Cite this: Green Chem., 2011, 13, 824

www.rsc.org/greenchem

## COMMUNICATION

## Hydrotalcite-supported gold-nanoparticle-catalyzed highly efficient base-free aqueous oxidation of 5-hydroxymethylfurfural into 2,5-furandicarboxylic acid under atmospheric oxygen pressure†

Navneet Kumar Gupta,<sup>a</sup> Shun Nishimura,<sup>a</sup> Atsushi Takagaki<sup>b</sup> and Kohki Ebitani<sup>\*a</sup>

Received 12th December 2010, Accepted 24th January 2011 DOI: 10.1039/c0gc00911c

Green synthesis of 2,5-furandicarboxylic acid, one of the most important chemical building blocks from biomass, *via* oxidation of 5-hydroxymethylfurfural has been demonstrated using hydrotalcite-supported gold nanoparticle catalyst in water at 368 K under atmospheric oxygen pressure without addition of homogeneous base.

Renewable biomass resources have considerable potential to serve as a sustainable supply of fuels and chemicals.<sup>1,2</sup> One of the most important biorefinery processes is the efficient chemical transformation of the most abundant cellulosic biomass into chemicals (Scheme 1).<sup>3</sup> Nowadays, 5-hydroxymethylfurfural (HMF), a versatile key intermediate, has been successfully synthesized from sugars including fructose, glucose and cellulose using efficient homogeneous biphasic system,<sup>4</sup> metal chloridecontaining ionic liquids<sup>5</sup> and heterogeneous acid–base catalysts.<sup>6</sup>



Scheme 1 2,5-Furandicarboxylic acid (FDCA) synthesis *via* oxidation of 5-hydroxymethylfurfural (HMF).

2,5-Furandicarboxylic acid (FDCA) which is obtained from HMF via oxidation, is a promising platform of biomass

"School of Materials Science, Japan Advanced Institute of Science and Technology (JAIST), 1-1 Asahidai, Nomi, 923-1292, Japan. E-mail: ebitani@jaist.ac.jp; Fax: +81-761-51-1625; Tel: +81-761-51-1610 derivatives<sup>7</sup> because it has a large potential as a replacement for terephthalic acid, a widely used component in various polyesters, and intermediates for other polymers, fine chemicals, pharmaceuticals and agrochemicals.<sup>1,3</sup> Therefore FDCA synthesis is considered to be a representative biorefinery process as alternatives for chemical production from petroleum.

HMF oxidation into FDCA was examined using stoichiometric oxidant like KMnO4<sup>8</sup> and homogeneous metal salts (Co/Mn/Br) by autooxidation under high pressure (70 bar air),<sup>9</sup> which is currently used for terephthalic acid production. Heterogeneous catalysts also afforded FDCA via HMF oxidation with molecular oxygen. Supported platinum catalysts were first demonstrated with the aid of homogeneous base, resulting in near quantitative FDCA yield.<sup>10</sup> Direct synthesis of FDCA from fructose has been also attempted using a solid acid and PtBi/C in water/MIBK, affording 25% FDCA yield with 50% selectivity.11 Although high conversion with excellent FDCA selectivity (99%) was obtained from fructose in the presence of Co(acac)-SiO<sub>2</sub> bifunctional catalyst, reaction was performed under harsh conditions (433 K, 20 bar).<sup>12</sup> Recently, two noticeable examples were reported using supported gold catalysts for aqueous HMF oxidation.<sup>13,14</sup> Gorbanev et al. demonstrated that Au/TiO<sub>2</sub> could oxidize HMF into FDCA in 71% yield at near room temperature.<sup>13</sup> Casanova et al. showed Au/CeO<sub>2</sub> was more active and selective.14 However, these catalysts require addition of homogeneous base (1-20 equiv. NaOH) and high oxygen pressure (10-20 bar). Alternatively, Taarning et al. reported production of the diester (2,5-dimethylfuroate) from HMF through oxidative esterification using Au/TiO<sub>2</sub> catalyst in sodium methoxide-containing methanol solution under oxygen pressure.15 Casanova et al. demonstrated base-free oxidative esterification of HMF into the diester using Au/CeO<sub>2</sub> catalyst in methanol under 10 bar oxygen in an autoclave reactor.<sup>16</sup>

