Supplementary Material (ESI) for Green Chemistry

Electronic Supplementary Information (ESI) for

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

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Experimental

Materials:

The following reagents and products were used for the experiment: 5-Hydroxymethyl-2-furfural (HMF) was purchased from Sigma-Aldrich. 2,5-Furandicarboxylic acid (FDCA) (98%) was received form Alfa Aesar (A Johnson Matthey company). 5-Formyl-2-furancarboxylic acid (FFCA) was obtained from Tokyo Chemical Industry Co. Ltd., 5-Hydroxymethyl-2-furancarboxylic acid (HMFCA) was purchased from Toronto Research Chemicals Inc. Gold standard solution was received from Wako Pure Chemical Ind., Ltd. And de-ionized water was used for catalyst experiment.

The following reagents were used for the catalyst preparation: Hydrogen tetrachloroaurate (III) tetrahydrate ($HAuCl_4•4H_2O$), ammonia solution (NH_3, 25%), magnesium nitrate hexahydrate ($Mg(NO_3)_2•6H_2O$), aluminium nitrate nonahydrate ($Al(NO_3)_3•9H_2O$), sodium carbonate decahydrate ($Na_2CO_3•10H_2O$), sodium hydroxide (NaOH) and activated carbon (C) were supplied by Wako Pure Chemical Ind., Ltd. MgO and SiO_2 were purchased from Kanto Chemical Co. Inc. Al_2O_3 was purchased from Sumitomo, Japan.

Preparation of hydrotalcite (HT):

Mg-Al hydrotalcite (Mg/Al = 5) were prepared as follows: $Na_2CO_3•10H_2O$ (30 mmol), NaOH (70 mmol) and water (60 mL) were taken into 100 mL of beaker. $Mg(NO_3)_2•6H_2O$ (50 mmol), $Al(NO_3)_3•9H_2O$ (10 mmol) and water (100 mL) were added in another 200 mL of beaker, waited until completely dissolved and dropped into the 100 mL of beaker at the speed of 1 mL/min while pH was kept to be 10. Pure white gel was obtained and aged for 3 h at 338 K, filtered and washed with water (2 L), thoroughly up to neutral pH. The obtained solid was dried in oven overnight at 373 K.

Preparation of hydrotalcite supported gold catalyst (Au/HT):

Au/HT catalyst was prepared by deposition-precipitation (DP) methods as follows. $HAuCl_4$ (0.1 mmol, 0.0412 g) was dissolved in 40 ml of water. To the solution hydrotalcite (Mg/Al =5, 1.0 g) was added followed by addition of NH_3 aq. (25%, ~0.4 ml) until pH was maintained to 10. Solution was vigorously stirred for 6 h and refluxed for 30 min at 373 K. The resulting solid was filtered, washed thoroughly with water and dried at 473 K for 4 h. Finally, the ruby-colored solid catalyst (BET surface area; 87.5 $m^2\ g^{-1}$) was obtained.

Preparation of gold catalysts on different support (Au/MgO, Au/C, Au/Al_2O_3, Au/SiO_2):

Au/MgO, Au/C, Au/Al_2O_3 and Au/SiO_2 were prepared by the same method as used for the synthesis of Au/HT.

Characterization:

Catalyst samples were characterized by transmission electron microscopy (TEM) (H-7100, Hitachi), X-ray diffraction (XRD) (RINT-2000, Rigaku) and X-ray absorption fine structure measurement (XAFS). Au XAFS spectra were recorded at room temperature by the fluorescence method using a Si(111) monochromator at the BL01B1 station in the SPring-8 synchrotron radiation facility, Japan (Proposal No. 2010A1598).

Oxidation of HMF:

Oxidations were carried out in the Schlenk tube attached with reflux condenser under O_2 flow. In each reaction the reactor was charged with 126 mg of HMF (1 mmol) in 6 ml of water. Subsequently adequate amount of supported metal catalyst was added and oxygen was introduced at the flow rate of 50 ml/min at 368 K for a given period under stirring (500 rpm). After the reaction, resultant solution was diluted 15-30 times with water and then filtered off the solid catalyst using Millex syringe filter. A sample solution was taken out for HPLC (Water) analysis (Aminex HPX-87H column from Bio-Rad Laboratories, Inc. Co. Ltd., flow rate 0.5ml/min, solvent 10 mM H_2SO_4, 323 K). The products were analyzed using a refractive index (RI) detector. The retention times for detected compounds were 22.8, 26.8, 31.3 and 38.8 for FDCA, HMFCA, FFCA and HMF, respectively.

