

## Supplementary Information

### Selective Hydrogenolysis of Carbon-Oxygen Bond with Formic Acid over a Au-Pt Alloy Catalyst

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### Experimental Section

*Materials.* All chemicals were of analytical grade and were used as received without further purification. CeO<sub>2</sub>, polyvinylpyrrolidone (PVP, K-30), formic acid, activated carbon (AC), and SiO<sub>2</sub> were obtained from Aladdin Chem. Co.; NaBH<sub>4</sub>, H<sub>2</sub>PtCl<sub>6</sub>, HAuCl<sub>4</sub>, 2-methoxy-4-methylphenol, vanillin, and 4-hydroxymethyl-2-methoxyphenol, tetrahydrofuran were obtained from Tianjin Guangfu Chemical Co.; PdCl<sub>2</sub> was from Zhejiang Metallurgical Research Institute Co.

*Synthesis of bimetallic Au-Pt colloid and Au-Pt/CeO<sub>2</sub>.* In a typical synthesis, 100 mg of PVP was added to 150 mL of HAuCl<sub>4</sub> (0.240 mmol/L) and H<sub>2</sub>PtCl<sub>6</sub> (0.243 mmol/L) solution and stirred at 0 °C for 3 h. Then, 10 mL of NaBH<sub>4</sub> solution (40 mg of NaBH<sub>4</sub>) was rapidly added under vigorous stirring at 0 °C for 1 h. Finally, the liquor was dialyzed for 96 h to remove the ions (*e.g.*, Na<sup>+</sup> and Cl<sup>-</sup>) to obtain ~150 mL of Au-Pt

colloid solution. The Au-Pt/CeO<sub>2</sub> was prepared by impregnation of the Au-Pt colloid with CeO<sub>2</sub>. Typically, 1 g of CeO<sub>2</sub> powder was added to the as-synthesized Au-Pt colloid solution, followed by ultrasonic treatment for 10 min and stirring for 1 h at room temperature. After evaporating the water under vacuum, the solid powder was dried at 100 °C for 12 h, followed by calcination at 400 °C for 5 h in air. Finally, the Au-Pt/CeO<sub>2</sub>, with Au and Pt loadings of 0.77 and 0.92 wt%, was obtained. The Au and Pt loadings on the Au-Pt/CeO<sub>2</sub> could be adjusted by changing the metal amount in the bimetallic Au-Pt colloid. In this work, the Au and Pt loadings in the Au-Pt/CeO<sub>2</sub> were 0.77 and 0.92 wt%, respectively.

The other bimetallic catalysts of Au-Pt/AC, Au-Pt/SiO<sub>2</sub> and Au-Pd/CeO<sub>2</sub> were synthesized following the same procedure of Au-Pt/CeO<sub>2</sub>, except for the use of different supports and bimetallic colloids.

*Synthesis of Au/CeO<sub>2</sub>, Pt/CeO<sub>2</sub>, Au/SiO<sub>2</sub>, Pt/C, Pd/CeO<sub>2</sub>.* These samples were synthesized by precipitation. In a typical synthesis of Au/CeO<sub>2</sub>, 1 g of CeO<sub>2</sub> was added to 300 mL of HAuCl<sub>4</sub> (0.25 mmol/L) and urea (10 mmol/L) solution. After stirring at 90 °C for 4 h in a closed reactor, the liquid mixture was cooled to 0 °C in an ice bath, followed by the addition of 10 mL of NaBH<sub>4</sub> solution (40 mg of NaBH<sub>4</sub>). Then, the solid sample was filtered and washed with a large amount of water, dried at 100 °C for 12 h, and calcined at 400 °C for 5 h in air to obtain Au/CeO<sub>2</sub>. Pt/CeO<sub>2</sub>, Au/SiO<sub>2</sub>, Pt/C, Pd/CeO<sub>2</sub> were synthesized following the same procedure, except for the use of different supports and metal precursor.