Herein, we report a much more environmentally benign and safe process for FDCA synthesis using hydrotalcite-supported gold nanoparticle catalyst (Au/HT). Au/HT catalyst was found to exhibit remarkable activity for FDCA synthesis *via* HMF oxidation in water at 368 K under an ambient oxygen pressure without addition of homogeneous base. Regarding product purification, the diester is easily purified compared to FDCA (diacid) as mentioned by Taaring *et al.*<sup>15</sup> However, the oxidative

<sup>&</sup>lt;sup>b</sup>Department of Chemical System Engineering, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, 113-8656, Japan

<sup>†</sup> Electronic supplementary information (ESI) available: Experimental procedure, XRD, XANES, TEM, color indicator test, and a proposed mechanism for HMF oxidation. See DOI: 10.1039/c0gc00911c

Entry	Catalyst	HMF/metal (mol/mol) <sup>*</sup>	HMF conv. (%)	FDCA selec. (%)	Yield (%)		
					HMFCA	FFCA	FDCA
1	Au/HT	40	>99	>99	0	0	>99
$2^{c}$	Au/HT	40	>99	81	11	1	81
3	$Au/HT^{d}$	150 (13)	>99	83	12	3	83
4	$Au/HT^{d}$	200 (13)	>99	72	22	4	72
5	Au/HT <sup>e</sup>	40	73	1	64	7	1
6	Au/MgO	40	>99	21	65	13	21
7	$Au/Al_2O_3$	40	35	9	22	5	3
8	Au/C	40	28	4	6	1	1
9	Au/SiO <sub>2</sub>	40	0	0	0	0	0
10 <sup>g</sup>	HT	0	0	0	0	0	0
11	Blank	0	0	0	0	0	0

Table 1 HMF oxidation in water using supported gold catalysts in the presence of oxygen without addition of homogeneous base<sup>4</sup>

<sup>*a*</sup> Reaction conditions: HMF (1 mmol), H<sub>2</sub>O (6 ml), HMF/metal = 40 (mol/mol), under O<sub>2</sub> flow (50 ml min<sup>-1</sup>), 368 K, 7 h. 1.92 wt% Au/HT. 2 wt% Au was used for different supports. <sup>*b*</sup> Values in the parentheses are reaction time (h). <sup>*c*</sup> Air atmosphere. <sup>*d*</sup> 1.03 wt% Au. <sup>*e*</sup> Catalyst not reduced. <sup>*f*</sup> Activated carbon. <sup>*s*</sup> 0.25 g of HT was used.

esterification needs higher temperature than the boiling point of methanol, such as 403 K, resulting in a requirement for a pressure-resistant reactor.<sup>15,16</sup> In contrast, FDCA formation in water using Au/HT could be operated even at 368 K using a conventional glass reactor through atmospheric oxygen flow.

HT, consisting of layered clays with HCO<sub>3</sub><sup>-</sup> and OH<sup>-</sup> groups on the surface, is known to exhibit high activity for basecatalyzed reactions such as aldol condensation, Knoevenagel condensation and transesterification.<sup>17</sup> In addition, metals supported on HTs functioned as excellent catalysts for alcohol oxidation owing to a combination of creation of active sites of metal species and basicity of the support.<sup>18</sup> Recently Kaneda *et al.* reported Au/HT acts as an efficient catalyst for oxidation of various monoalcohols and diols to corresponding carbonyl compound and lactones in the presence of molecular oxygen as well as deoxygenation of epoxides into alkenes.<sup>19</sup>

Au/HT catalyst was prepared by deposition-precipitation (DP) methods<sup>20</sup> using NH<sub>3</sub> aqueous solution followed by calcination at 473 K (see ESI, experimental<sup>†</sup>). The X-ray diffraction measurement confirmed that the crystal structure of Au/HT is identical to that of parent HT (Fig. S1 in ESI<sup>†</sup>). The amount of loaded gold was determined to be 1.92 wt% analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES). Au L<sub>III</sub>-edge X-ray absorption near-edge structure (XANES) study revealed that Au/HT catalyst has completely reduced Au metal on HT (Fig. S2<sup>†</sup>). Fig. 1 shows a TEM image and particle size distribution of Au/HT catalyst, indicating that Au nanoparticles of 3.2 nm in average size ( $\sigma = 1.2$ ) are highly dispersed on HT.

