CHEMISTRY & SUSTAINABILITY
CHEMSUSCHEM
ENERGY & MATERIALS

Supporting Information

Conversion of Biomass-Derived Levulinate and Formate Esters into γ-Valerolactone over Supported Gold Catalysts

Xian-Long Du, Qing-Yuan Bi, Yong-Mei Liu, Yong Cao,* and Kang-Nian Fan[a]

cssc_201100483_sm_miscellaneous_information.pdf

Materials

Levulinic acid (LA, 98 %), γ-valerolactone (GVL, 98 %), formic acid (FA, 97 %), *n*-butanol (99 %), H_2SO4 (99 %) were purchased from Alfa Aesar; cellulose (microcrystalline) was purchased from Sigma-Aldrich.

Catalyst preparation

Preparation of Au/TiO_2 catalyst

A slightly modified deposition-precipitation (DP) procedure[S1] has been employed to prepare the Au/TiO_2 sample. TiO_2 (1.0 g, Degussa P25, specific surface area: 45 m^2/g nonporous, 70 % anatase and 30 % rutile, purity > 99.5 %) was added to 100 mL of an appropriate amounts of aqueous solution of $[Au(en)_2]Cl_3$ at a fixed pH = 9.4 adjusting with 0.2 M NaOH at 40 °C. The mixture was aged for 2 h, after which the suspension was cooled to room temperature. Extensive washing with deionized water was then followed until it was free of chloride ions. The samples were dried under vacuum at room temperature for 12 h, and then reduced in 5 vol% H_2/Ar (30 mL/min) at 300 ^oC for 2 h. A large fraction of the Au particles in this catalyst was within 1.2-2.3 nm in diameter. Elemental analysis results revealed that the real gold loading was 0.98 wt % in Au/TiO_2.

Preparation of Au/SiO_2 catalyst

Au/SiO_2 catalyst was prepared by following the modified DP procedure as described above[S2]. 2.0 g of SiO_2 (Aldrich, Davisil) was introduced into the appropriate amount of $HAuCl_4$ solution in order to prepare catalysts with 1.0 wt% gold content. After stirring at 75 ^oC for 1 h the solution was cooled down to room temperature. Then the pH was adjusted to 9.0 by dropwise addition of 0.25 M NH_4OH. After 6 h stirring at room temperature the catalyst was washed five times with deionized water and separated by filtration. The samples were dried at 110 ^oC in a forced air oven for 1 h and reduced in flowing 5 vol% H_2/Ar at 350 ^oC for 2 h.

Preparation of Au/C catalyst

Au/C catalyst was prepared by the procedure as described previously[S3]. In a typical preparation, the poly vinyl alcohol (PVA) was added (Au/PVA =1.5:1 mg mg^{-1}) to a aqueous solution containing 5.0×10^{-4} M $HAuCl_4$ at room temperature under vigorous stirring. The obtained solution was then left under stirring for 10 min. A following rapid injection of an aqueous solution of NaBH4 0.1 M (Au/$NaBH_4$ =1:5 mol mol^{-1}), led to formation of a dark orange-brown solution, indicating the formation of the gold sol. Activated carbon (pretreated with 2.5 wt% HNO_3 solution at 93 ^oC for 6 h) was then added to the colloidal gold solution under stirring and kept in contact until total adsorption (1 wt % of gold on the support) occurred. After 2 h, the slurry was filtered and the total absorption of gold was checked by ICP analysis of the filtrate.

Preparation of Pt/ZrO_2, Ru/ZrO_2 and Pd/ZrO_2 catalysts

1 wt% Pt/ZrO_2, Ru/ZrO_2 and Pd/ZrO_2 catalysts were prepared by an incipient wetness technique. ZrO_2 (1.0 g as prepared ZrO_2) was added to 1 mL of an aqueous solution containing appropriate amounts of $H_2PtCl_6{\cdot}6H_2O$, $RuCl_3$ or $PdCl_2$. After a perfect mixing of the corresponding slurries, the samples were dried under vacuum at room temperature for 12 h and then reduced in 5 vol% H_2/Ar at 400 ^oC for 2 h.

Preparation of Pd/C and Ru/C catalysts

The activated carbon was pretreated with dilute solution of HNO_3 (2.5 wt%) at 93 ^oC for 6 h, then washed with distilled water until pH=7, and eventually dried in a vacuum at 25 ^oC overnight. Ru/C and Pd/C catalysts were prepared by a conventional incipient wetness technique. A desired volume of H_2PdCl_4 or $RuCl_3$ aqueous solution with 5 M, the nominal metal loading of 1 wt %, was added into an aqueous suspension of the pretreated activated carbon. Then the pH of solution was adjusted to 10-11 by addition of NaOH solution; eventually the precipitated metals were reduced by hydrazine hydrate.

