI, model Technai G2 microscope with an acceleration voltage of 200 kV using carbon-coated 200 mesh copper grids. XPS measurements were carried out on a Thermo Fischer Scientific K-alpha using monochromatized Al K α radiation (hv = 1486.6 eV) and processed using Thermo Avantage software. The specific surface area of the resins was determined in a BET surface analyzer (Bruanuer-Emmett-Teller, ASAP2010, Micromeritics, USA) using N_2 as the adsorbent at liquid nitrogen temperature (77 K) in a relative pressure (P/P_0) range of 0 to 0.25. The resin samples (in powder form) were degassed in air for over 12 h at 100 °C prior to analysis. The conversion of HMF and the selectivity of the products, including FDCA were determined using high-performance liquid chromatography (HPLC, Agilent 1200 series) equipped with a refractive index (RI) detector and an Aminex HPX-87H column (Bio-Rad laboratories, Inc.). The HPLC analysis conditions were as follows: eluent, 0.01 N H₂SO₄; flow rate, 0.6 mL min⁻¹; and column temperature, 45 °C. Prior to the HPLC analysis, all samples were subjected to dilution with water (HPLC grade) to prevent signal overload and damage to the system.NMRSynthetic HMF was characterized by HPLC and confirmed by ¹H NMR (400 MHz, JNM-AL400, JEOL), which was processed by the Delta program (ver. 4.3.6). Elemental chemical analysis of the samples was determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Thermo Scientific, U.K., iCAP 6000 Series) by digesting the sample in a concentrated HNO₃ and H₂SO₄ mixture (4:1). The loading of "N" content (mmol/g) in the resins were determined by a CHN elemental analysis (Automatic Elemental analyzer, FLASH 2000 Series, Thermo Scientific, USA). Each resin was analysed 3 times and the average amount of nitrogen over sample weight were calculated and presented in Table 3.

2.3. Procedures

Preparation of catalysts: A calculated amount of metal/metals (2 wt% of resins) in the form of the chloride salt was completely dissolved in 200 mL of ethanol (a high Pd content requires more time to dissolve). Five grams of resin (the commercial resin was dried overnight under vacuum at 313 K and then used) was then added and stirred slowly for 24 h without breaking the resin beads. The metal/metals were reduced using an excess of sodium boro hydride (5equiv). The metal/metals-supported resin was filtered and washed with 400 mL of hot ethanol and then dried under vacuum for 12h before being used as the oxidation catalyst.

Oxidation of HMF into FDCA: The experiment was conducted in a high-pressure reactor (Series 4560 Mini Reactors, Parr Instrument Company) starting with 2mM of HMF, 200mg of resin catalyst, and 2mM of Na₂CO₃ in 20 mL H₂O. Oxygen (10 bar) was used as the oxidative agent at 373K, with continuous mechanical stirring at 300 rpm for 4 h. After the reaction, the aqueous sample was taken and analyzed by HPLC. After isolation, FDCA was characterized by ¹H NMR.

3. Results and Discussion

3.1. Characterization of catalyst

The SEM-EDX analysis of 2 wt% Au-Pd supported on the anion-exchange resin (2% Au-Pd/IRA-743) showed that Au and Pd were homogeneously dispersed both on the surface and inside the resin. This meant that the resin swelled in the solvent during the synthesis, and the metal gained access to the interior of resin because of macroporous nature of IRA-743 (Fig. 2a and 2b). TEM images of this metal supported on resins showed 5-20 nm metal nanoparticles dispersed throughout the material (Fig. 2c and 2d).



Fig. 2. SEM-EDX analysis of the (a) surface and (b) cross-section of Au-Pd/IRA-743 and TEM images of (c) IRA-743 and (d) Au-Pd/IRA-743.

To investigate the chemical state and surface composition of the metal catalysts, XPS analysis was carried out. Two binding energy peaks, positioned at 83.9 and 87.6 eV, appear with an energy separation of 3.7 eV and an intensity ratio of 0.75, which clearly represent the spin orbit splitting of metallic Au⁰. The binding energies of the Au 4f_{7/2} for 2% Au/IRA-743 and 2% Au-Pd(1:1)/IRA-743 were 83.95 eV and 83.91 eV, respectively (Fig 3a and 3b). A slight shift towards lower binding energy was observed in 2% Au-Pd(1:1)/IRA-743. On the other hand, the binding energy of the Pd 3d_{5/2} for 2% Au-Pd(1:1)/IRA-743 was 335.94 eV, which was shifted to a high value compared with that for 2% Pd/IRA-743 (335.38 eV) (Fig 3b). This shift indicated that two metal elements (Au and Pd) formed an alloy [18,28] and this Au-Pd alloy was expected to enhance the catalytic activity via the electron transfer between Au and Pd [29].