*Characterization.* Powder X-ray diffraction (XRD) patterns were obtained with a Rigaku D/MAX 2550 diffractometer with CuK $\alpha$  radiation ( $\lambda=0.1542$  nm). The metal content was determined by inductively coupled plasma spectroscopy (ICP, Perkin-Elmer 3300DV). X-ray photoelectron (XP) spectroscopy was performed on a Thermo ESCALAB 250 with Al K $\alpha$  radiation at  $\theta=90^\circ$  for the X-ray sources. The binding energies were calibrated using the C1s peak at 285.0 eV. A JEOL JEM-3000F

microscope equipped with a field-emission gun, operated at 300 kV, was used for high-resolution transmission electron microscopy (HR-TEM) observation and analysis. The point-to-point resolution was 0.19 nm. An energy dispersive X-ray spectroscopy (EDX) detector with an ultra-thin window was used to conduct chemical analysis of the samples. The powders were dispersed in ethanol by sonicating for 5 min. One drop was placed on a holey carbon film supported on a copper grid, followed by 10 min heating on the heating stage at 200 °C. IR spectra were recorded using a Nicolet NEXUS 670 FT-IR spectrometer equipped with a MCT detector and ZeSe windows and a high temperature reaction chamber. ~15 mg of the solid catalyst placed in the sample cell was treated in flowing Ar (30 sccm) at 300 °C for 30 min, then the cell was decreased at 50 °C and acetone was introduced into the cell with the flowing Ar gas. After adsorption for 30 min at 50 °C, the sample was swept with Ar at 50 °C for another 30 min, then the spectra were collected. The temperature programmed reduction by H<sub>2</sub> (H<sub>2</sub>-TPR) was performed on a FINETEC Finesorb-3010 instrument equipped with a thermal conductivity detector (TCD). The sample was placed in a quartz tube reactor in an oven. Typically, 50 mg of the sample was pre-treated in a pure He flow (15 sccm) at 480 °C for 1 h and then cooled to 50 °C. After introducing 10% H<sub>2</sub>/He mixed gas to the sample (15 sccm), the reactor was heated to 600 °C at a ramp rate of 10 °C/min to collect the signals by TCD. The Raman spectra were recorded using a JY HR800 instrument. The sample after FA dehydrogenation treatment was separated from the reaction liquor, dried under vacuum, and quickly transferred to the sample cell with flowing Ar (30 sccm). Then the Raman spectra were collected at room temperature.

*Catalytic tests for HDO.* The HDO reactions using FA were performed in a high-pressure autoclave with a magnetic stirrer (1000 rpm). In a typical run for the HDO of vanillin with FA, powder catalyst, vanillin, and water solvent were mixed in the reactor by stirring for 0.5 h at room temperature. After the addition of FA and the introduction of nitrogen to the desired pressure, the reactor was heated to a given temperature (the temperature was measured with a thermometer in an oil bath). After

the reaction, the reactor was cooled to room temperature, and ethanol was added to blend the liquor. After separation of the catalyst by centrifugation, the liquor was diluted with tetrahydrofuran analyzed by gas chromatography (GC-14C, Shimadzu, with a flame ionization detector) with a flexible quartz capillary column coated with OV-17 and FFAP. The product yields were calculated using dodecane as an internal standard. The mass balances were greater than 98.5% for the reactions.

The recyclability of the catalyst was tested by separating it from the reaction system by successive centrifugation, washing with a large quantity of methanol/water, and drying at 90 °C for 2-4 h. To fully understand the recyclability of the catalyst, the reaction time in the recycling HDO tests for each run was shortened to 2.0 h for lower vanillin conversion.

The HDO reactions using H<sub>2</sub> were performed following to the same procedures for the reactions using FA, except for the use of H<sub>2</sub> as the hydrogen source.

*Catalytic tests for the dehydrogenation of FA.* The reaction was performed in a high-pressure autoclave with a magnetic stirrer (1000 rpm). In a typical run, powder catalyst, FA, and water solvent were mixed in the reactor in an ice bath. After removing the air in the reactor and introducing nitrogen (2% argon in N<sub>2</sub>) to the desired pressure, the reaction system was quickly heated to a given temperature (the temperature was measured with a thermometer in an oil bath). After the reaction, the gaseous product was removed from the reaction system and analyzed by gas chromatography using a thermal conductivity detector with a TDX-1 column with argon as internal standard. The amount of FA was analyzed using an acid-base titration method, and corrected by the amount of CO and CO<sub>2</sub>. The TOFs were calculated from the total amount of metal sites (Au and Pt) in the reaction system. After measuring the dependence of FA conversion on time at the start of the reaction, straight lines were obtained by fitting these points. Then, the TOFs were calculated on the basis of the slopes (*k*) of these straight lines according to the following equation:

$$\text{TOF} = (m_{\text{FA}}/m_{\text{AuPt}}) \times k$$

where  $m_{\text{FA}}$  is the moles of FA in the system before the reaction,  $m_{\text{AuPt}}$  is the moles of Au and Pt atoms in the system, and  $k$  is the slope of the straight lines.

