Supplementary Information for

# Au-Pd alloy cooperates with covalent triazine frameworks for the catalytic oxidative cleavage of $\beta$ -O-4 linkage

Li Zhao,<sup>a,b</sup> Song Shi,<sup>a\*</sup> Guozhi Zhu,<sup>a,b</sup> Meng Liu,<sup>a,b</sup> Jin Gao<sup>a</sup> and Jie Xu<sup>a\*</sup>

<sup>a</sup> State Key Laboratory of Catalysis, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023,

P. R. China. E-mail: shisong@dicp.ac.cn, xujie@dicp.ac.cn

<sup>b</sup> University of Chinese Academy of Sciences, Beijing, 100049, P. R. China

## **Table of Contents**

## **Part I Materials and methods**

## Part II General synthesis procedures and catalytic reactions

- 1. Synthesis of the lignin model compounds and deuterated compounds;
- 2. Reaction procedures and products analysis;
- 3. Extraction of lignin and catalytic oxidative conversion of organosolv lignin.

## Part III Characterizations of the catalysts and reaction analysis

Fig. S1 TEM images and particle size distribution histograms of Au-Pd-CTFs samples;

**Fig. S2** The N<sub>2</sub> sorption isotherms of Au-Pd-CTFs samples;

Fig. S3 The pore size distributions of Au-Pd-CTFs samples;

**Table S1** Catalytic conversion of  $\beta$ -O-4 model compound **1** over the catalysts;

**Table S2** Radical trapping experiments for the conversion of lignin model 1;

Fig. S4 Yields of identified monomer products after the catalytic cleavage of organosolv lignin;

Fig. S5 The reaction time profile of  $\beta$ -O-4 model compound 1;

**Fig. S6** The linear fit of  $\ln(C_t/C_0)$  against the reaction time of (a) 2-phenoxy-1-phenylethanol, (b)  $C_{\alpha}$ -deuterium-labelling 2-phenoxy-1-phenylethanol and (c) 2-phenoxyacetophenone;

Fig. S7 The peroxide verification experiments;

Fig. S8 The detection of possible intermediates;

**Fig. S9** The linear fit of  $ln(C_t/C_0)$  against the reaction time of (a) 2-phenoxyacetophenone and (b)  $C_{\alpha}$ -deuterium-labelling 2-phenoxyacetophenone;

 Table S3 Catalytic conversion of ketone compound 7 over the catalysts;

**Fig. S10** The linear fit of  $ln(C_t/C_0)$  against the reaction time of 2-phenoxyacetophenone over the catalysts (a) CTFs, (b) Au-CTFs, (c) Au<sub>1</sub>-Pd<sub>1.5</sub>-CTFs and (d) Pd-CTFs.

## NMR spectra of the compounds

#### Part I Materials and methods

ZnCl<sub>2</sub>, methanol and phenol were supplied by Tianjin Kermel Chemical Reagent Co., Ltd. 2-bromoacetophenone and 2,2,6,6-tetramethylpiperidine-1-oxyl was purchased from Aladdin Chemistry Co., Ltd. Butylated hydroxytoluene, polyvinyl alcohol, guaiacol, HAuCl<sub>4</sub>·4H<sub>2</sub>O and NaBH<sub>4</sub> were purchased from Sinopharm Chemical Reagent Co., Ltd. PdCl<sub>2</sub> was from Beijing Chemical Works. 1, 4-dicyanobenzene was purchased from Enrgy chemical. 2-bromo-4'-methoxyacetophenone and 2-bromo-3', 4'-dimethoxyacetophenone were purchased from Adamas Reagent Co., Ltd. Benzyl phenyl ether was purchased from SIGMA-ALDRICH Co., Ltd. Unless otherwise noted, all the other reagents were commercially available and used as received.

