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Pd-modified Au on Carbon as an Effective and Durable Catalyst for the Direct Oxidation of HMF to 2,5-Furandicarboxylic Acid

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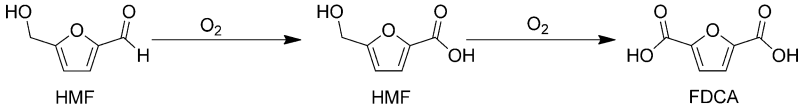
We show that the modification of a Au/C catalyst with Pt or Pd produces stable and recyclable catalysts for the selective oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-furandicarboxylic acid (FDCA). This finding is a significant advance over current conversion technology because of the technological importance of FDCA. Indeed, FDCA has been identified as one of twelve potential building blocks for the production of value-added chemicals derived from biosources.[1] FDCA is a potential replacement source of terephthalic acid; the monomer is currently used for the production of polyethylene terephthalate (PET) and derived from hydrocarbon sources.[2]



Scheme 1. Reaction pathway for aqueous HMF oxidation.

FDCA is commonly synthesized through oxidation of HMF, which is produced through cellulose depolymerisation and subsequential dehydration.[3] The synthesis of FDCA from HMF has been reported using stoichiometric amounts of oxidants, such as $KMnO_4$, and homogeneous metal salts (Co/Mn).[4,5] A green alternative to $KMnO_4$ involves the use of molecular oxygen, in the presence of a heterogeneous catalyst, with water as the solvent. Different systems using the classic Pt-, Pd- or Ru-based heterogeneous catalysts have been reported for the selective oxidation of HMF to FDCA,[6,7] but these systems are generally lacking stability or selectivity. In addition to catalyst type it has been demonstrated by Verdeguer et al. that basicity has a major influence on catalytic activity (and selectivity) of Pt/Pb-supported catalysts.[8] Furthermore, these authors showed that the production of FDCA occurred in two steps. In the first step, 5-hydroxymethyl-2-furancarboxylic acid (HFCA) is formed by oxidation of the aldehyde group. Subsequent oxidation of the hydroxyl group forms FDCA (Scheme 1).

Recently, a supported Au catalyst has been found to be active in the oxidation of HMF, and many studies have been performed to increase the yield to FDCA by optimising the reaction conditions (especially temperature), HMF/metal or HMF/base ratios and support selection, that is, CeO_2, TiO_2 and AC.[9–11] Studies by Davis et al. showed that Au catalysts were more active than Pt in the first step of the oxidation reaction (HMF to HFCA),[11] but they exhibited a lower activity for the successive conversion of HFCA to FDCA. Interestingly, the use of basic supports such as hydrotalcite has been reported to be beneficial in enhancing the formation of FDCA even in the absence of a free base.[12] It should be noted that the role of a basic environment can be beneficial from different points of view as it reduces degradation of HMF (at 100 °C in water HMF degrades by 30% in 2 h), but also enhances the activity of the Au catalysts.

However, although the activity of the Au catalyst is good, they deactivate rapidly.[9] This deactivation is attributed to the irreversible absorption of intermediates.[11,13] Recently, Pasini et al. showed that alloying Cu with Au/TiO_2 resulted in a catalyst with significantly higher activity and drastically enhanced stability.[14] However, in these stability studies the final product was mainly HFCA instead of the desired FDCA.

The catalysts presented here overcome these limitations, making them suitable for industrial-scale applications. Indeed, we show that Au nanoparticles supported on activated carbon (AC) under realistic reaction conditions are able to catalyze the oxidation of HMF to FDCA. Similarly prepared Pd and Pt catalysts showed high selectivity to the intermediate HFCA and not FDCA. Moreover, by modifying Au/AC with Pd or Pt we obtained catalysts that catalyzed both steps of the reaction (HMF to HFCA and HFCA to FDCA), showing an excellent stability during the recycling test.