**Table S1.** The Au and Pt loadings of various Au-Pt catalysts.<sup>a</sup>

Catalyst	Au loading (wt%)	Pt loading (wt%)
Au-Pt/SiO <sub>2</sub>	0.70	0.96
Au-Pt/AC	0.81	0.89
Au-Pt/CeO <sub>2</sub>	0.77	0.92
Au-Pd/CeO <sub>2</sub>	0.80	0.89 <sup>b</sup>

<sup>a</sup> By ICP analysis; <sup>b</sup> Pd loading.

**Table S2.** HDO of vanillin with FA into MMP over Au-Pt/CeO<sub>2</sub> catalyst with different Au and Pt loadings.

Entry	Au loading (wt%)	Pt loading (wt%)	Vanillin Conv. (%) / MMP Sel. (%)
1	0.80	0	3.1 / 2.2
2	0.77	0.92	99.9 / 99.8
3	0.55	1.00	99.9 / 80.1
4	0.23	1.73	85.6 / 81.6
5	0	0.90	16.1 / 2.9

Reaction conditions: 0.8 mmol of vanillin, 40 mg of catalyst, 8 mmol of FA, 10 mL of water, 15 bar N<sub>2</sub>, 150 °C, and 4.5 h.

The bimetallic catalyst with Au and Pt loading at 0.77 and 0.92 wt% gave higher vanillin conversion and MMP selectivity than other catalysts. Normally, Au-Pt/CeO<sub>2</sub> in this work denoted the catalyst with Au and Pt loadings at 0.77 and 0.92wt%, respectively.

**Table S3.** Catalytic data in HDO of vanillin over Au/CeO<sub>2</sub>, Pt/CeO<sub>2</sub>, and Au-Pt/CeO<sub>2</sub> synthesized from different methods.<sup>a</sup>

Catalyst	Synthesis method	Conv. of vanillin (%)	Selectivity (%)	
			MMP	HMP
Au/CeO <sub>2</sub>	colloid immobilization	1.2	6.5	94.5
	precipitation	3.1	2.2	97.8
Pt/CeO <sub>2</sub>	colloid immobilization	16.9	2.0	98.0
	precipitation	16.1	2.9	97.1
Au-Pt/CeO <sub>2</sub>	colloid immobilization	>99.0	99.8	0.2
	precipitation	>99.0	80.0	20.0

<sup>a</sup> Reaction conditions: 0.8 mmol of vanillin, 40 mg of catalyst, 8 mmol of FA, 10 mL of water, 15 bar N<sub>2</sub>, 150 °C, and 4.5 h.

For comparison, Au-Pt was loaded on CeO<sub>2</sub> by precipitation method for obtaining another Au-Pt/CeO<sub>2</sub> sample with larger Au-Pt nanoparticle (Figure S5). The monometallic Au or Pt was loaded on CeO<sub>2</sub> by colloid immobilization method for obtaining another Au/CeO<sub>2</sub> and Pt/CeO<sub>2</sub> sample as referenced catalysts (Figure S4). Their catalytic data are presented in Table S3.

