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AuPd–Fe₃O₄ nanoparticle-catalyzed synthesis of furan-2,5dimethylcarboxylate from biomass-derived 5hydroxymethylfurfural under mild conditions

Ahra Cho,^[a] Sangmoon Byun,^{[a],[b]} Jin Hee Cho,^[a] and B. Moon Kim*^[a]

Dedication ((optional))

Abstract: Efficient one-pot oxidative esterification of 5hydroxymethylfurfural (HMF) to furan-2,5-dimethylcarboxylate (FDMC) has been achieved under extremely mild reaction conditions through the use of AuPd alloy nanoparticles (NPs) supported on Fe₃O₄. High yield of FDMC (92%) was obtained at room temperature under atmospheric O2. The reaction proceeded through the synergistic effects of the AuPd heterobimetallic catalyst system. The most effective molar ratio of noble metal contents for HMF oxidation was 1.00:1.18. On the other hand, when Au-Fe₃O₄ NPs were used as the catalyst, selective synthesis of 5-hydroxymethylfuroic acid methyl ester (HMFE) was achieved. Additionally, the AuPd-Fe₃O₄ catalyst could be successfully reused.

Introduction

Biomass is widely considered to be one of the most important sources for sustainable chemicals, which can be transformed into various value-added molecules.^[1] The production of value-added chemicals from renewable biomass using high performance metal catalysts has attracted much attention from scientists and engineers in recent years. Specially, 5-hydroxymethylfurfural (HMF) is a key intermediate in industry because of its versatility as a platform material for valuable chemicals such as fuel,^[2] pharmaceuticals,^[3] and polymers.^[4] One particularly useful chemical transformations of HMF is its oxidation to 2,5furandicarboxylic acid (FDCA),^[5] which can be a monomer of new polymers, that can replace the fossil fuel-derived polyethylene terephthalate (PET) polymer.^[6] Polyethylene furanoate (PEF), consisting of ethylene glycol and FDCA, is a bio-derived polymer. PEF exhibits better physical properties with higher glass transition temperature and gas impermeability than PET.^[7] Additionally, the enzymatic hydrolysis of PEF films is reported to be faster than that of the common PET films.[8]

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In the past few years, various synthetic reactions have been developed for FDCA that employ heterogeneous catalysts such as Pd,^[9] Pt,^[10] Au,^[11] Ru,^[12] bimetallic NPs,^[1b,13] and homogeneous catalysts.^[14] Despite significant progress in FDCA production, there have been difficulties in its direct application in industry because of its low solubility in most solvents.^[15] Also, product purification is cumbersome and another drawback. Though FDCA synthesis proceeds in high yields, quantitative isolation in high purity for polymerization has proven difficult.^[16] Owing to the limitation of FDCA, furan-2,5-dimethylcarboxylate (FDMC), which is soluble in most common solvents, has generated a lot of interest in the past decade as it has more suitable properties for polymerization.^[15] Typically, synthesis of FDMC involves alcohol oxidation of the corresponding alcohol to aldehyde in methanol followed by oxidative esterification of the aldehyde to esters in one-pot, which obviates the isolation of intermediates. There are, however, relatively fewer studies of direct FDMC synthesis in comparison to those of FDCA. Reactive heterogeneous catalysts such as Au,^[17] Co,^[18] and PdCoBi^[19] have been developed for the production of FDMC. Corma and coworkers used Au-CeO2 NPs for the oxidative esterification of HMF, and achieved high conversion and selectivity at 130 °C, under 10 bar bubbled O₂ in methanol.^[17b] Grassi and coworkers developed gold nanoparticles supported on nanoporus multiblock copolymer matrix (AuNP-sPSB), which show tunable selectivity to the oxidation of HMF.^[17c] For the selective synthesis of FDMC using AuNP-sPSB, 3.5 MPa O2 and 110 °C were required. Xu and coworkers established a base-metal catalyst system that provided high yield of FDCA at 100 °C, under 0.6 MPa O₂ in methanol.^[18b] They reported CoOx-N/C NPs with α-MnO₂ as the active catalyst system and instead of alkali metal base additives, the pyridinic-N on the doped carbon could act as a Lewis base. In these reports. high temperature and pressure were essential for the successful synthesis of FDMC from HMF. Most recently. Fu group have developed a new reaction utilizing PdCoBi/C as a catalyst, which produces FDMC in 96% vield under atmospheric oxvgen at 60 °C.^[19] To our best knowledge, however, elevated temperature is crucial for high yields of FDMC, as evidenced in all the previously reported cases (Table 1). Usually, catalytic oxidation of HMF using Au NPs at room temperature under 1 atm O₂ proceeds primarily at the aldehyde functional group and forms 5hydroxymethylfuroic acid methyl ester (HMFE) as the major product. Riisager and co-workers chose Au-TiO₂ as a catalyst for the oxidation of HMF,^[20] and succeeded in the selective formation of HMFE (73% yield) at r.t. under 1 atm O₂ with KOMe as a base.