Fig. 3. XPS spectra of (A) Au 4f profile of Au/IRA-743, (B) Au 4f profile of AuPd/IRA-743, (C) Pd 3d profile of Pd/IRA-743, (D) Pd 3d profile of AuPd/IRA-743

ICP analysis of the samples were done to find out the extent of the metal loading on to the surface of the resin and the results of the selected samples were given in Table 1

Name	Calcu	ılated	Analysed		
	Au (wt %)	Pd (wt %)	Au (wt %)	Pd (wt %)	
2% AuPd(1:1)/IRA-743	1.00	1.00	0.53	0.58	
1% Pd/IRA-743	0	1.00	0	0.58	
1% Au/IRA-743	1.00	0	0.73	0	

Table 1. ICP analysis of the AER-supported Au-Pd alloy nanoparticles

This shows with the reported synthetic route only a portion of metal was loaded on to the surface of the resin. Au supported materials showed relatively higher loading than Pd supported or Au-Pd supported AERs.

3.2. Oxidation of HMF into FDCA

To elucidate the activity of the catalysts, oxidation of HMF into FDCA was studied in water with 10 bar of oxygen at 373 K (Table 2). Equimolar Na₂CO₃ to HMF was used as the base. The anionexchange resin (IRA-743) in the absence of an active metal showed only a 2.3% FDCA selectivity with a 68.7% conversion efficiency (Entry 1). The resin containing monometallic gold showed a high conversion of HMF but a relatively low FDCA selectivity: both 1% Au/IRA-743 and 2% Au/IRA-743 gave 100% HMF conversion with 27.6% and 39.1% FDCA selectivities, respectively (Entry 2-3). In the case of resin containing monometallic palladium, 80.4% and 83.5% conversion efficiencies with 7.0% and 17.4% FDCA selectivities were observed for 1% Pd/IRA-743 and 2% Pd/IRA-743 catalyst, respectively (Entry 4-5). However, the addition of palladium to gold on the supported resin enormously influenced the FDCA selectivity, the 1:1 Au-Pd catalyst with a 2% total metal loading (2% AuPd(1:1)/IRA-743) showed a ~93% selectivity with 100% conversion (Entry 6). A simple mixture of the two monometallic catalysts (1% Au/IRA-743 plus 1% Pd/IRA-743) gave only a 52.0% FDCA selectivity (Entry 7), which could support the bimetallic effect of the Au-Pd catalyst. This result is comparable with the recent results on bimetallic catalysts with a minimum base concentration [19-23]. Though reports are available for base-free heterogeneous catalytic HMF oxidation to FDCA, the leaching of solid base materials into water and the partial solubility of FDCA makes this reaction technically complex [13,18,30]. The catalyst leaching study was performed by taking the active catalyst in solvent and the base without the reactant, and the reaction was conducted for 2 h. Then, the reaction catalyst was filtered, HMF was added to the used solvent, and the reaction was conducted; no activity was observed.

Entry	Catalyst	HMF Conversion (%)	FDCA Selectivity (%)
1	IRA-743	68.7	2.3
2	1% Au/IRA-743	100	27.6

Table 2. Oxidation of HMF into FDCA using AER-supported Au-Pd alloy nanoparticles^a

3	2% Au/IRA-743	100	39.1
4	1% Pd/IRA-743	80.4	7.0
5	2% Pd/IRA-743	83.5	17.4
6	2% AuPd(1:1)/IRA-743	100	93.2
7*	2% AuPd(1:1)/IRA-743	56.3	5.8
8	1% Au/IRA-743 + 1% Pd/IRA-743	100	52.0

^a Reaction conditions: HMF (2 mM),catalyst (200 mg), Na₂CO₃ (2 mM), O₂ (10 bar), H₂O (20 mL), 373 K, 4 h. * Reaction conditions same as above without Na₂CO₃