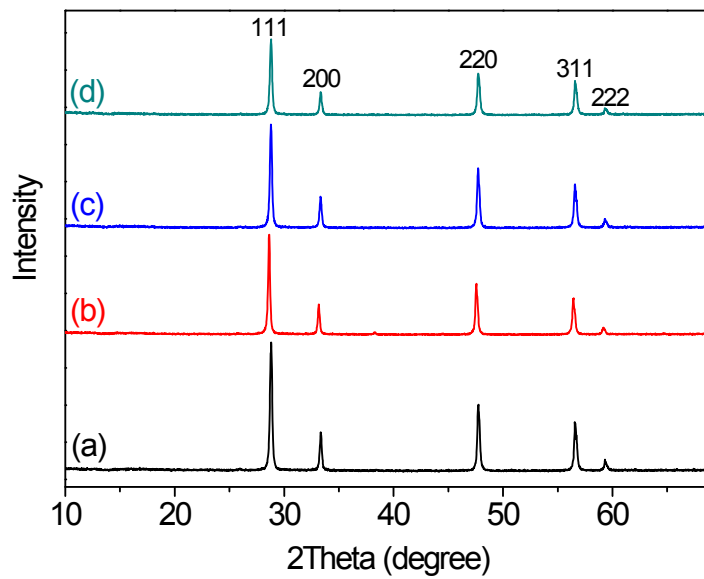
**Note:** If there is no special mark, the Au-Pt/CeO<sub>2</sub> in this manuscript is the catalyst synthesized from colloid immobilization method. Au/CeO<sub>2</sub> and Pt/CeO<sub>2</sub> are the catalysts synthesized from precipitation method.

**Table S4.** Catalytic data in HDO of vanillin over Au-Pt/CeO<sub>2</sub> using H<sub>2</sub>.<sup>a</sup>

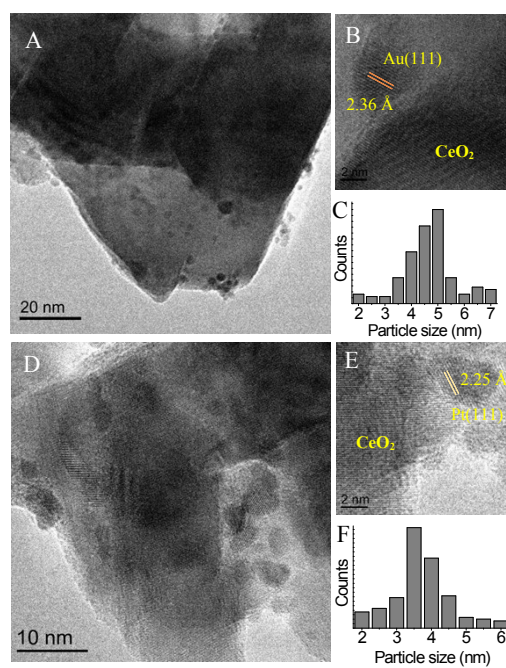
Conv. of vanillin (%)	Selectivity (%)	
	MMP	HMP
90.0	41.1	58.9

<sup>a</sup> Reaction conditions: 0.8 mmol of vanillin, 40 mg of catalyst, 10 mL of water, 10 bar of H<sub>2</sub>, 150 °C, and 4.5 h.