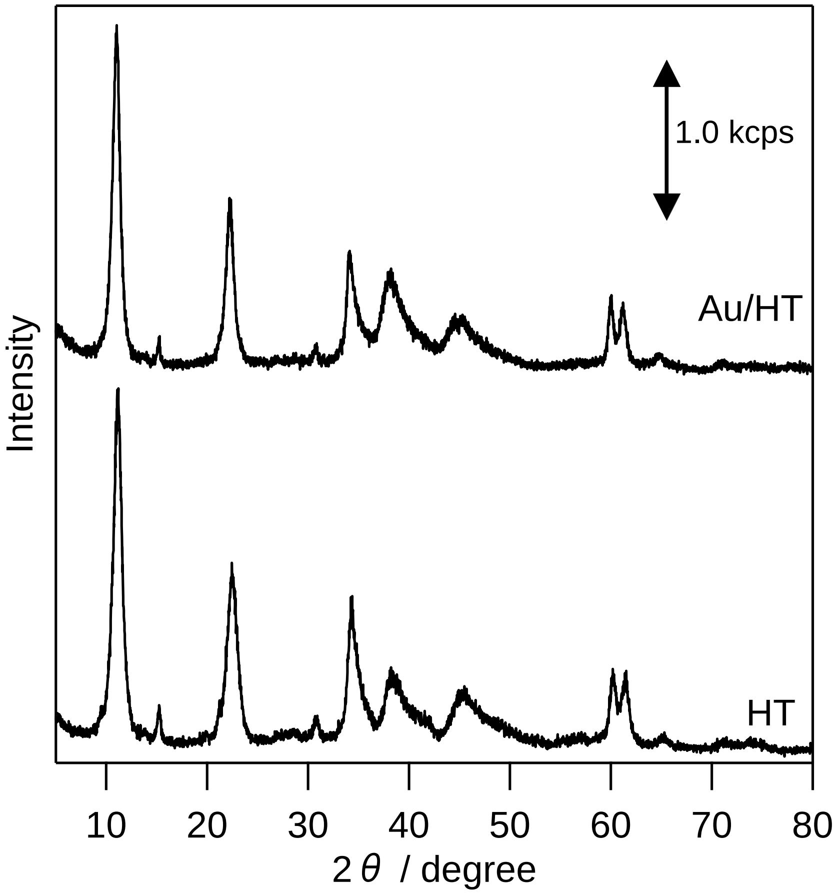


Figure S1. X-ray diffraction patterns for Au/HT and HT.