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HO O Catalyst Conditions MeO O O OMe								
Entry	Catalyst	HMF/met al (mol/mol)	Pres sure (bar)	T (°C)	Yield (%)			
1 ^[17a]	Au-TiO ₂	313	4	130	98			
2 ^[17b]	Au-CeO ₂	300	10	130	99			
3 ^[18a]	Co _x O _y -N@C	40	10	100	53			
4 ^[18b]	CoO _x -N/C + α-MnO ₂	8	6	100	95.6			
5 ^[19]	PdCoBi/C	10	1	60	96			
This work	AuPd–Fe ₃ O ₄	100	1	r.t.	92			

Table 1. Previous research results of FDMC synthesis with heterogeneous

Therefore, it is a challenge to find a catalyst that is capable of converting HMF to FDMC under mild conditions (room temperature and atmospheric O_2). Most known reactions using catalysts to produce FDCA or FDMC from HMF require either high temperature or high pressure. To secure a high yield of the desired product under mild reaction conditions, it is necessary to develop a new catalyst that can facilitate oxidation at low temperature. In recent years, several reports have been published on bimetallic^[13] or even trimetallic^[19] catalysts for HMF oxidation at <100 °C under 1 atm O_2 . However, an elevated temperature is still necessary for high yields in this reaction (Table S4) because the conversion of HMF with most of known catalysts is very sluggish at room temperature under atmospheric O_2 .^[21]

Studies abound on the catalytic oxidation of alcohols to aldehydes or carboxylic acids using molecular oxygen as an oxidant.^[22] In particular, syntheses of benzaldehyde or benzoic acid from benzyl alcohol using Au or AuPd alloy catalysts have been amply documented.^[23] In benzyl alcohol oxidation catalyzed by various heterogeneous metal species, [24] reactions employing bimetallic alloy AuPd have shown a synergistic effect compared to those using monometallic Au or Pd nanoparticle (NP) catalysts.^[25] Therefore, several studies on the synthesis of FDCA using AuPd NPs have been carried out.[13b,26] Reactions employing AuPd NPs showed better results than those utilizing Au monometallic NPs, however in most cases reactions generally require 60-100 °C heating under oxygen pressure ranging 1-10 bars. Although AuPd NPs are known to possess a better catalytic effect in alcohol oxidation compared to Au or Pd NPs, reports on AuPd-catalyzed HMF conversion to FDMC are scarce. Herein, we have described our approach of using a bimetallic alloy nanoparticle catalyst consisting of Au and Pd for FDMC synthesis under exceptionally mild conditions (room temperature, 1 atm O₂). The catalytic activity was compared with that of Au-Fe₃O₄ including the oxidations of furfuryl alcohol and furfural. Kinetic studies were also performed for the reactions employing both AuPd–Fe₃O₄ and Au–Fe₃O₄ NPs. Catalysts with different metal ratios (Au:Pd) were prepared and their activities were compared. Additionally, the catalytic stability of AuPd–Fe₃O₄ was investigated in comparison with Au–Fe₃O₄ by recycling experiments.