3.3. Time course study

To understand the mechanism of this oxidation using our catalyst, time on stream investigations were performed for FDCA. 1% Au/IRA-743 converted 85% of HMF in 1 h of reaction time with a 5-hydroxymethylfuran-2-carboxylic acid (HMFCA) selectivity of 77%. As time progressed, the FDCA selectivity increased from <5% at 0.5 h to 36% at 5 h at the expense of HMFCA, but the selectivity of 5-formylfuran-2-carboxylic acid (FFCA) remained ~20% throughout the reaction. Though additional FDCA may be formed for longer reaction intervals, it may not be economical for fine chemicals (Fig 4a). 1% Pd/IRA-743 reacted different than Au did, i.e. the HMFCA selectivity remained ~50% from 0.5 h to 5 h; similarly FFCA and FDCA selectivities also remained stable throughout the reaction.



Fig. 4. Time course investigation on the oxidation of HMF using (a) 1% Au/IRA-743, (b) 1% Pd/IRA-743, and (c) 2% Au-Pd(1:1)/IRA-743 (reaction conditions: HMF (2 mM), catalyst (200 mg), Na₂CO₃ (2 mM), O₂ (10 bar), H₂O (20 mL), 373 K.

This seems that the catalyst did not have the tendency to shift the equilibrium towards FDCA (Fig 4b). 2% AuPd(1:1)/IRA-743 showed a 95% HMF conversion with a 61% FFCA selectivity in 0.5 h of reaction time. As time progressed, the selectivity of FDCA also increased, reaching a 91%

selectivity in 3 h and 95% in 5 h (Fig 4c). The time on stream study also confirmed that the FDCA produced was stable under the reaction conditions for a long time which makes it suitable for industrial production. Interestingly, 2,5-diformylfuran (DFF) was not observed under our reaction conditions unlike stoichiometric oxidant KMnO4 [31], enzyme [32-34], ruthenium-based catalysts [35,36], oxidizing HMF to FDCA via DFF intermediate, but HMF oxidation proceeded via HMFCA intermediate. It meant that the AER-supported Au-Pd alloy nanoparticles could catalyze the oxidation from aldehyde to carboxylic acid more effectively than the oxidation from alcohol to aldehyde. The possible mechanism of this oxidation reaction is given in Fig. 4 and which similar to what was already observed by Albonetti et. al [23].

3.4. Effect of polymeric-supports and metal ratios

To understand the influence of the supporting resin, IRA-743 (macroporous-type resin) was compared with other anion-exchange resins having different support morphologies like IRA-900 (gel-type resin) and IRA-400 (macroreticular-type resin) and characterization of each anion-exchange resin was summarized in Table 3. Au-Pd (1:1) was supported on different resins and the oxidation ability was studied. Among the supports, IRA-743 was found to be highly active. 2% Au-Pd(1:1)/IRA-400 showed a 98% conversion with a 26% FDCA selectivity and 2% Au-Pd(1:1)/IRA-900 showed a 91% conversion with a 5% FDCA selectivity (Table 4). From this result, the macroporous morphology appears beneficial for access to substrate (HMF). However, BET surface area analyses of 2% AuPd(1:1)/IRA-743, 2% AuPd(1:1)/IRA-400 and 2% AuPd(1:1)/IRA-900 are 19 m²/g, 0 m²/g and 2 m^2/g , respectively. The surface areas of all catalysts were very low, and they did not have a significant influence on catalytic behavior. Instead, it was noticed that basicity of the resins could affect the oxidation ability because the terminal functional groups of IRA-400 and IRA-900 are tetraalkyl ammonium salts; on the other hand, the terminal fucntional group of IRA-743 is tertiary amine, having a weaker basicity than the others [37]. To examine the influence of the palladium on the gold, the ratio of Au-Pd was varied from 6:1 to 0.5:1 by maintaining a total metal loading of 2wt%, and the results are given in Fig. 5. As the palladium concentration increased, the selectivity of FDCA also increased, i.e. 2% AuPd(6:1)/IRA-743 had 100% conversion with a 55.1% FDCA selectivity whereas 2% AuPd(1:1)/IRA-743 had 100% conversion with a 93.2% selectivity. A further increase in palladium concentration did not show improvement in the FDCA selectivity, which might be due to the decrease of the active metal (Au) concentration. The turnover number (TON) calculated for the active 2% AuPd(1:1)/IRA-743 catalyst after 4 h was 65, which is comparable to other active catalysts reported in the literature.