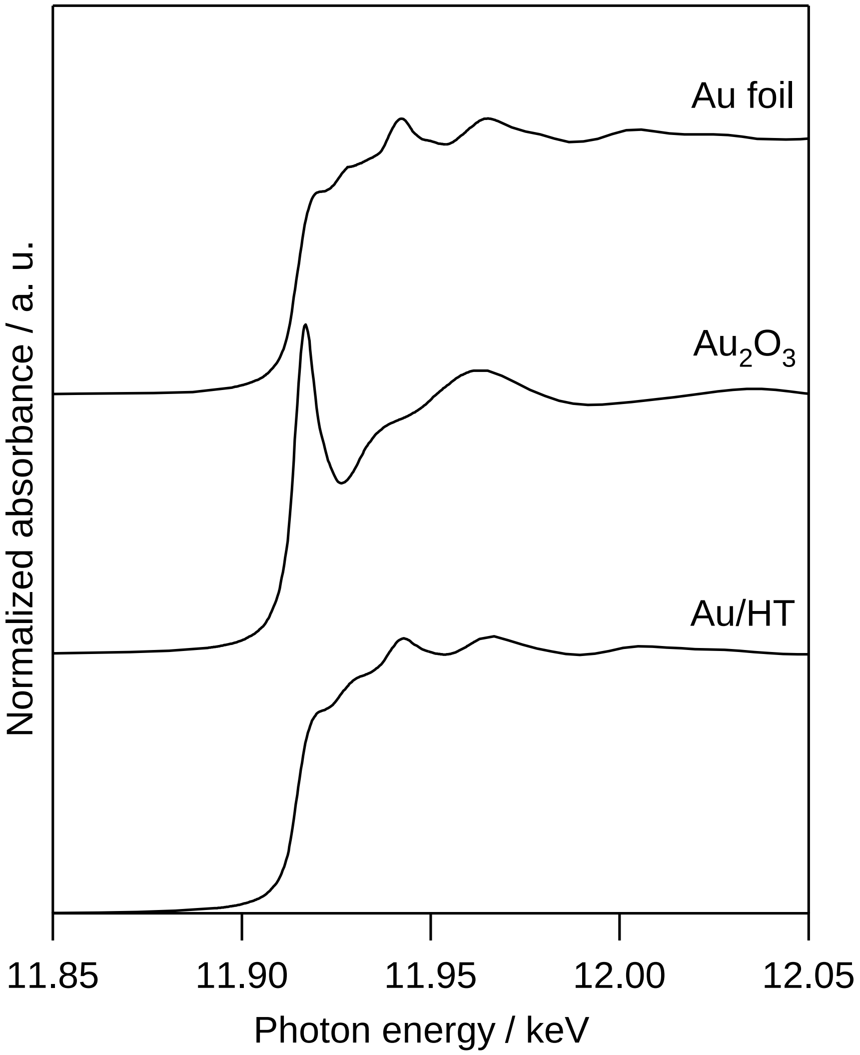


Figure S2. Au L_{III}-edge XANES spectra for Au/HT catalyst.