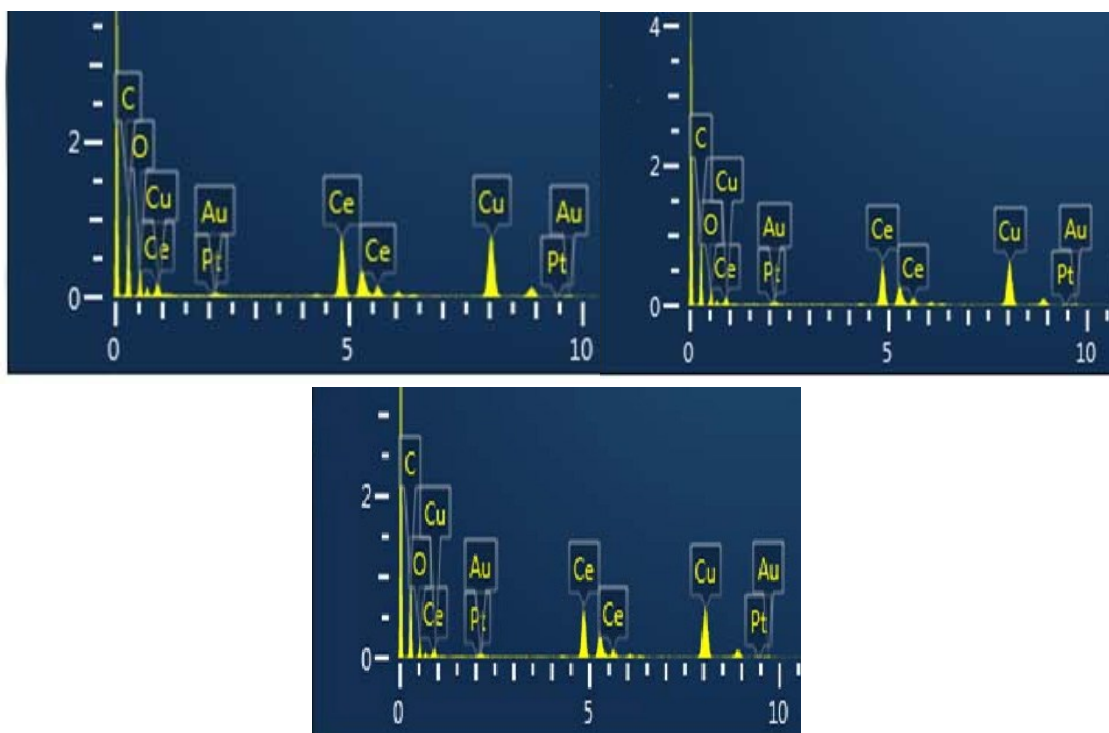




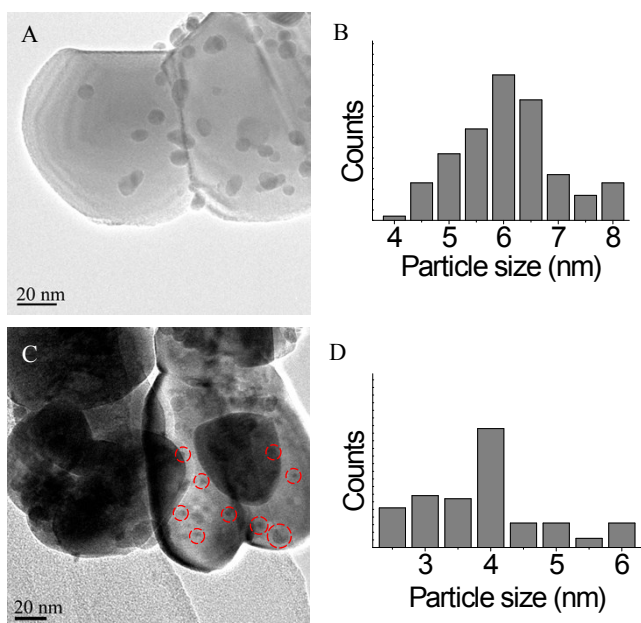
**Figure S1.** XRD patterns of the (a) CeO<sub>2</sub>, (b) Au/CeO<sub>2</sub>, (c) Pt/CeO<sub>2</sub>, and (d) Au-Pt/CeO<sub>2</sub>. These patterns show only peaks associated with CeO<sub>2</sub>, while the peaks related to metallic Au or Pt are absent, which might be due to the low loading and high dispersion of metal nanoparticles on CeO<sub>2</sub>.



**Figure S2.** TEM images and metal nanoparticle size distribution of (A-C) Au/CeO<sub>2</sub> and (D-F) Pt/CeO<sub>2</sub> samples.

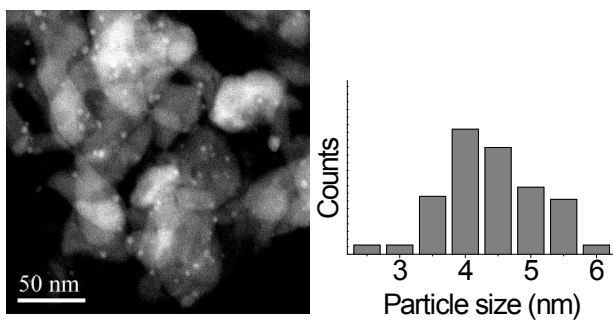


**Figure S3.** EDX analysis of the randomly selected regions on the Au-Pt/CeO<sub>2</sub>. The  $x$  axis is the Energy (keV),  $y$  axis is the Counts (a.u.).

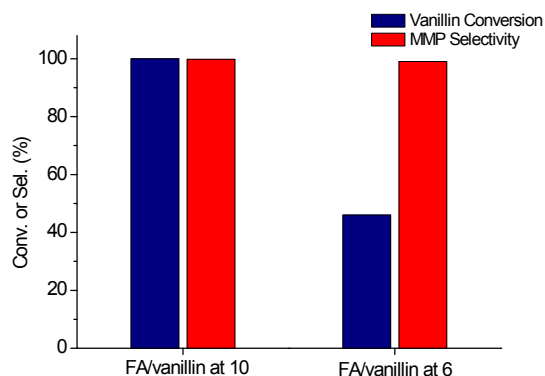


**Figure S4.** TEM and particle size distribution of (A and B) Au/CeO<sub>2</sub> and (C and D) Pt/CeO<sub>2</sub> synthesized by colloid immobilization method.