HMF oxidations were carried out in a Schlenk glass tube attached with a reflux condenser under oxygen flow. In each reaction the reactor was charged with 1 mmol of HMF in 6 ml of water. Subsequently, an adequate amount of supported metal catalyst was added and oxygen was introduced at a flow rate of 50 ml min<sup>-1</sup> at 368 K with stirring under atmospheric pressure. After the reaction, resultant solution was diluted 15–30 times with water and the solid catalyst was filtered off before the HPLC measurement (see ESI, experimental<sup>+</sup>).<sup>21,22</sup>

Table 1 lists the results for HMF oxidation in water using supported gold catalysts without addition of homogeneous



**Fig. 1** (a) TEM image of Au/HT (Au: 1.92 wt%). (b) Au particle size distribution.

base. Au/HT catalyst afforded FDCA with >99% selectivity at total conversion of HMF (entry 1). Au/HT could catalyze the reaction at high HMF/metal ratios, 150 and 200 (entries 3 and 4), reaching high turnover numbers of at least 138 (entry 4), which was simply calculated by moles of Au. It should be noted that high selectivity of FDCA (81%) was also achieved under air atmosphere with total HMF conversion at 368 K (entry 2). In contrast, unreduced Au/HT (without calcination) showed negligible FDCA yield (1%) (entry 5). The activity of Au/HT was much higher than those of Au/Al<sub>2</sub>O<sub>3</sub>, Au/C and Au/SiO<sub>2</sub> (entries 7-9). HT itself could not convert HMF (entry 10). The neutral supports of Al<sub>2</sub>O<sub>3</sub> and C rarely showed the activity, and acidic SiO2 was inactive.20 Au/HT also exhibited higher activity than Au/MgO (entries 1 and 6) although MgO is more basic as determined by color indicator test (Table S1).23 This indicates that not only solid basicity of support but also formation of metal active sites played important roles for the reaction. A TEM measurement of Au/MgO (Fig. S3<sup>†</sup>) showed that Au particles with large size (>10 nm) were aggregated on MgO, which was responsible for low catalytic activity.

Fig. 2 shows the time course of product formation for HMF oxidation over Au/HT. By monitoring the reaction progress with time, we observed the formation of 5-hydroxymethyl-2-furancarboxylic acid (HMFCA) and 5formyl-2-furancarboxylic acid (FFCA) intermediates at the



**Fig. 2** Time course of product formation for HMF oxidation over Au/HT catalyst in water using atmospheric pressure of oxygen at 368 K. *Reaction conditions*: HMF (1 mmol),  $H_2O$  (6 ml), HMF/Au = 40 (mol/mol), under  $O_2$  flow (50 ml min<sup>-1</sup>), 368 K. HMF conversion (closed circle), HMFCA yield (open square), FFCA yield (open triangle) and FDCA yield (closed diamond).

initial stage of the reaction, and other oxidation products such as the corresponding dialdehyde (furan-2,5-diformylfuran) were absent. Both intermediates gradually converted into the final product FDCA (Scheme 1). This tendency is in good agreement with previous study using Au/TiO<sub>2</sub> and Au/CeO<sub>2</sub> under different reaction conditions.<sup>13,14</sup>

For elucidation of reaction mechanism, a radical scavenger (2,6-di-tert-butyl-p-cresol) was added to the reaction medium, which hardly influenced the oxidation of HMF (FDCA yield 78%). This result indicates that oxidation of HMF did not proceed by the free radical mechanism. As shown in Fig. 2, oxidation of aldehyde groups of HMF to form corresponding monocarboxylic acid (HMFCA) was easily occurred. The initial oxidation smoothly proceeded even at room temperature (HMFCA yield 87%; HMF conversion >99%) (Table 2). This first step oxidation was very fast via the formation of the intermediate hemiacetal<sup>14</sup> owing to the basicity of HT. For the synthesis of the dicarboxylic acid (FDCA), the rate-determining step is considered to be oxidation of hydroxyl group, that is transformation of HMFCA to FFCA.13,14 HMFCA is converted to FFCA by the formation of metal alcoholate species via metal-hydride shift with the aid of basicity of HT.<sup>19,24</sup> FFCA