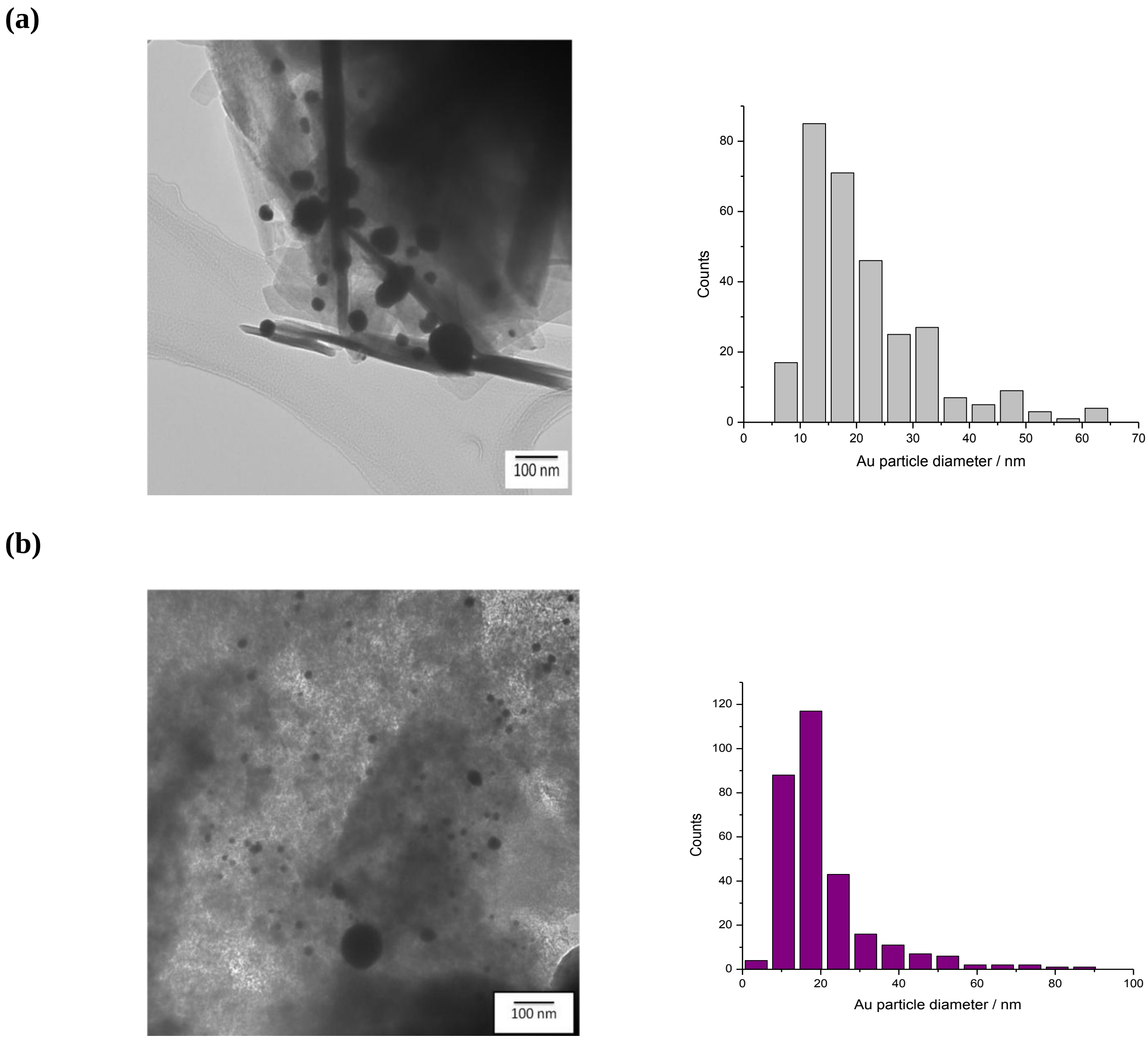


Figure S3. TEM images and Au particle size distributions for (a) Au/MgO (b) Au/C.

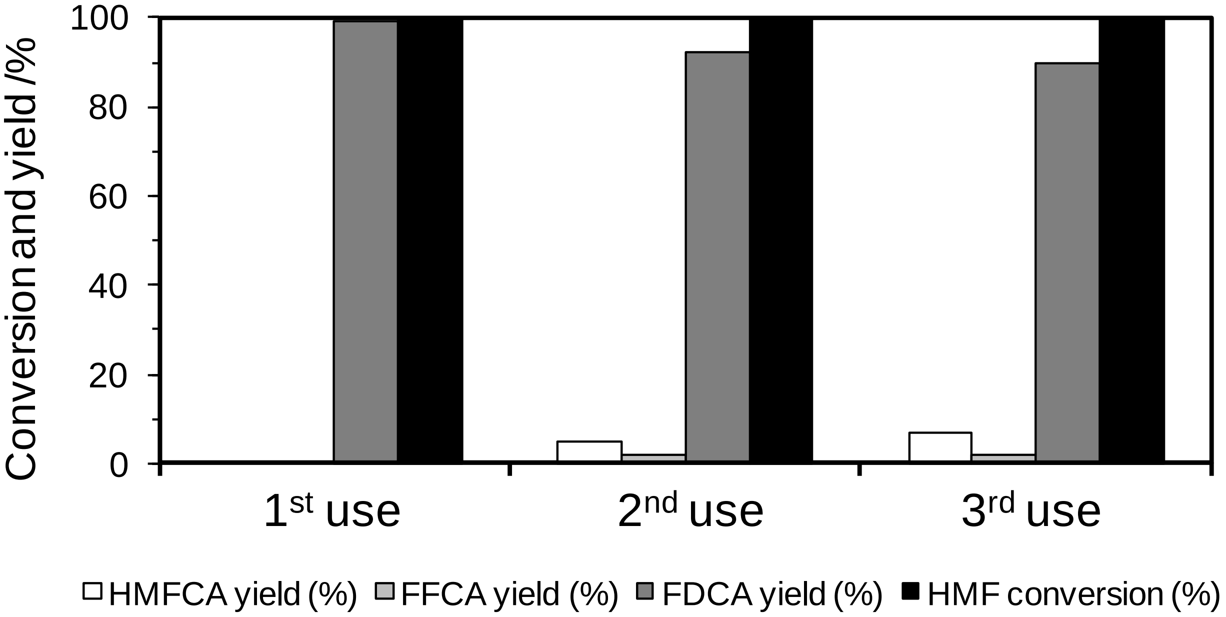


Figure S4. Recycling of Au/HT catalyst. *Reaction condition*: HMF (1 mmol), H_2O (6 ml), HMF/Au = 40 (mol/mol), under O_2 flow (50 ml/min), 368 K, 7 h.