Synthesis of CTFs: CTFs material was synthesized according to the report.<sup>1</sup>

**Synthesis of Au-Pd-CTFs samples:** The samples were prepared by a solimmobilization method.<sup>2</sup> Typically, To a mixed aqueous of PdCl<sub>2</sub> and HAuCl<sub>4</sub> of the desired content, the required amount of a PVA solution (0.75 wt%) was added (PVA/(Au+Pd) (wt/wt)=1.2), a freshly prepared solution of NaBH<sub>4</sub> (0.1 M, NaBH<sub>4</sub>/(Au+Pd) (mol/mol)=5) was then added to form a dark brown sol. After 30 min of sol generation, the colloid was immobilized by adding the CTFs support, the theoretical total metal loading was 1 wt%. After vigorous stirring for 2 h, the slurry was filtered, and washed thoroughly with distilled water (neutral mother liquors) and dried at 120 °C overnight. For example, the material was noted as Au<sub>1</sub>-Pd<sub>0.5</sub>-CTFs when the Au/Pd molar was 1:0.5, and so on. Other supported catalysts have the same preparation method except the support was exchanged.

#### Characterization

The X-ray powder diffraction (XRD) patterns were obtained using Empyrean-100 powder diffraction system with Cu K $\alpha$  radiation ( $\lambda$ =0.15406 nm) between 5 and 80 ° (40 KV, 40 mA). The specific surface area and pore volume was determined by N<sub>2</sub> adsorption-desorption at 77 K on QUADRASORB SI, the samples were degassed under 120 °C before determination. The morphologies of the materials were examined by transmission electron microscopy (TEM) on HITACHI H7700 electron microscope and high angle annular dark-field scanning TEM (HAADF-STEM) images were detected on JEM-2100F electron microscope. X-ray photoelectron spectroscopy (XPS) was performed on a Thermofisher ESCALAB 250Xi spectrometer using AlK $\alpha$  radiation. The binding energies were calibrated using the C 1s level (284.6 eV) as the internal standard reference. The real content of Au and Pd was determined on AVANCE III 400 MHz spectrometer at room temperature.

#### Part II General synthesis procedures and catalytic reactions

1. Synthesis of lignin model compounds and deuterated compounds



2-phenoxyacetophenone was prepared by the literature procedures.<sup>3</sup> Typically, a 500 mL bottle was charged with phenol (6.9 g, 73 mmol) and  $K_2CO_3$  (10.4 g, 75 mmol) in acetone (150 mL) and stirred at RT for 30 min. To this solution, 2-bromoacetophenone (14.0 g, 70 mmol) was added, the resulting suspension was stirred at RT for 24 h, after which the suspension was filtered and concentrated *in cacuo*. The solid was dissolved in ethyl acetate and washed with NaOH aqueous (5%, 30 ml) and water (30 ml). The organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The crude product was recrystallized from ethanol to give 2-phenoxyacetophenone as a white solid.



Then 2-Phenoxy-1-phenylethanol was synthesized as follows.<sup>4</sup> A 100 mL pressure bottle was charged with 2-phenoxyacetophenone (2.12 g, 10 mmol) and THF/water solvent (50 mL, 4:1 volume ratio) was added. NaBH<sub>4</sub> (0.76 g, 20 mmol) was added in one portion and stirred at r.t. for 1 h. Then, an excess of saturated NH<sub>4</sub>Cl aqueous solution (30 mL) was added. The crude product was extracted with ethyl acetate ( $3 \times$ 20 mL). The combined organic extracts were washed with brine (100 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The organic solvent was distilled under vacuum to 2-phenoxy-1-phenylethanol as a white solid. Spectral data were in accordance with those previously reported. For the other methoxyl substituted 2-phenoxy-1-phenylethanol, the preparation procedure is the same as described above except using different starting materials.



According to the literature to synthesize 2-phenoxy-1-phenylpropane-1,3-diol.<sup>5</sup> A solution of 2-phenoxyacetophenone (848.0 mg, 4.00 mmol) and HCHO (aqueous solution, 36 wt%, 0.6 mL, 7.3 mmol) in EtOH/acetone (1:1, 20 mL) was treated with  $K_2CO_3$  (0.6 g, 4.3 mmol) and the reaction mixture was stirred at room temperature for 4 h. The solvent was then evaporated and the residue was diluted with ethyl acetate and washed with water and brine. The organic phase was concentrated and the resulting crude materials were purified by column chromatography with hexane/EtOAc (15:1 to

1:1) to give 1-phenyl-3-hydroxy-2-phenoxy propan-1-one compound, then the ketone was reduced as the above method to give diol compound.