Monometallic polyvinyl alcohol (PVA)-protected Au, Pd, and Pt nanoparticles were prepared on AC supports by impregnation following a previously reported procedure.[15] All the catalysts showed a similar mean particle diameter of 2.9–3.9 nm as estimated from TEM studies (Figures S1 and S2 in the Supporting Information). The activity of these catalysts was evaluated by oxidizing 0.15 M of HMF in water with 2 equivalents of NaOH, at 60 °C and 3 bar O_2 (HMF/metal = 200 mol/mol). The

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conditions were the same as those reported in the literature to allow for an easier comparison.[11,14] Profiles showing the percent fraction of HMF, HFCA and FDCA as a function of time are shown in Figure 1. From these results it is clear that the Au/AC catalyst showed a higher selectivity to FDCA, converting nearly all the intermediate HFCA at 80% completion. In contrast, the Pd and Pt catalysts only converedt 9 and 20% of the HMF to FDCA, respectively. The majority of the products are trapped in the form of the HFCA intermediate, indicating that the Pd and Pt materials was deactivated.

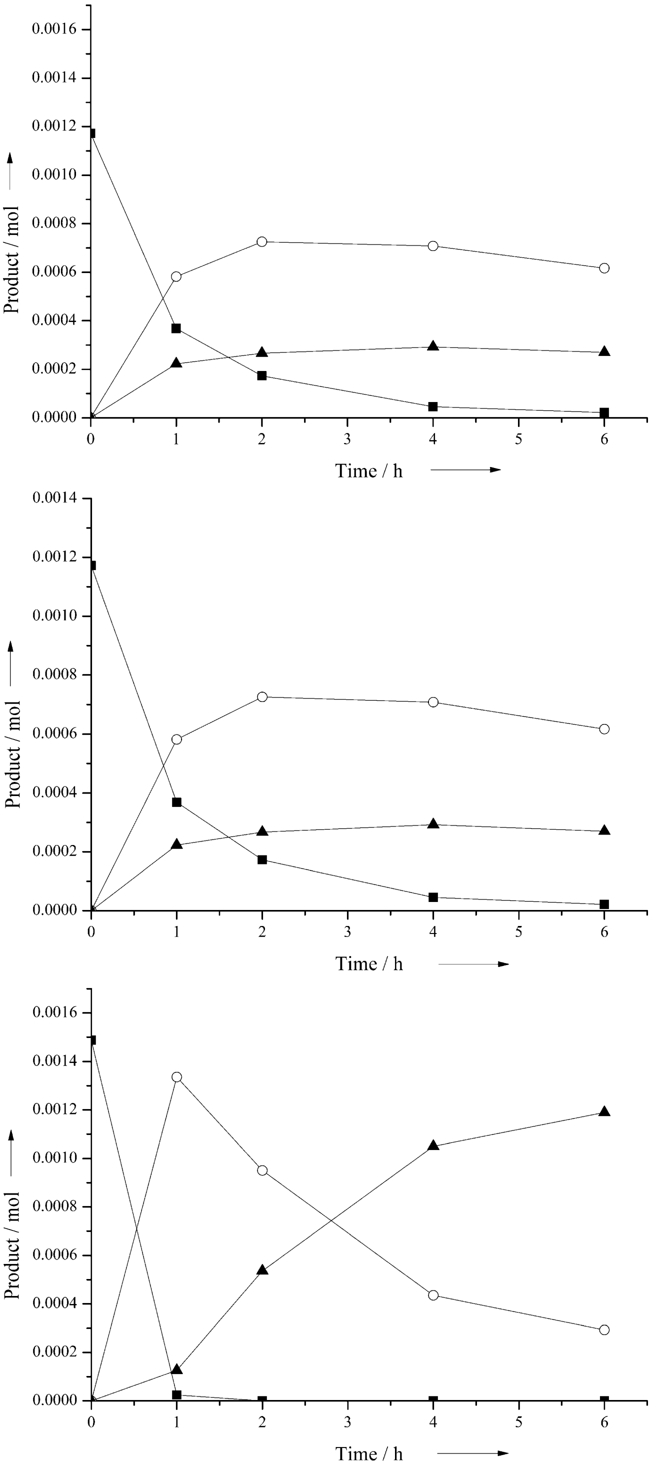

Figure 1. Product distribution (■ HMF, ○ HFCA, ▲ FDCA), for a) Pt/AC, b) Pd/AC and c) Au/AC.