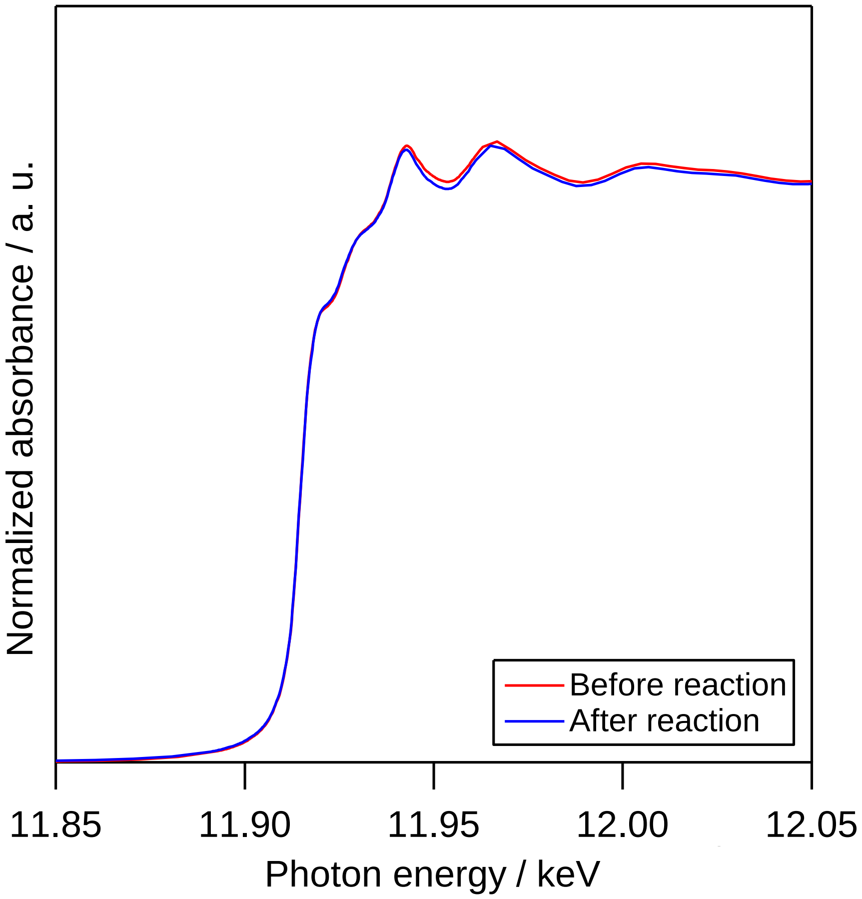


Figure S5. Au L_{III}-edge XANES spectra for fresh and used Au/HT catalysts.