In order to study the catalytic performances of Au and Pt catalysts synthesized from different method. Au/CeO<sub>2</sub> and Pt/CeO<sub>2</sub> were synthesized from colloid immobilization method, which exhibits Au and Pt particles sizes at 4.0-8.0 and 2.5-6.0 nm with lightly larger mean size than Au/CeO<sub>2</sub> and Pt/CeO<sub>2</sub> synthesized from precipitation method (Figure S2). As presented in Table S3, the Au/CeO<sub>2</sub> or Pt/CeO<sub>2</sub> catalysts synthesize from different method exhibit comparable catalytic performances.

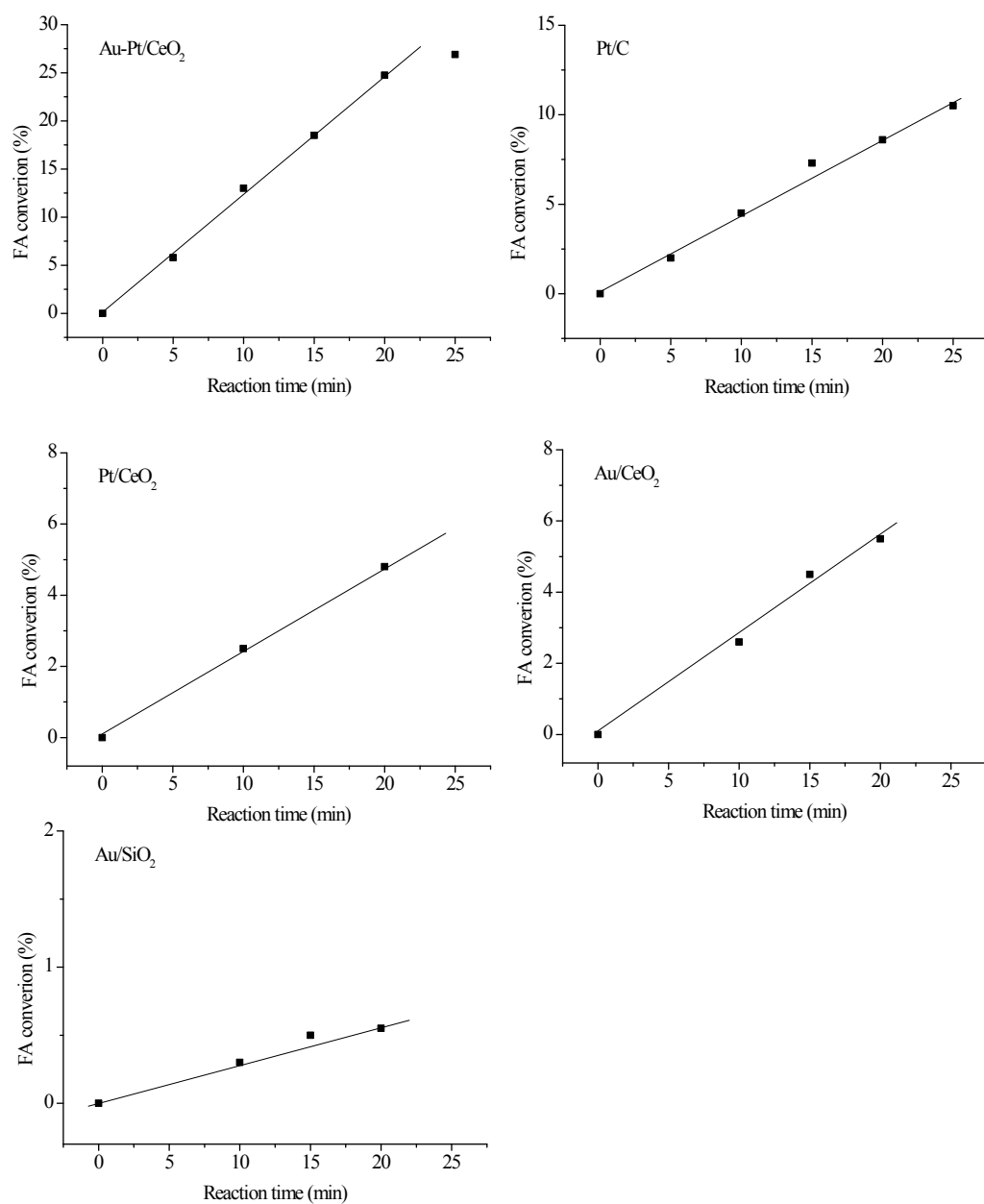


**Figure S5.** TEM and particle size distribution of bimetallic Au-Pt/CeO<sub>2</sub> catalyst synthesized by precipitation method.

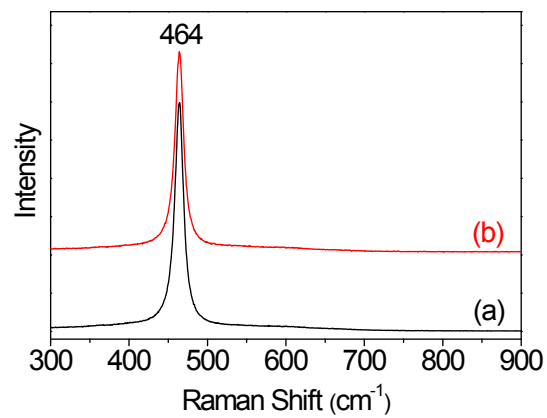