To quantify the effect of support on the reaction, different carbon-based supports were investigated: AC, graphite (Graph), carbon nanofibers (CNFs) and carbon nanotubes (CNTs). The supports were impregnated as before by using a Au_{PVA} solution. There are numerous differences between the various forms of carbon. Among the most important variables for catalysis are the graphitic content and the surface functionality of the carbon. Comparing the D/G band ratios using Raman spectroscopy confirmed the predicted graphitization trends based on graphite form, that is, Graph > CNT > AC > CNF (Table S3, Supporting Information).[16]

Analysis of X-ray photoelectron spectroscopy (XPS) data revealed significant differences in oxygen concentrations on the carbon surfaces. AC (8 at%), CNF ($\approx$7 at%) > CNT ($\approx$2 at%) $\gg$ Graph (0 at%).[17,18] The AC support did contain approximately 1—2 at% K on the surface of the carbon, which is a by-product of the carbon source. Analysis of the Au particles sizes, through TEM studies (Figure 2), revealed that the average particle sizes increased with decreasing oxygen content and disorder: Au/AC (2.9 nm) > Au/CNFs (3.8 nm) > Au/CNTs (4.6 nm) > Au/graph (5.4 nm) (Figure S1, Supporting Information). This is not surprising as higher disorder and oxygen groups provide nucleation sites to trap and stabilize the supported Au clusters. However, despite the variation in size, the absolute magnitude of variation was quite small indicating that in all cases excellent particle distributions were obtained. It should be noted that in the case of the CNTs some empty tubes and Au aggregates were observed.

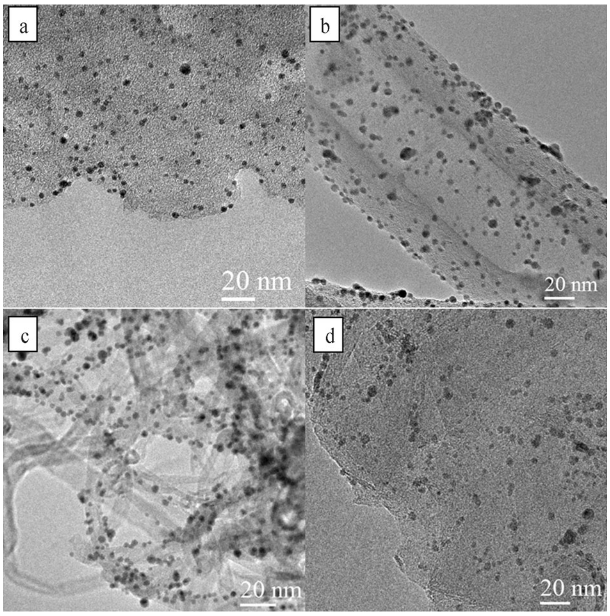

Figure 2. TEM images of a) Au/AC, b) Au/CNFs, c) Au/CNTs and d) Au/Graph.

Table 1. HMF oxidation using Au based catalysts.

Catalyst[a]	Time of reaction [h]	Conversion [%]	Selectivity [%] HFCA	FDCA
monometallic				
Au/AC	2	> 99	64	36
	6	> 99	20	80
Pd/AC	2	85	92	8
	6	> 99	91	9
Pt/AC	2	88	80	20
	6	> 99	80	20
Au/CNFs	2	> 99	98	2
	6	> 99	94	6
Au/K-CNFs	2	> 99	95	5
	6	> 99	98	2
Au/CNTs	2	> 99	81	19
	6	> 99	61	39
Au/Graph	2	> 99	87	13
	6	> 99	74	26
bimetallic				
Au_6-Pd_4/AC	2	> 99	5	95
	4	> 99	–	> 99
Au_8-Pd_2/AC	2	> 99	1	99
	4	> 99	–	> 99
Au_6-Pt_4/AC	2	> 99	38	62
	4	> 99	6	94
Au_8-Pt_2/AC	2	> 99	24	76
	4	> 99	3	97
base-free experiments				
Au/AC	6	5	–	–
Au_8-Pd_2/AC	6	3	–	–

[a] Reaction conditions: 0.15 M, p_{O_2} = 3 bar, stirring at 1250 rpm, 60 °C, HMF/metal = 200 mol/mol, 2 eq NaOH.