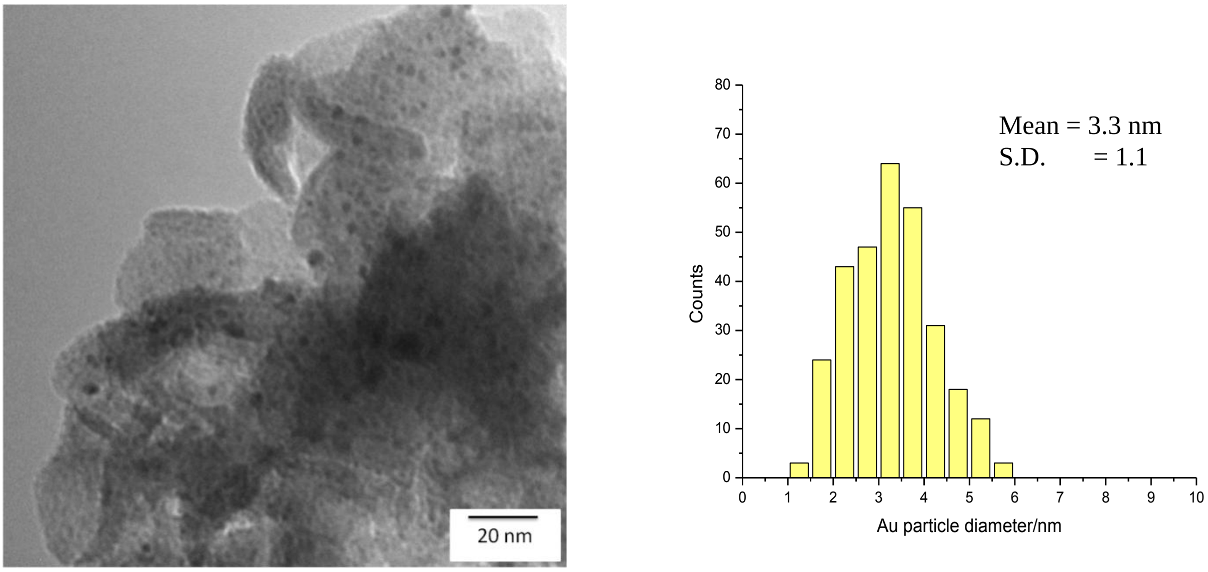


Figure S6. TEM image and Au size distribution for used Au/HT catalyst.