Results and Discussion

Catalyst characterization

The bimetallic alloy AuPd-Fe₃O₄ catalyst was synthesized by a hydrothermal method that was reported previously for a one-pot nitro-reduction and reductive amination.[27] The catalyst was analyzed through the use of scanning electron microscopy (SEM), high resolution transmission electron microscopy (HR-TEM), energy dispersive X-ray spectroscopy (EDS), scanning transmission electron microscopy (STEM) and X-ray photoelectron spectroscopy (XPS) (Figure 1). The SEM and STEM images (Figure 1 (a) and 1 (b)) indicate that the Au and Pd metal particles were well deposited on the Fe₃O₄ support. The STEM-EDS images show that Au and Pd were located as random alloy particles on the Fe₃O₄ support (Figure 1 (c)). The alloy AuPd metal particles were 3.4-7.5 nm size and evenly dispersed throughout the NPs. To determine the chemical state and electronic properties of the AuPd-Fe₃O₄ NPs, XPS analysis was carried out (Figure 1 (d) and S3). Two binding energy peaks, Au $4f_{7/4}$ and $4f_{5/4}$, of Au-Fe₃O₄ were positioned at 83.2 and 86.9 eV, respectively, which indicated the presence of metallic Au(0). The binding energy peaks of AuPd-Fe₃O₄, detected at 82.9 and 86.6 eV, were slightly shifted. This shift demonstrated that the catalytic activity and selectivity could be changed by the electron transfer of Au and Pd metals. Also, inductively coupled plasma atomic emission spectroscopy (ICP-AES) showed that AuPd-Fe₃O₄ NPs



Figure 1. (a) SEM image (b) STEM image and EDS image (c) HR-TEM image of AuPd-Fe₃O₄ (Au:Pd = 1.00:1.18, molar ratio), (d) XPS peaks of Au-Fe₃O₄ and AuPd-Fe₃O₄ (Au:Pd = 1.00:1.18, molar ratio).

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HO CO HMFE HO CO HMFE HO CO HME FDMC OME

Scheme 1. Synthetic pathway of oxidative esterification from HMF to FDMC.

have 7.34 wt % of Au and 4.70 wt % of Pd with a molar ratio of 1.00:1.18 (Table S3). Additional information on catalyst characterization is in supporting information.

Catalyst test

There are two possible oxidative pathways from HMF to FDMC (Scheme 1). If the conversion of the aldehyde to an ester functionality in HMF is faster than alcohol oxidation, HMFE would be a dominant reaction intermediate (path a). On the other hand, if alcohol oxidation is faster than aldehyde oxidation, 2,5diformylfuran (DFF) would be formed predominantly in the initial stage of the reaction (path b). To explore the catalytic activity of alloy AuPd-Fe₃O₄ NPs (molar ratio of Au:Pd is 1.00:1.18) towards the oxidative esterification of HMF, the effect of different bases and catalysts was evaluated under atmospheric pressure of O2 at room temperature. First, several bases were screened. As seen in Table 2, no oxidation was observed without the presence of a base (Table 2, Entry 1). Reaction in the presence of sodium carbonate led to 63% conversion and 37% yield of the desired product (Table 2, Entry 2), confirming that a base is needed to promote the oxidation. Oxidation in the presence of organic bases such as trimethylamine (TEA) and 1.8-diazabicyclo[5.4.0]undec-7-ene (DBU) was investigated (Table 2, entries 3 and 4). With the use of TEA, HMF was converted to HMFE (38% conversion), but FDMC was not detected (Table 2, entry 3). The conversion and vield increased to 55% and 26%, respectively, with DBU (Table 2, entry 4). When oxidation was carried out with 1 equivalent of either LiOH or K₂CO₃, excellent yields of the desired product were obtained (Table 2, entries 5 and 6, respectively). However, in the case of the reaction using LiOH a significant amount of leaching from AuPd-Fe₃O₄ was confirmed by SEM images obtained after the reaction (Figure S9). Thus, K₂CO₃ was selected as the optimal base that led to the formation of the desired FDMC in 92% yield (Table 2, entry 6). Owing to the very mild reaction conditions, no degradation of HMF or saponification reaction could be detected, which has often been reported in more harsh reaction conditions in a basic medium.^[28] The presence of molecular O_2 was absolutely necessary as an oxidant for both alcohol oxidation and aldehyde esterification. When the reactions were carried out under argon or air, the conversion of HMF to HMFE (only product) were 13% and 36%, respectively (Table 2, entries 7 and 8). In addition, when 2 mol% AuPd-Fe₃O₄ catalyst was used, the same yield of FDMC was obtained in 10 h (Table 2, entry 9). The highest yield of FDMC (96%) was obtained when oxidation was carried out with 5 mol% AuPd-Fe₃O₄ catalyst (Table 2, entry 11). In addition, when Fe₃O₄ alone was tested as catalyst for the oxidation of HMF, only 3% conversion was observed and the desired FDMC was not obtained (Table 2, entry 12). Based on these results, it was concluded that the optimal reaction