Table 2Effect of reaction temperature on product distribution ofHMF oxidation in water using  $Au/HT^a$ 

				Yield (%)			
Reaction temperature/K	HMF conv. (%)	HMFCA	FFCA	FDCA			
303	>99	87	1	7			
323	>99	62	2	31			
353	>99	20	2	76			
368	>99	0	0	>99			

<sup>*a*</sup> Reaction conditions: HMF (1 mmol),  $H_2O$  (6 ml), HMF/metal = 40 (mol/mol), under  $O_2$  flow (50 ml min<sup>-1</sup>), 7 h. 1.92 wt% Au/HT.

again rapidly converted *via* hemiacetal intermediate into FDCA (Scheme S1, ESI†).<sup>14</sup> This mechanism could be supported by the results of temperature dependence of product distribution where decrease of HMFCA yield corresponded with increase of FDCA yield with increase of reaction temperature (Table 2).

The Au/HT catalyst could be reused at least three times without significant loss of activity (Fig. S4†). The catalyst was simply reused again after washing thoroughly with water at room temperature followed by drying *in vacuo*. The catalytic activity was almost constant. HMF was completely converted for all cases and FDCA yields were >99%, 92% and 90% for 1st, 2nd and 3rd uses, respectively. No change of gold oxidation state, morphology and particle size of the reused Au/HT catalyst was observed by XANES and TEM measurements (Fig. S5 and S6†).

The possibility of leaching of the gold catalyst was also verified by carrying out the oxidation reaction. The reaction was stopped after 3 h of reaction and catalyst was filtered. The reaction mixture was again reacted up to 10 h under the same reaction condition (Fig. S7†). As a result, after the catalyst removal no change of each product yield was observed. Furthermore, ICP analysis gave no gold species in the filtrate solution.<sup>25</sup> These results indicate that gold species were not leaching out of the support.

Fig. 2 shows that at the initial stage of reaction most HMF was selectively transformed into HMFCA and HMFCA remained at high yield for a while, as reported by Casanova *et al.*,<sup>14</sup> indicating that oxidation of the hydroxyl group was much slower than the aldehyde oxidation. For FDCA synthesis from HMF it is necessary to oxidize both the aldehyde group and the hydroxyl group considered as the rate-determining step should be improved. Further study is necessary to develop highly active gold catalyst on hydrotalcite for oxidation of alcohols in water.

In conclusion, we have found that gold nanoparticles supported on hydrotalcite (Au/HT) is a highly effective heterogeneous catalyst for selective oxidation of HMF into FDCA using molecular oxygen in water under homogeneous base-free condition, and the catalyst could be reusable at least three times without significant loss of activity and selectivity. The role of the basic support HT on the oxidation could be attributable to formation of intermediate hemiacetals from aldehydes (HMF and FFCA) and formation of metal alcoholate species *via* metalhydride shift from HMFCA.

This work was supported by a Grant-in-Aid for Scientific Research (C) (No. 10005910) of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

## Notes and references

- A. Corma, S. Iborra and A. Velty, *Chem. Rev.*, 2007, **107**, 2411; J. N. Chheda, G. W. Huber and J. A. Dumesic, *Angew. Chem., Int. Ed.*, 2007, **46**, 7164.
- 2 G. W. Huber, J. N. Chheda, C. J. Barrett and J. A. Dumesic, *Science*, 2005, **308**, 1446; T. P. Vispute, H. Zhang, A. Sanna, R. Xiao and G. W. Huber, *Science*, 2010, **330**, 1222.
- 3 X. Tong, Y. Ma and Y. Li, Appl. Catal., A, 2010, 385, 1.
- 4 Y. Román-Leshkov, J. N. Chheda and J. A. Dumesic, *Science*, 2006, 312, 1933.
- 5 H. Zhao, J. E. Holladay, H. Brown and Z. C. Zhang, *Science*, 2007, **316**, 1597; J. B. Binder and R. T. Raines, *J. Am. Chem. Soc.*, 2009, **131**, 1979.