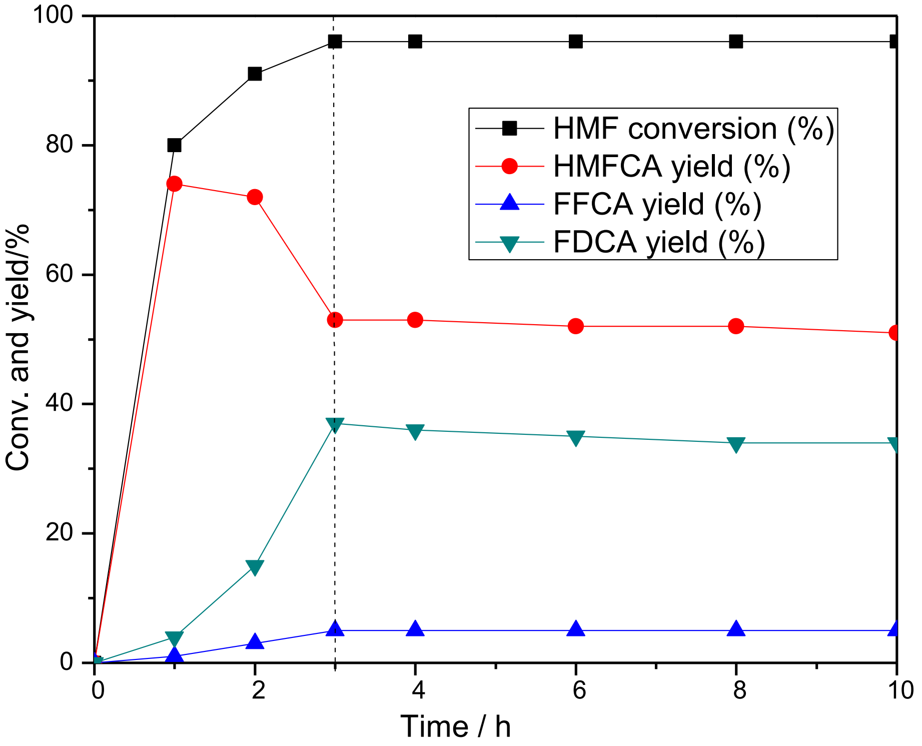
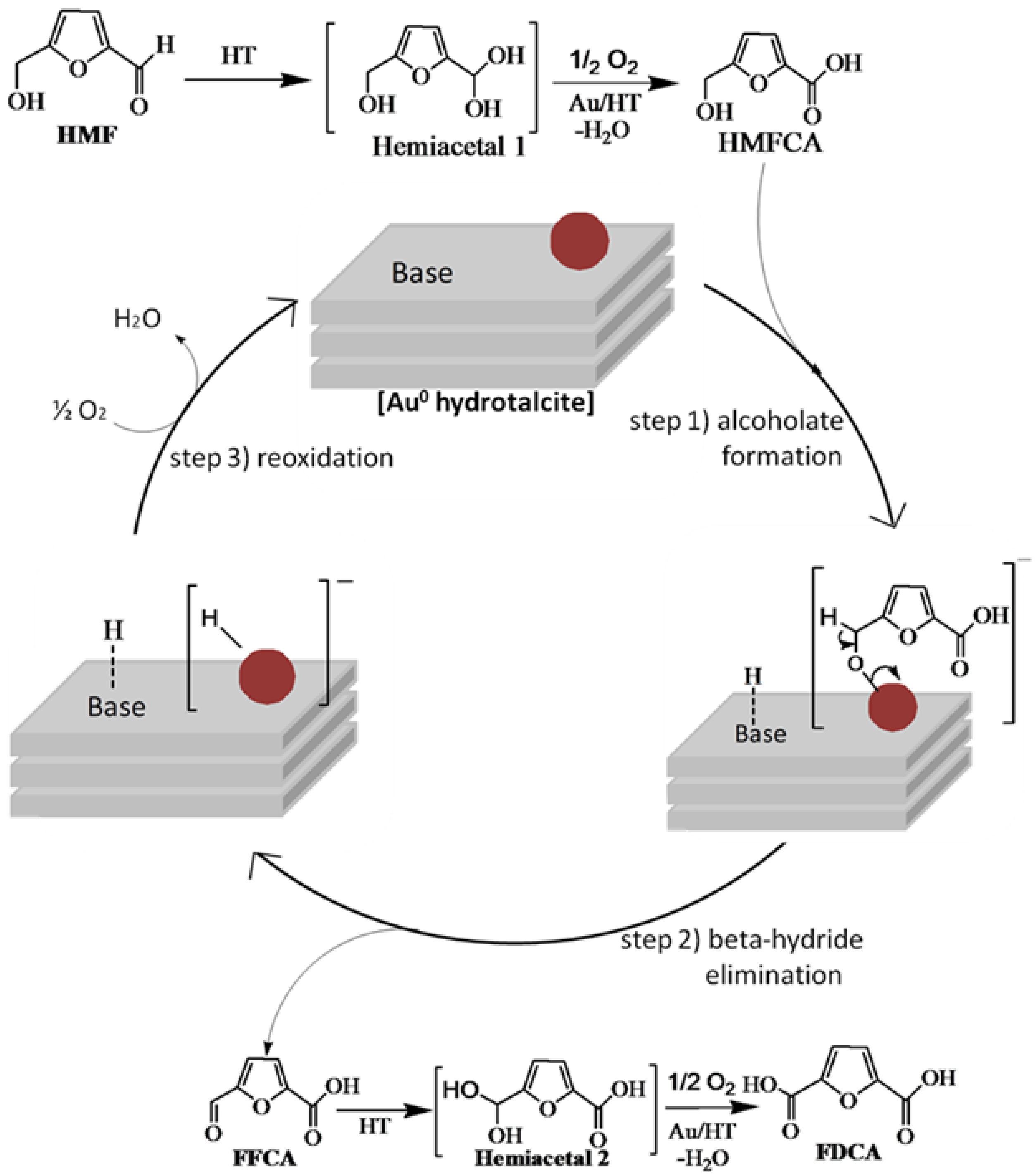


Figure S7. Time course of product distribution after filtration of Au/HT catalyst. ***Reaction conditions*****: 1.92 wt % Au/HT, HMF/Au=40 (mol/mol), HMF 1 mmol, water 6 ml, 368 K, 3h. O_2 flow rate 50 ml/min. After 3 h the catalyst was filtered off.**

Table S1. Estimation of base strength of hydrotalcite and MgO by using color indicators.[a]

Catalyst	Indicator		
	Phenolphthalein *p*Ka = 9.6	Brilliant cresyl blue *p*Ka = 11	2,4-dinitroaniline *p*Ka = 15
Hydrotalcite (Mg/Al =5)	+	—	—
MgO	+	+	+

[a] Conditions: 0.1 g of sample was added in benzene followed by a drop of 0.01 M indicator-containing benzene solution. +: basic color, —: acidic color



Scheme S1. A proposed reaction mechanism.