Table 2. Optimization of reaction conditions for the oxidative esterification of HMF. ^[a]										
HO	C Base, T 1 atr	atalyst ∵ime, MeOH, m O ₂ , RT	HO +		р ₊ но + МеО	HMFE HMFE COCOME FDMC				
En try	Catalyst (on Fe ₃ O ₄)	Base	Ti me (h)	Conv . (%)	Yield (%)	Selectivity (HMF:HMFE: DFF:FDMC) [[] e]				
1	1 mol% AuPd	-	24	0	0	100:0:0:0				
2	1 mol% AuPd	Na ₂ CO ₃	24	63	37	37:19:7: 37				
3	1 mol% AuPd	TEA	24	38	0	62:38:0:0				
4	1 mol% AuPd	DBU	24	55	26	45 : 25 : 4 : 26				
5	1 mol% AuPd	LiOH	24	100	90	0:10:0:90				
6	1 mol% AuPd	K_2CO_3	24	100	92	0:8:0:92				
7 ^[c]	1 mol% AuPd	K_2CO_3	24	13	0	87:13:0:0				
8 ^[d]	1 mol% AuPd	K_2CO_3	24	36	0	64 : 36 : 0 : 0				
9	2 mol% AuPd	K_2CO_3	10	100	92	0:8:0:92				
10	2 mol% AuPd	LiOH	10	100	88	0 : 12 : 0 : 88				
11	5 mol% AuPd	K_2CO_3	3	100	96	0:4:0:96				
12	Fe ₃ O ₄ only	K ₂ CO ₃	24	3	0	97:0:3:0				
13	2 mol% Pd	K ₂ CO ₃	24	25	2	75 : 5 : 14 : 2				
14	2 mol% Au	K₂CO₃	24	92	0 (92) ^[b]	8:92:0:0				

Reaction conditions: [a] 0.5 mmol HMF, 1 equiv base, 5 mL MeOH, 1 atm O₂, room temperature, mol% of AuPd-Fe₃O₄ based on Pd, Au:Pd = 1.00:1.18 (molar ratio). [b] HMFE yield. [c] 1 atm Ar. [d] 1 atm air. [e] Selectivity was determined by NMR. TEA : trimethylamine, DBU : 1,8-diazabicyclo[5.4.0]undec-7-ene.

conditions should include K_2CO_3 and 1 atm O_2 for the oxidative esterification. Under this optimized reaction condition with 1 mol% AuPd catalyst (Table 2, entry 6), the catalyst exhibited turnover number (TON) of 92. Compared to the previously reported nanoparticle catalysts^[17a,17b,18,19] used for the synthesis of FDCA or FDMC, the AuPd–Fe₃O₄ catalyst showed an acceptable TON value despite the mild reaction conditions (room temperature and atmospheric pressure) (see Table S7).

To study the role of the bimetallic catalyst and compare to that of the monometallic $Pd-Fe_3O_4$ and $Au-Fe_3O_4$ catalyst, reactions using each kind of NPs were carried out under the optimized

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Figure 2. Kinetic curves of (a) HMFE synthesis with 2 mol% Au–Fe₃O₄, (b) FDMC synthesis with 1 mol% AuPd–Fe₃O₄, (c) FDMC synthesis with 2 mol% AuPd–Fe₃O₄, (d) 2–methylfurancarboxylate synthesis with 2 mol% Au–Fe₃O₄ and 1 mol% AuPd–Fe₃O₄. Reaction conditions: 0.5 mmol HMF or furfural, 1 equiv K₂CO₃, 5 mL MeOH, 1 atm O₂, room temperature, Au:Pd = 1.00:1.18 (molar ratio).