Catalyst characterization

BET analysis

The BET specific surface areas of the prepared catalysts were determined by adsorption–desorption of nitrogen at liquid nitrogen temperature, using a Micromeritics TriStar 3000 equipment. Sample degassing was carried out at 300 ^{o}C prior to acquiring the adsorption isotherm.

Elemental analysis

The metal loading of the catalysts was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Thermo Electron IRIS Intrepid II XSP spectrometer.

Transmission electron microscopy (TEM)

TEM images for supported catalysts were taken with a JEOL 2011 electron microscope operating at 200 kV. Before being transferred into the TEM chamber, the samples dispersed with ethanol were deposited onto a carbon-coated copper grid and then quickly moved into the vacuum evaporator.

X-ray photoelectron spectroscopy (XPS)

XPS analysis was performed using a Perkin Elmer PHI 5000C system equipped with a hemispherical electron energy analyzer. The Mg Kα (hv = 1253.6 eV) was operated at 15 kV and 20 mA. The energy scale was internally calibrated by setting the C 1s peak at 284.6 eV.

Catalytic activity measurements

Multi-phase water-gas-shift (WGS) reaction

A mixture of CO (3.2 MPa at room temperature, equivalent to 20 mmol CO), Au (0.1 mol%), water (60 mmol) and *n*-butanol (120 mmol) were placed into a 25-mL Hastelloy-C high pressure Parr reactor. The resulting mixture was vigorously stirred at 170 °C for given reaction time at a stirring speed of 800 rpm. The gaseous products were identified by a gas chromatography (GC) analyzer equipped with a TDX-01 column and a thermal conductivity detector (TCD) detector.

Decomposition of formic acid

A mixture of FA (20 mmol), Au (0.1 mol%), water (60 mL), and *n*-butanol (120 mmol) were charged into a 25-mL Hastelloy-C high pressure Parr reactor and stirred at a rate of 800 rpm for given reaction time. The mixture of substrate and catalyst were heated to 170 ^{o}C in less than 15 minutes. After the reaction, the concentration of residual FA was analyzed by a HPLC (HP 1100, Agilent, USA) system consisting of a Platisil ODS C18 column and a refractive index detector. H_2SO_4 (0.5 mM) was used as the mobile phase at a flow rate of 1 mL min^{-1}. Both of the column temperature and the detector temperature were 40 ^{o}C.

Decomposition of butanol

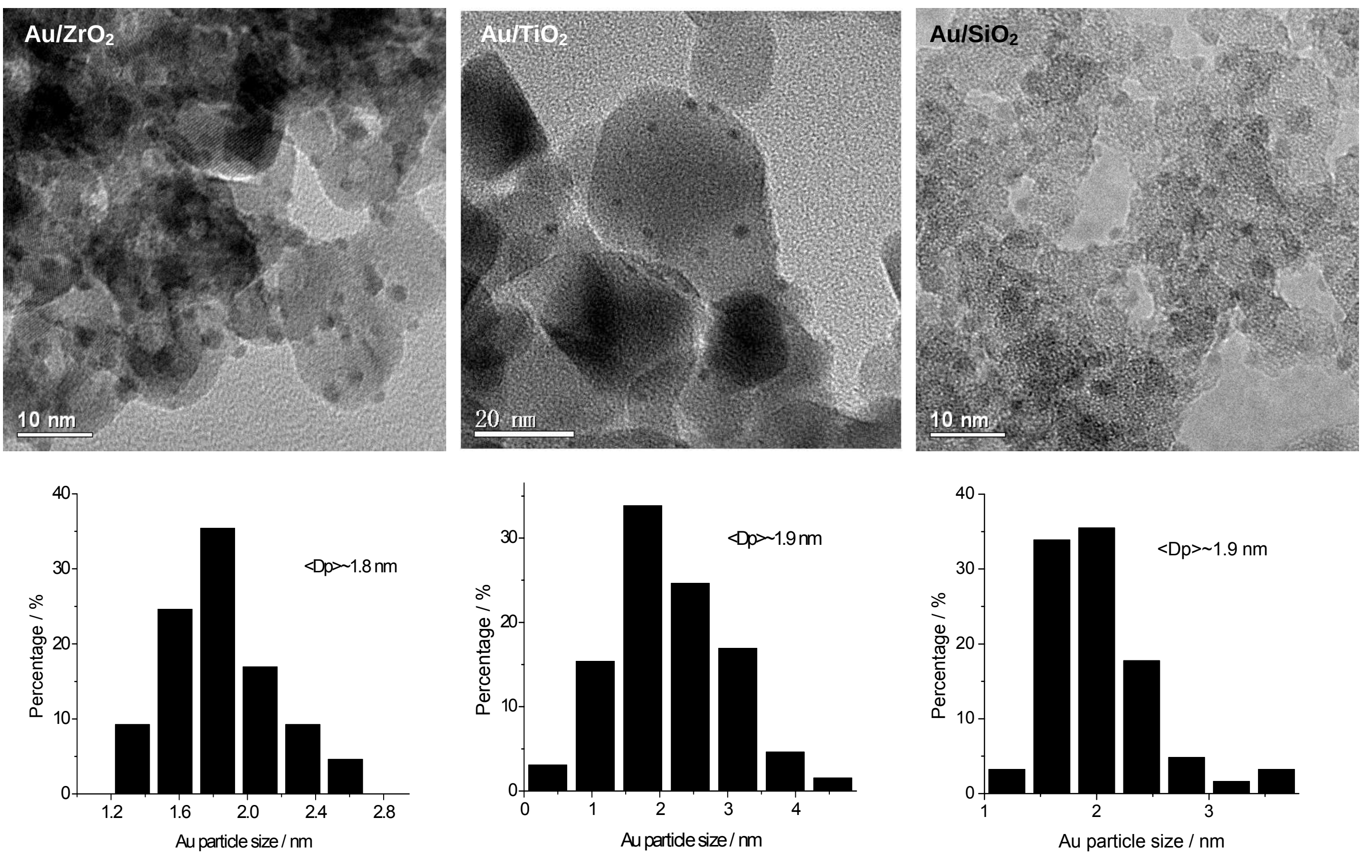
To check whether there is any decomposition of butanol with Au/ZrO_2, a mixture of butanol (120 mmol, 10 mL) and Au/ZrO_2 catalyst (Au 0.1 mol%) were charged into a 25-mL Hastelloy-C high pressure Parr reactor and stirred at a rate of 800 rpm under 0.1 MPa N_2 atmospheres at 170 ^{o}C. After the reaction, the concentration of residual FA was analyzed by a Shima- dzu GC-17A gas chromatograph equipped with a capillary column HP-FFAP (30 m × 0.25 mm) and FID detector (external standard: 2-methoxyethyl ether). The concentration of butanol was constant after 15 h, verifying that the butanol was very stable under the examined reaction conditions.