- 6 C. Carlini, M. Giuttari, A. M. R. Galletti, G. Sbrana, T. Armaroli and G. Busca, *Appl. Catal.*, A, 1999, **183**, 295; A. Takagaki, M. Ohara, S. Nishimura and K. Ebitani, *Chem. Commun.*, 2009, 6276.
- 7 Top Value Added Chemicals from Biomass, US Department of Energy report, August 2004, ed. T. Werpy and G. Petoser, http://www1.eere.energy.gov/biomass/pdfs/35523.pdf.
- 8 T. Miura, H. Kakinuma, T. Kawano and H. Matsuhisa, U.S. Patent, US-7411078, 2008.
- 9 W. Partenheimer and V. V. Grushin, *Adv. Synth. Catal.*, 2001, **343**, 102.
- 10 P. Vinke, W. V. Poel and H. van Bekkum, *Stud. Surf. Sci. Catal.*, 1991, 59, 385.
- 11 M. Kroger, U. Prube and K. D. Vorlop, Top. Catal., 2000, 13, 237.
- 12 M. L. Ribeiro and U. Schuchardt, Catal. Commun., 2003, 4, 83.
- 13 Y. Y. Gorbanev, S. K. Klitagaard, J. M. Woodley, C. H. Christensen and A. Riisager, *ChemSusChem*, 2009, 2, 672.
- 14 O. Casanova, S. Iborra and A. Corma, ChemSusChem, 2009, 2, 1138.
- 15 E. Taarning, I. S. Nielsen, K. Egeblad, R. Madsen and C. H. Christensen, *ChemSusChem*, 2008, 1, 75.
- 16 O. Casanova, S. Iborra and A. Corma, J. Catal., 2009, 265, 109.
- 17 H. Hattori, *Chem. Rev.*, 1995, **95**, 537; M. L. Kantam, B. M. Choudary, C. V. Reddy, K. K. Rao and F. Figueras, *Chem. Commun.*, 1998, 1033; B. M. Choudary, M. L. Kantam, B. Kavita, C. V. Reddy, K. K. Rao and F. Figueras, *Tetrahedron Lett.*, 1998, **39**, 3555.

- 18 T. Matsushita, K. Ebitani and K. Kaneda, *Chem. Commun.*, 1999, 265; T. Nishimura, N. Kakiuchi, M. Inoue and S. Uemura, *Chem. Commun.*, 2000, 1245; B. M. Choudary, N. S. Chowdari, S. Madhi and M. L. Kantam, *Angew. Chem.*, *Int. Ed.*, 2001, 40, 4619.
- 19 T. Mitsudome, A. Noujima, T. Mizugaki, K. Jitsukawa and K. Kaneda, Adv. Synth. Catal., 2009, **351**, 1890; T. Mitsudome, A. Noujima. T. Mizugaki, K. Jitsukawa and K. Kaneda, Green Chem., 2009, **11**, 793; T. Mitsudome, A. Noujima, Y. Mikami, T. Mizugaki, K. Jitsukawa and K. Kaneda, Angew. Chem., Int. Ed., 2010, **49**, 5545.
- 20 M. Haruta, CATTECH, 2002, 6, 102.
- 21 10 g L<sup>-1</sup> of FDCA was insoluble in water (solubility is *ca.* 1 g L<sup>-1</sup>).<sup>22</sup> However, after addition of Au/HT into aqueous solution, FDCA was completely dissolved due to change of pH value to *ca.* 10 by solid basicity of support.
- 22 S. M. Payne and F. M. Kerton, Green Chem., 2010, 12, 1648.
- 23 The base amount of HT used was estimated to be 0.64 mmol  $g^{-1}$  from titration for glycerol carbonate synthesis through transesterification by the addition of benzoic acid as a titrant<sup>26</sup>.
- 24 A. Abad, A. Corma and H. Garcia, Chem.-Eur. J., 2008, 14, 212.
- 25 The detection limit of ICP was 0.2 ppm.
- 26 A. Takagaki, K. Iwatani, S. Nishimura and K. Ebitani, *Green Chem.*, 2010, **12**, 578.