Scheme 2. Oxidative esterification of furfuryl alcohol with Au– and AuPd–Fe $_3O_4$ (Au:Pd = 1.00:1.18, molar ratio).

conditions (Table 2, entries 13 and 14). HMF oxidation conversions using Pd-Fe₃O₄ or Au-Fe₃O₄ catalysts were 25% and 92%, respectively, and represented oxidations catalysed by both Au and Pd catalysts. It should be noted that when Pd-Fe₃O₄ was used, the oxidation of the primary alcohol of HMF producing mostly DFF was preferred to the oxidative esterification (path b, Scheme 1). Interestingly, when $Au-Fe_3O_4$ was employed as the catalyst, only HMFE was obtained as a product with high conversion and high selectivity. As can be seen from the kinetic studies on the reaction using Au-Fe₃O₄ catalyst, there was a gradual increase in the amount of HMFE (Figure 2 (a)). There was no formation of DFF intermediate during the reaction, which indicated selective aldehyde oxidation with the monometallic Au-Fe₃O₄ catalyst (path a). In contrast, bimetallic AuPd-Fe₃O₄ showed high activity and selectivity toward the formation of FDMC, unlike monometallic Au-Fe₃O₄ or Pd-Fe₃O₄. Apparently, both types of oxidation appeared to be effective with the alloyed AuPd metal catalyst, i.e., alcohol oxidation and aldehvde oxidation/esterification. A more detailed kinetic study using 1 mol% AuPd-Fe₃O₄ NPs was conducted under the optimized conditions (Figure 2 (b)). It was found that HMF was consumed within 5 h, while the desired product, FDMC, was formed slowly over 24 h. A major intermediate of this reaction was HMFE. FDMC was formed as HMFE was consumed over time while the concentration of methyl 5-formylfuran-2-carboxylate (FMF) was





negligible. This demonstrated that the aldehyde esterification is faster than the alcohol oxidation using the AuPd catalyst. The fact that DFF was not detected suggested that the reaction employing the AuPd-Fe₃O₄ catalyst preferentially followed path a. Both Au-Fe₃O₄ and AuPd–Fe₃O₄ showed high catalytic activity toward the formation of methyl 2-furancarboxylate from furfural providing 100% and 86% yields, respectively, while the yield from the reaction employing the Pd-Fe₃O₄ catalyst was 25% (Scheme S1). The kinetic profiles in Figure 2 (d) allow a comparison of the activities of Au and AuPd NPs in the oxidative esterification of furfural; the AuPd catalyst exhibited much higher activity than Au NPs. Methyl 2-furancarboxylate was quantitatively formed within 3 h in the reaction employing AuPd-Fe₃O₄ NPs. To compare the activities of Au-Fe₃O₄ and AuPd-Fe₃O₄ as an oxidation catalyst, the synthesis of methyl 2-furancarboxylate from furfuryl alcohol was investigated (Scheme 2). While furfuryl alcohol oxidation did not occur when Au-Fe₃O₄ was used as the catalyst, the reaction proceeded successfully with AuPd-Fe₃O₄ to provide methyl 2furancarboxylate in up to 85%. As in the case of oxidative esterification of HMF, AuPd-Fe₃O₄ catalyst exhibited versatile activity towards both furfuryl alcohol oxidation and furfural oxidative esterification and high yields of the desired products were achieved.

Effect of support material and metal content ratio of bimetallic AuxPdy catalysts on FDMC synthesis