Evaluation of the catalysts supported on different carbons revealed significant variation in activity compared to the Au/AC samples, Table 1. The Au particles on CNTs, Graph, and CNFs are as active as Au on AC in the first step of the oxidation to produce HFCA.

However, the catalysts are extremely poorly active for the subsequent oxidation of HFCA to FDCA. The selectivity to FDCA after 6 h was 80 % for Au/AC, 6 % for Au/CNFs, 39 % for Au/CNTs and 26 % for Au/Graph, respectively (Table 1). Clearly, Au/AC was more active in the oxidation of the hydroxyl group of HFCA, producing more FDCA compared to the other catalysts. This result indicates the importance of the support in mediating the overall activity and selectivity towards Au particle size. However, we believe the difference in particle size plays a minor role as Au/CNF, which has a mean particle size very similar to Au/AC (3.8 vs. 2.9 nm), completely differs in activity for the oxidation of HFCA. Therefore, support chemistry is likely the dominant factor in mediating activity. We note that AC did have a small concentration of residual K on the surface, which may influence the basicity of the catalyst in a manner similar to the work reported on hydrotalcite.[12] For determining the possible active role of K content, we doped the CNF support with K following the procedure reported elsewhere.[19] Therefore, 2 at % K was added to CNF and K-CNF was used as the support for Au_{PVA} nanoparticles. Alternatively, we also impregnated Au/CNF with a solution of KBr (1 wt %). The catalytic tests, however, revealed in both cases similar activity and selectivity of Au/CNF and Au/K-CNF (Table 1), thus excluding a positive effect of K.

Further efforts focused on the recyclability and stability of the Au/AC catalyst. The catalyst was allowed to react for 6 h each run and was then filtered and reused without further treatment in the following run (Figure 3). The catalyst showed good product selectivity, but it underwent deactivation, losing 20 % of conversion efficiency after the fifth run. No Au leaching from the catalyst was detected, as reported for other Au catalysts; thus, this deactivation was possibly ascribed to irreversible adsorption of intermediates or Au particle agglomeration.[9,13]

For the liquid-phase alcohol oxidation, we recently found that it is possible to increase the activity and the stability of the Au catalysts by alloying Au with Pd or Pt.[20,21] Moreover, we found that varying the Au/precious metal ratio, the catalyst activities varied depending on the nature of the alcohol.[22–24] We hypothesized that these findings could also be applied to HMF oxidation. Au bimetallic catalysts, with different Au/Pd (or Pt) molar ratios (6:4 and 8:2) were prepared following a previously reported procedure, which ensured formation of alloyed bimetallic nanoparticles.[23] Characterization of these catalysts revealed similar metallic-particle dimensions (3.1–3.5 nm, Figures S1 and S2 in the Supporting Information).

Comparing the activity of these catalysts with the pure Au materials, we found that all the bimetallic catalysts showed an