Name of resin	Morphology of resin	Chemical structure of terminal group	Surface area (m²/g)	Loading level of 'N' content (mmol/g)
Amberlite IRA-743	Macroporous		18.76±0.08	1.9
Amberlite IRA-400	Gel	H ₃ C,⊕,CH ₃ M ^N CH ₃ x [⊝]	0.03±0.02	3.3
Amberlite IRA-900	Macroreticular	H ₃ C,⊕,CH ₃ M [×] CH ₃ X [⊖]	20±0.01	3.8

 Table 3. Characterization of anion-exchange resins

	Table 4. HMF	conversion	according to	the mor	phology o	f the resir	supports
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Catalyst	HMF Con%	FFCA Sel%	FDCA Sel%	HMFCA Sel%	Others Sel%
2%AuPd (1:1)/IRA743	100.0	3.3	93.2	0.0	3.5
2%AuPd (1:1)/IRA900	91.5	42.6	5.0	39.6	12.8
2%AuPd (1:1)/IRA400	97.8	48.3	25.9	12.9	12.9



Fig. 5. According to the ratio of Au/Pd metals, the HMF conversion (red) and selectivity of FDCA (green) are shown. Reaction conditions: HMF (2 mM), catalyst (200 mg), Na₂CO₃ (2 mM), O₂ (10 bar), H₂O (20 mL), 373 K, 4 h.

3.5. Reusability

Immediately after the reaction, the catalyst was filtered, washed with water, dried in vacuum and used for new reaction; the results are given in Table 5. The catalyst was reusable up to 6 cycles without any marginal change in the conversion and selectivity. No leaching of Au or Pd was detected in the filtrates, and the reaction times were similarly kept for all runs; this proves the potential of the catalyst to be extended for industrial production.

Table 5. HMF conversion and the selectivity of FFCA and FDCA using recycled AuPd(1:1)/IRA-743. The reaction conditions are the same as **Fig. 5**

Cycle No	HMF Con. (%)	FFCA Sel. (%)	FDCA Sel. (%)
1 cycle	100	2.7	96.8
2 cycle	100	5.0	95.0
3 cycle	100	8.0	92.0
4 cycle	100	6.5	93.5
5 cycle	100	6.7	93.3
6 cycle	100	6.9	93.1

3.6. Practical approach

For bringing this reaction close to a practical application, HMF produced from our laboratory (KITECH HMF) using high fructose corn syrup (HFCS) was used for this oxidation [38]. Both Aldrich HMF and our HMF were studied under similar reaction conditions, and both showed 100% conversion and FDCA selectivities of 93.2% and 91.9% respectively. It is clear that our catalyst was not only active for pure commercial HMF but also for crude HMF synthesized in our laboratory. The reaction was also conducted using air as the oxidant. Previously, HMF oxidation to FDCA using Au-Pd alloy supported on carbon nanotube [18] or zinc hydroxycarbonate [22] used molecular oxygen as an oxidant. The AER-supported Au-Pd afforded 100% HMF conversion with 82.9% FDCA selectivity using an air pressure of 40 bar (Table 6).

	HMF Conversion (%)	Selectivity (%)			
Source		HMFCA	FFCA	FDCA	
Aldrich HMF	100	0	3.3	93.2	
KITECH HMF	100	0	8.9	91.9	
Aldrich HMF ^b	100	14.9	2.2	82.9	

Table 6. Influence of HMF source on oxidation ^a

^a Reaction conditions: HMF (2 mM), Au-Pd(1:1)/IRA-743 (200 mg), Na₂CO₃ (2 mM), O₂ (10 bar), H₂O (20 mL), 373 K, 4 h

^b Air (40 bar) used instead of O₂.

4. Conclusion

In summary, we report the simple synthesis of Au-Pd alloy nanoparticles supported on basic anionexchange resins and its application to efficient oxidation of HMF to FDCA. Cross-sectional SEM-EDX analysis confirms that alloy particles are present both on the surface and in the cross-section of the resin spheres and XPS shows that the Au- and Pd metals exist in an alloy form. A 1:1 ratio of Au-Pd supported on Amberlite IRA-743 resin having a terminal functional group of a tertiary amine gives FDCA from HMF in a great yield (93.2%) with O₂ (10 bar) at 373 K in an equimolar Na₂CO₃ aqueous solution and this catalyst can be used 6 times without any significant loss of activity. FDCA is also obtained from HMF with an 82.9% yield in air (40 bar).

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