**Figure S6.** Catalytic conversion and selectivity in the hydrodeoxygenation of vanillin with formic acid over AuPt/CeO<sub>2</sub> with different amount of formic acid. Reaction conditions: 0.8 mmol of vanillin, 40 mg of catalyst, 10 mL of water, 15 bar N<sub>2</sub>, 150 °C, and 4.5 h. The carbon balances are over 99% for both the tests.

Note: In the hydrodeoxygenation of vanillin, the stoichiometric ratio of formic acid (or hydrogen) to vanillin should be 2:1. When the hydrodeoxygenation of vanillin was performed with FA/vanillin ratio at 6, the Au-Pt/CeO<sub>2</sub> catalyst gave relatively low conversion of vanillin (46.0%), but the MMP selectivity is still as high as 99.0%.

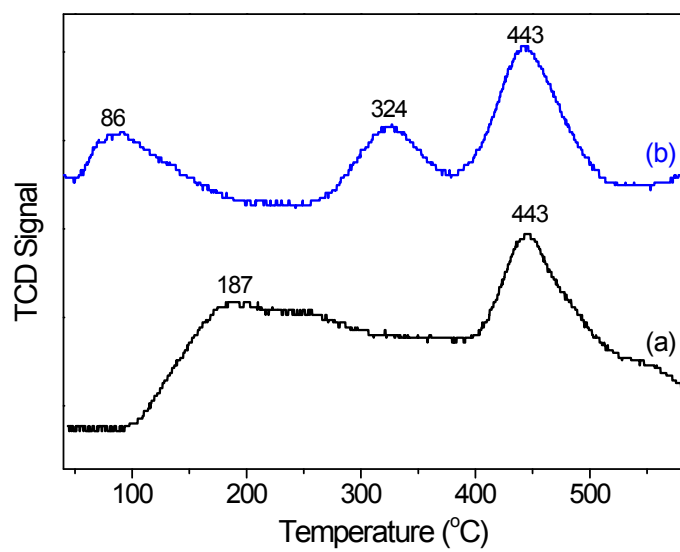


**Figure S7.** Dependences of FA conversion on time over various catalysts. The FA conversion over Pt/CeO<sub>2</sub>, Au/CeO<sub>2</sub>, and Au/SiO<sub>2</sub> were calculated from the amount of gaseous products.