Mean sizes of metal particles in various heterogeneous catalysts

The mean sizes of metal particles in various supported catalysts derived from TEM observations by counting ca. 150-200 particles are summarized in Table S1. Many catalysts possessed metal particles with similar mean sizes (2-3 nm), but they exhibited quite different formate ester decomposition activity (see Table 2 in main text). Therefore, we think that the noble metal and the nature of support play a role in the catalytic activity of BF decomposition.

Table S1. Mean sizes of metal particles in various heterogeneous catalysts used for BF decomposition

Entry	Catalyst	Mean size of metal [nm]
1	Au/ZrO_2	1.8
2	Au/TiO_2	1.9
3	Au/SiO_2	1.9
4	Au/C	4.0
5	Ru/C	2.2
6	Pd/C	2.0
7	Pt/ZrO_2	1.9
8	Ru/ZrO_2	2.1
9	Pd/ZrO_2	2.0



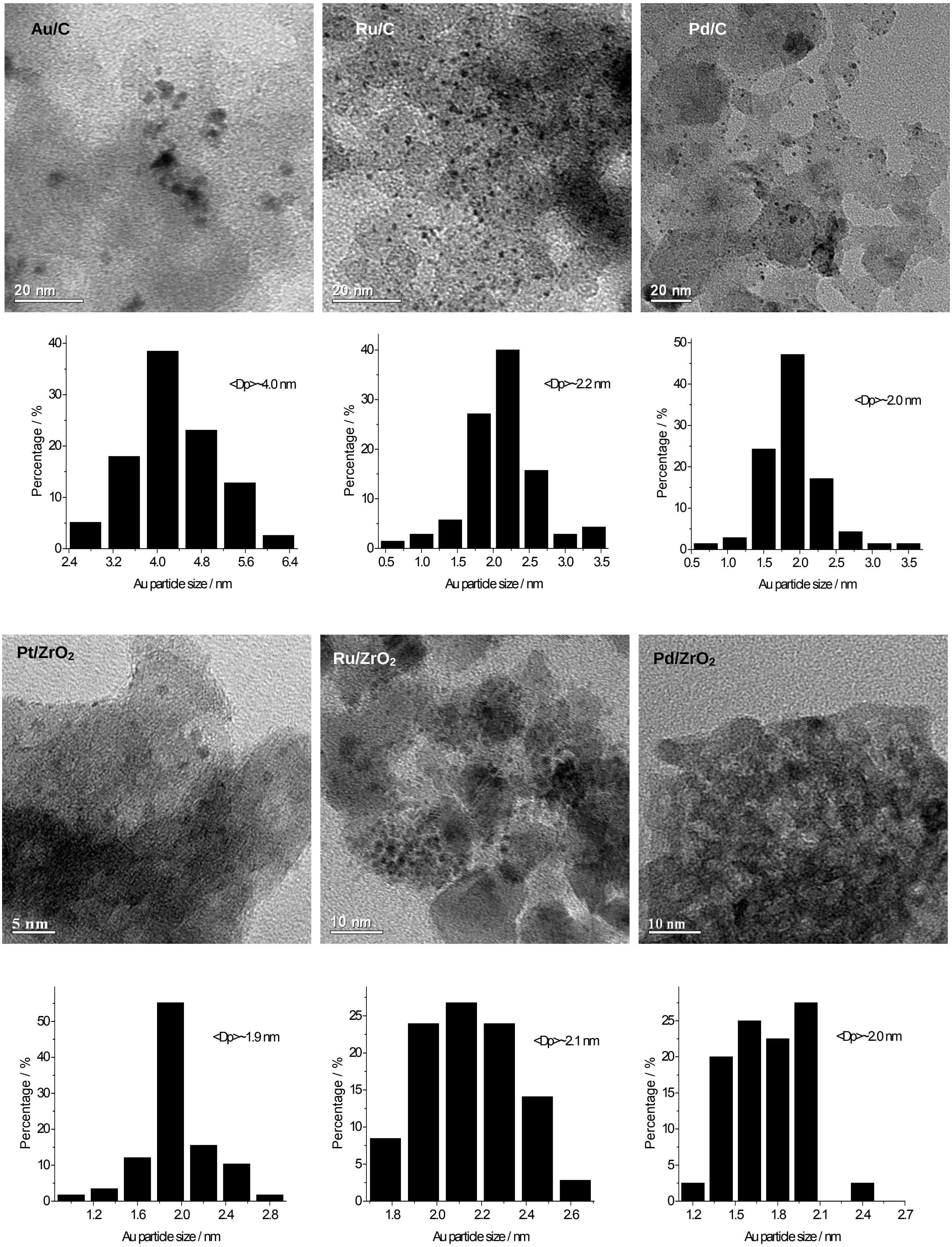
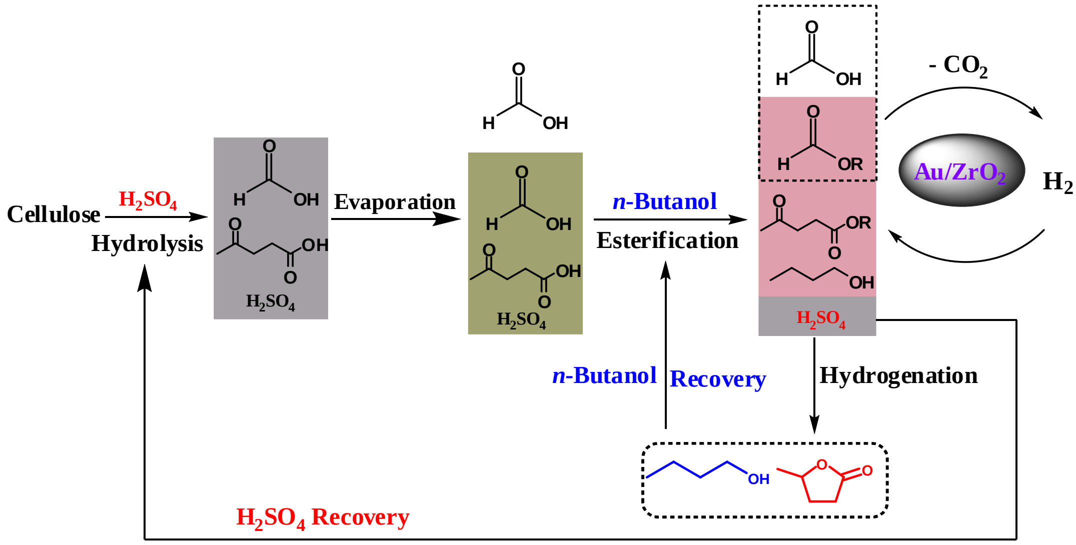


Figure S1. Representative TEM image and size distribution of various catalysts.



Scheme S1. The conversion of cellulose to GVL through esterification of concentrated LA and FA solution, followed by hydrogenation of BL with H_2 produced from decomposition of BF and FA.

[S1] L. He, L. C. Wang, H. Sun, J. Ni, Y. Cao, H. Y. He, K. N. Fan, *Angew. Chem. Int. Ed.* **2009**, *48*, 9538-9541.

[S2] X. L. Du, L. He, S. Zhao, Y. M. Liu, Y. Cao, H. Y. He, K. N. Fan, *Angew. Chem. Int. Ed.* **2011**, *50*, 7815-7819.

[S3] F. Porta, L. Prati, M. Rossi, S. Coluccia, G. Martra, *Catal. Today* **2000**, *61*, 165-172.