The yields of alcohol oxidation products were dependent on the nature of the supports and preparation methods of nanoparticles and also varied according to the Au and Pd ratio.^[29] We investigated first the activities of AuPd nanoparticles on different supports, which were synthesized by following the same hydrothermal method as for AuPd-Fe₃O₄ NPs.^[27] Thus, AuPd-C, AuPd-CeO₂, and AuPd-TiO₂ were applied to the synthesis of FDMC (Table S1 and S2, Figure S7). When AuPd-C catalyst was used, 97% conversion and 55% yield were observed with HMFE (42%) as a major side product. In the case of AuPd-CeO₂ NPs, the conversion and yield were 74% and 44%, respectively, with similar amounts of HMFE (16%) and DFF (15%) as side products. The yield of FDMC with AuPd–TiO₂ NPs as the catalyst was 34% with 75% conversion and 32% of HMFE. These results imply that the AuPd-Fe₃O₄ NPs exhibit the best activity in HMF oxidation. Next, five different Au_xPd_y catalysts on Fe_3O_4 (x:y = 1.0:0.25, 1.0:0.60, 1.00:1.18, 0.52:1.0 and 0.37:1.0) were prepared to explore the effect of metal composition on the catalytic activity (Table 3 and Figure S8). In the cases of Au₁Pd_{0.25}-Fe₃O₄ NPs and Au₁Pd_{0.6}-Fe₃O₄ NPs, the conversions were 70, and 73% and the desired product was obtained in 30 and 42% yields, respectively (Table 3, entries 1 and 2). When Au_{0.52}Pd₁-Fe₃O₄ NPs and Au_{0.37}-Pd1-Fe3O4 NPs were used, 93 and 73% of the starting material were oxidized, and 72 and 35% yields of the desired product were obtained (Table 3, entries 4 and 5). The best conversion and yield of the desired product were achieved when the nanoparticles of nearly equal amounts of Au and Pd were used as a catalyst (Table 3, entry 3). As shown in Table 3, the activities of the alcohol oxidation and oxidative esterification were the highest as the ratio of Au and Pd metals was almost one. The synergistic effect of AuPd bimetallic surface for the O2 activation compared to Au surface alone has been well documented.^[30] Mullin^[30a] and Li^[30b] groups reported that the propensity of O₂ adsorption is correlated with the coverage of isolated Pd active sites by Au atoms. When isolated Pd sites surrounded by Au are neighboured, O2 activation is promoted. In addition, according to the study by Molina et al.[31] the catalytic activity and oxidation selectivity of Au_xPd_y NPs can be related to the binding affinity of reaction intermediates (i.e. metal-alkoxy, metal-hydride) on the metal surface. In the case of pure Au NPs, intermediates are too weakly bound, which means the catalysts are not active enough to initialize the reactions. On the other hand, pure Pd metals bind so strongly with intermediates that the reaction rates are decreased due to poisoning of the Pd sites. Based on the above results, we assume that the almost equal distribution of Au and Pd metals ensure proper stability of the reaction intermediates, which leads to the highest activity for both alcohol oxidation and oxidative esterification of aldehyde, resulting in the best selectivity for the production of FDMC.

Reusability test

Iron oxide is the useful supporter of nanocatalysts which can easily recyclable using magnetic property.^[32] To investigate the recyclability of AuPd-Fe₃O₄ NPs for oxidative esterification of HMF, recycling experiments were performed using either K₂CO₃ or LiOH as a base since good yields of the desired product were obtained with either of these two bases. During three repetitive reactions with 1 mol% AuPd–Fe₃O₄ NPs, yields of the desired

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Figure 3. Recycling test results. Reaction condition : 0.5 mmol HMF, 1 equiv K_2CO_3 , 5 mL MeOH, 1 atm O_2 , room temperature, Au:Pd = 1.00:1.18 (molar ratio).

product decreased noticeably in both cases using K₂CO₃ and LiOH (Figure 3). Therefore, the reusability test was conducted with 2 mol% AuPd-Fe₃O₄ NPs with a shorter reaction time of 10 h. The product yields were almost constant with the use of K₂CO₃ in comparison to LiOH as can be seen in Figure 3. This was expected from the fact that LiOH as a stronger base led to increased leaching of the metals during the reactions. This was corroborated by SEM images (Figure S9). The stability of AuPd-Fe₃O₄ catalyst was also examined in comparison with Au-Fe₃O₄ in terms of metal leaching and morphological changes after recycling experiments. In the case of monometallic Au-Fe₃O₄ NPs, the production of HMFE tended to decrease slightly after recycling 3 times under optimized conditions, but yields of >80% were maintained (Figure S10). The morphology and remaining metal content of spent Au-Fe₃O₄ catalysts were investigated using HR-TEM and ICP-AES (Figure S10 and Table S3). Leaching of dispersed Au NPs on Fe₃O₄ support was confirmed after the third reaction. The amount of Au remaining after the reuse reaction was 12.32%, which is 3.98% lower than that of fresh Au-Fe₃O₄ catalyst (16.3%). In contrast, the metal content change of AuPd-Fe₃O₄ after recycling was relatively lower than that of Au-Fe₃O₄ under the same optimized reaction conditions (Figure S11); Au and Pd contents decreased by only 0.26% and 0.04%, respectively (Table S3). Interestingly, agglomeration of nanoparticles^[33] was not observed in either SEM or HR-TEM images of AuPd-Fe₃O₄ NPs. These results confirmed that AuPd-Fe₃O₄ had better catalytic stability than Au-Fe₃O₄ in the HMF oxidation reactions. Mild reaction conditions such as room temperature and low oxygen pressure appear to be critical for the stability of the catalyst.^[33.34] AuPd-Fe₃O₄ NPs can allow for reactions under extremely mild conditions because of the improved catalytic activity rendered by synergistic electron transfer of Au and Pd. To the best of our knowledge, AuPd-Fe₃O₄ is the first catalyst to be used for the synthesis of FDMC through

oxidative esterification of HMF under atmospheric O_2 at room temperature.