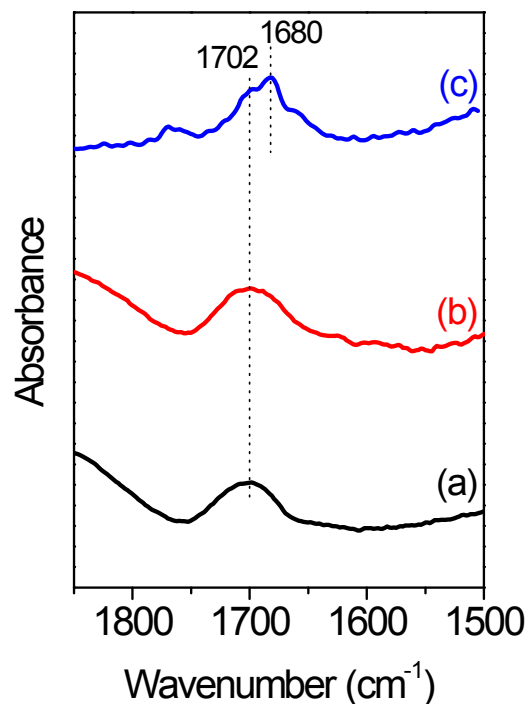


**Figure S8.** Raman spectra of the CeO<sub>2</sub> sample: (a) Fresh and (b) FA-treated for 1 h.

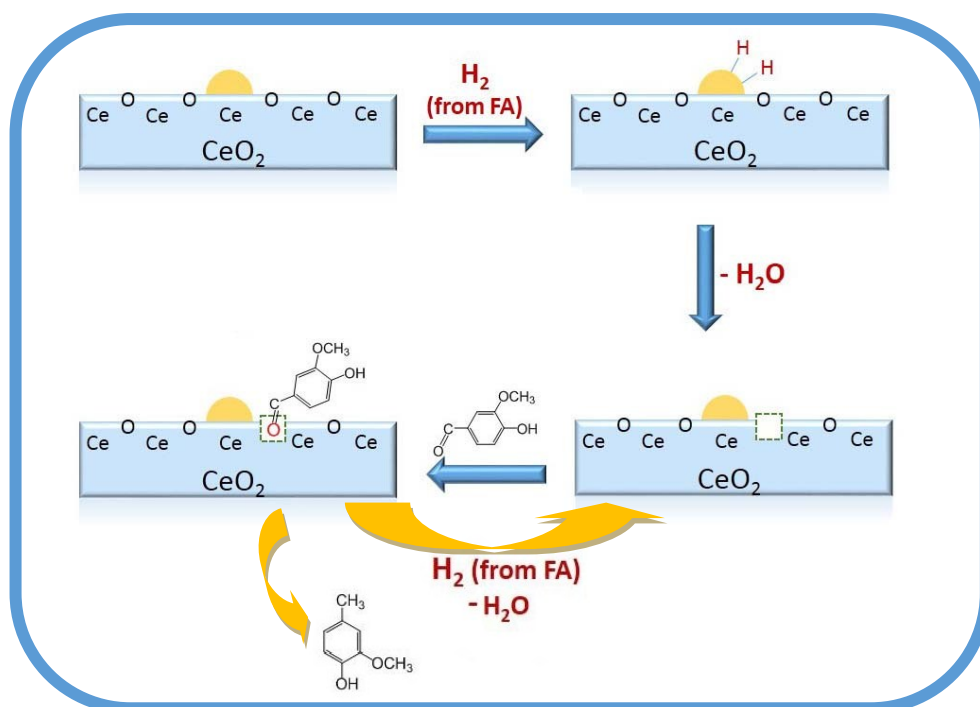




**Figure S9.** H<sub>2</sub>-TPR profiles of the (a) CeO<sub>2</sub> and (b) Au-Pt/CeO<sub>2</sub> catalysts.



**Figure S10.** FT-IR spectra of (a) CeO<sub>2</sub>, (b) Au-Pt/CeO<sub>2</sub>, and (c) FA dehydrogenation-treated Au-Pt/CeO<sub>2</sub> after competitive adsorption of water and acetone. In this case, the treated Au-Pt/CeO<sub>2</sub> shows a C=O stretching band at 1680 cm<sup>-1</sup>, which is distinguishable from that (1669 cm<sup>-1</sup>) in the case using pure acetone, suggesting that water influences the adsorption of acetone on the catalyst. In addition, the band at 1680 cm<sup>-1</sup> has a red shift of 22 cm<sup>-1</sup> from the general C=O band on acetone (1702 cm<sup>-1</sup>).



**Scheme S1.** Proposed process of HDO of vanillin over the Au-Pt/CeO<sub>2</sub> catalyst with FA.