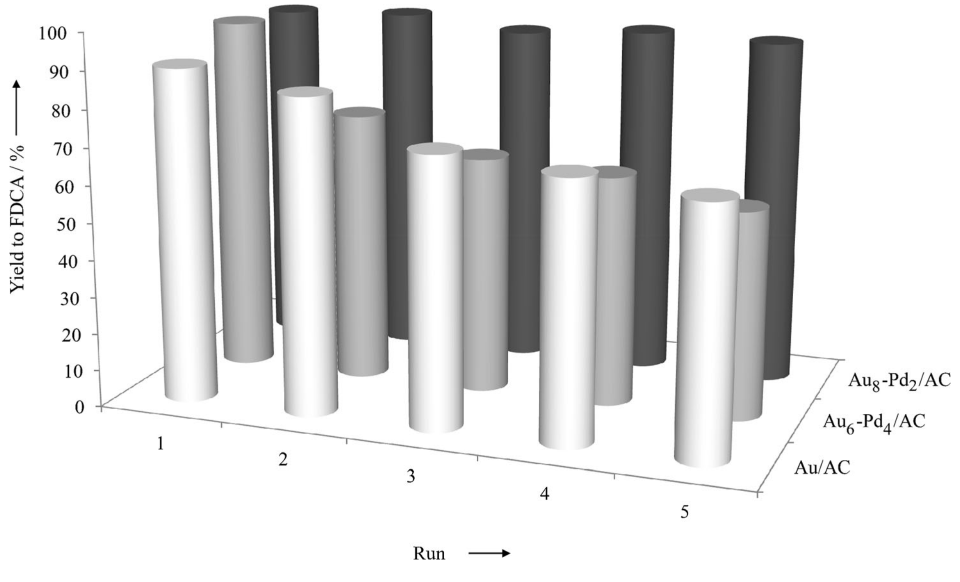

Figure 3. Stability tests for Au-based catalysts.

enhanced activity with respect to the corresponding monometallic counterpart (Table 1). AuPd catalysts appeared more active than AuPt ones, reaching almost full conversion to FDCA after only 2 h, whereas AuPt needed 4 h for reaching almost the same results. In both cases it was observed that the activity increased by increasing the Au content, Au_6M_4/AC being less active than Au_8M_2/AC, which is in agreement with the trend observed in glycerol or alcohols oxidations.[22–24] In addition, these catalysts were fully characterized elsewhere; they all presented randomly alloyed phases without any peculiar differences from a structural point of view.[23] Therefore, a possible explanation for the different activity of these two catalysts is likely attributable to different electronic properties derived from different isolation of active sites.

As our main concern was the durability of the catalysts, we carried out stability tests similar to those performed with Au/AC using the AuPd catalysts. In Figure 3, the conversions after 6 h reactions for Au/AC and 2 h reactions for Au_6Pd_4/AC and Au_8Pd_2/AC are compared. Au_6Pd_4/AC followed the same deactivation profile as observed for the Au/AC samples. Furthermore, as in the case of Au/AC, inductively coupled plasma (ICP) measurements did not reveal any leaching of Au or Pd. However, a different behaviour was observed for the Au_8Pd_2/AC catalyst. This catalyst was able to completely convert HMF at the same rate over all five runs, maintaining 99% selectivity to FDCA during the whole experiment. Thus, alloying Au with Pd in a 8:2 atomic ratio produced an active and stable catalyst for FDCA production from HMF, eliminating the deactivating phenomena shown by Au/AC catalysts.

We also tested Au_8Pd_2/AC and Au_6Pd_4/AC in the absence of a base. They were active also under these conditions, but the yield of FDCA and also of HFCA was very low ($<10\%$). These results did not surprise us as it was reported elsewhere that, by avoiding a basic environment, HMF rapidly degrades to levulinic and formic acids and FDCA to glycolic and formic acid.[14] Moreover, under such conditions also the stability of the catalysts was reduced.

In summary, mono-metallic (Au, Pd, Pt) and bi-metallic catalysts have been prepared by solution immobilization using PVA as a protective agent and carbon-based supports. Au/AC can effectively oxidize HMF to FDCA, whereas Pd and Pt rapidly deactivate during the oxidation of the intermediate HFCA to FDCA. The key factor influencing the activity of the Au-based catalyst seems to be the support. Indeed, when comparing Au supported on various carbon supports, only Au on AC effectively oxidized HMF to FDCA. Au/AC was not stable in recycling experiments. However, its stability (and activity) was increased extraordinarily by alloying Au with Pd. In particular, we showed that Au_8Pd_2/AC, where Au and Pd were present at a 8:2 ratio, presented a high activity and most importantly a high stability for the production of FDCA from HMF. Therefore, this latter catalyst could be proposed as a good candidate for the large-scale production of FDCA from HMF.

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