Conclusions

In this study, alloy AuPd-Fe₃O₄ nanoparticles were used for the first time as catalyst for one-pot oxidative esterification of HMF to FDMC under very mild conditions. Using this catalytic system, FDMC was synthesized with high activity and selectivity under atmospheric O₂ and room temperature. The catalytic activity strongly depended on the ratio of Au and Pd in the HMF oxidation reactions. In particular, 1.00:1.18 of Au:Pd showed the highest catalytic performance. Interestingly, the reactions employing Au-Fe₃O₄ NPs led to the selective synthesis of HMFE, which is one of the important synthetic intermediates in the pharmaceutical industry. Au-Fe₃O₄ and AuPd-Fe₃O₄ NPs demonstrated extraordinary selectivity, leading to two different products from HMF. The stability of the AuPd–Fe₃O₄ catalysts was evaluated by recycling tests. Both Au- and AuPd-Fe₃O₄ could be recycled efficiently using the magnetic properties of the iron oxide support. Also, the bimetallic alloy AuPd-Fe₃O₄ system exhibited more pronounced stability than mono-metallic Au-Fe₃O₄. Furthermore, the alloyed nanoparticles were structurally more stable than the monometallic nanoparticles, and consequently more resistant to leaching. Considering these features, this alloyed bimetallic catalytic system may be applicable to other biomass transformation reactions and we are currently exploring the possibilities.

Experimental Section

General: All commercially available chemicals were used as received without further purification. Gold chloride trihydrate (\geq 49% Au basis), palladium chloride (99% purity) and polyvinylpyrrolidone (PVP) were purchased from Sigma-Aldrich. Iron oxide nanoparticles (Fe₃O₄ Nps) were purchased from DK Nano. 5-Hydroxymethylfurfural, furfural, and furfuryl alcohol were purchased from Alfa-Aesar.

Synthesis of AuPd-Fe₃O₄ NPs: A mixture of palladium(II) chloride (PdCl₂, 0.044 g) and polyvinylpyrrolidone (PVP) (Mw ~10,000, 0.500 g) in 10 mL ethylene glycol was placed in a 25 mL round-bottom flask and heated at 100 °C for 1 h. Additionally, a mixture of gold(III) chloride trihydrate (HAuCl₄·3H₂O, 0.098 g) and PVP (Mw ~10,000) (0.250 g) in 10 mL water was stirred at 60 °C for 30 min. Commercially available Fe₃O₄ (0.250 g) was mixed with 75 mL water. The preheated palladium precursor solution was added dropwise into the Fe₃O₄ dispersion in water. After 5 min, the preheated gold solution was added dropwise, followed by the addition of sodium borohydride (0.025 g) in 10 mL water dropwise into the mixture containing Au, Pd, and Fe₃O₄. This mixture was stirred at 60 °C for 5 h. It was subsequently cooled to room temperature and collected with an external magnet. After removal of the solution, remaining AuPd NPs were dispersed in 50mL of ethanol and sonicated for 3 minutes, and the NPs were collected using and external magnet. Then the dark colored ethanol solution resulting from unloaded AuPd nanocolloids was removed. This process for completely washing unloaded AuPd colloids was repeated until decanted ethanol did not show any color. After repeated washing cycles (usually requiring ~10 cycles), the AuPd-Fe₃O₄ NPs were dried on a rotary evaporator to yield 480mg of NPs, which exhibit 1.00:1.18 molar ratio of Au:Pd.

Synthesis of Au–Fe₃O₄ NPs: Gold(III) chloride trihydrate (HAuCl₄·3H₂O, 0.098 g) and PVP (Mw ~10,000) (0.250 g) were mixed in 10 mL water and the mixture was stirred at 60 °C for 30 min. Fe₃O₄ (0.250 g) in 75 mL water was prepared and then the preheated gold precursor solution was added dropwise into the Fe₃O₄ solution, followed by the addition of sodium borohydride (0.025 g) in 10 mL water dropwise into the mixture containing Au and Fe₃O₄. This mixture was stirred at 60 °C for 5 h. The washing process of Au–Fe₃O₄ is the same as synthesis of AuPd–Fe₃O₄ NPs.

Synthesis of Pd–Fe₃O₄ NPs: A mixture of of palladium(II) chloride (PdCl₂, 0.044 g) and polyvinylpyrrolidone (PVP) (Mw ~10,000, 0.500 g) in 10 mL ethylene glycol was heated at 100 °C for 1 h. Fe₃O₄ (0.250 g) in 75 mL ethylene glycol was prepared and then the preheated palladium precursor solution was added dropwise into the Fe₃O₄ solution. This mixture was stirred at 100 °C for 24 h. The washing process of Pd–Fe₃O₄ is the same as synthesis of AuPd–Fe₃O₄ NPs.

Synthesis of Au_xPd_y-Fe₃O₄ NPs: To synthesize Au_xPd_y-Fe₃O₄, the same synthetic method as for AuPd-Fe₃O₄ NPs was employed, albeit using different quantities of metals and sodium borohydride. To prepare Au1Pd0.3-Fe3O4 NPs, 0.011 g of palldium(II) chloride together with 0.125 g of PVP (Mw ~10,000), 0.098 g of gold(III) chloride trihydrate together with 0.250 g of PVP (Mw ~10,000), and 0.025 g of sodium borohydride were reated. For the synthesis of Au1Pd0.5-Fe3O4 NPs, 0.022 g of palldium(II) chloride together with 0.250 g of PVP (Mw ~10,000), 0.098 g of gold(III) chloride trihydrate together with 0.250 g of PVP (Mw ~10,000), and 0.025 g of sodium borohydride were used. In the case of $Au_0 {}_5Pd_1 - Fe_3O_4$ NPs. 0.044 g of palldium(II) chloride together with 0.500 g of PVP (Mw ~10,000), 0.049 g of gold(III) chloride trihydrate with 0.125 g of PVP (Mw ~10,000) and 0.013 g of sodium borohydride were used. Lastly, for the preparation of Au_{0.4}Pd₁-Fe₃O₄ NPs, 0.044 g of palladium(II) chloride together with 0.500 g of PVP (Mw ~10,000), 0.033 g of gold(III) chloride trihydrate with 0.083 g of PVP (Mw ~10,000), and 0.008 g of sodium borohydride were reacted

Catalyst characterization: Scanning electron microscopy (SEM) images were obtained on a JSM-7600F at a voltage of 15 kV. Transmission electron microscopy (TEM) was performed using a JEM-2100 microscope at an accelerating voltage of 200 kV. Scanning transmission electron microscopy (STEM) images were obtained on a JEM-ARM200F (Cold field emission type, JEOL). X-ray photoelectron spectroscopy (XPS) was performed using SIGMA PROBE (ThermoVG, U.K.).

HMF oxidative esterification: The oxidative esterification of HMF was performed in a glass vial. A mixture of the catalyst, HMF (63 mg, 0.50 mmol), and a base (0.50 mmol) in 5 mL of methanol (>99%) were placed in a sealed 20.0 m glass vial, which was subsequently purged with O_2 . The mixture was stirred at room temperature under O_2 (balloon) for 24 h. After the reaction, the catalyst was separated using an external magnet, and washed with methanol. The organic layer was analyzed by gas chromatography/mass spectrometry (Hewlett Packard 5890 GC-Agilent 5793 Mass Selective Detector) with mesitylene as an internal standard. The catalyst collected after the reaction was reused for further reactions.

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Layout 2:

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We reported the first direct synthesis of furan-2,5-dimethylcarboxylate (FDMC) from 5-hydroxymethylfurfural (HMF) using bimetallic AuPd alloy nanoparticle catalyst under extremely mild reaction conditions.

Ahra Cho, Sangmoon Byun, Jin Hee Cho and B. Moon Kim *

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AuPd–Fe₃O₄ nanoparticle-catalyzed synthesis of furan-2,5dimethylcarboxylate from biomassderived 5-hydroxymethylfurfural under mild conditions