According to the literature.<sup>3</sup> 2-phenoxyacetophenone (0.50 g 2.36 mmol) was added to a vial with anhydrous  $K_2CO_3$  (0.126 g, 0.92 mmol) and 5 mL of D<sub>2</sub>O. The vial was caped. The reaction ran at 100 °C for 24 h. The D<sub>2</sub>O was decanted and replaced by fresh one. The reaction was maintained for additional 24 h at 100 °C. Then the solid was washed to remove the  $K_2CO_3$  residues. Finally, the solid was dried under vacuum to give deuterated compounds as a light yellow solid.



A 35 mL pressure bottle was charged with 2-phenoxyacetophenone (0.42 g, 2 mmol) and THF/D<sub>2</sub>O solvent (10 mL, 4:1 volume ratio) was added. NaBD<sub>4</sub> (0.15 g, 4 mmol) was added in one portion and stirred at r.t. for 1 h. Then, an excess of saturated NH<sub>4</sub>Cl aqueous solution (10 mL) was added. The crude product was extracted with ethyl acetate ( $3 \times 10$  mL). The combined organic extracts were washed with brine ( $3 \times 10$  mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The organic solvent was distilled under vacuum to deuterated 2-phenoxy-1-phenylethanol as a white solid.

#### 2. Reaction procedures and products analysis

Catalytic reactions were performed on a 60 mL of autoclave reactor with a Teflon insert inside. Typically, 0.2 mmol of substrate, 5 mL of methanol and 40 mg of catalyst were added into the reactor. Then, the reactor was charged with 0.5 MPa of  $O_2$  and heated to the desired temperature under magnetic stirring. When the reaction was complete, the reaction mixture was diluted to 10 mL for analysis. The products were identified by Agilent 6890N GC/5973 MS detector and quantitated by Agilent 7890A GC equipped with an Agilent HP-5 column (30.0 m × 0.530 mm) and flame ionization detector with p-dichlorobenzene as the internal standard.

#### 3. Extraction of lignin and catalytic oxidative conversion of organosolv lignin

#### **3.1 Extraction of lignin<sup>6</sup>**

To birch sawdust (20 g) was added 1,4-dioxane (144 mL) followed by 2N HCl (16mL) and the mixture was heated to a gentle reflux under a  $N_2$  atmosphere for 1 h. The mixture was then allowed to cool and the lignin containing liquor was collected by filtration. The collected liquor was partially concentrated in vacuo to give a gummy residue which was taken up in acetone/water (V:V=9:1, 25 mL) and precipitated by

addition to rapidly stirring water (250 mL). The crude lignin was collected by filtration and dried under vacuum. The dried crude lignin was taken up in acetone/methanol (V:V=9:1) and precipitated by dropwise addition to rapidly stirring Et<sub>2</sub>O (200 mL). The precipitated lignin was collected by filtration and dried under vacuum to give a purified birch lignin (1.42 g). This lignin was used in subsequent experiments without further processing.

#### 3.2 Catalytically oxidative cleavage of organosolv lignin

0.1g of lignin with 10 mL of methanol and 40 mg of Au<sub>1</sub>-Pd<sub>1.5</sub>-CTFs catalyst were added into a 60 mL Teflon insert reactor. Then the reactor was charged with 0.5 MPa of  $O_2$  and heated to 180 °C kept for 16 h under magnetic stirring. After the reaction was complete, the reaction mixture was centrifuged, solid catalyst was washed several times with methanol and the liquid was all collected and evaporated. DMSO-*d6* was added to determine the 2D HSQC NMR spectrum.



Part III Characterizations of the catalysts and reaction analysis





**Fig. S1** TEM images of (a1) Au-CTFs, (b1) Au<sub>1</sub>-Pd<sub>0.25</sub>-CTFs, (c1) Au<sub>1</sub>-Pd<sub>0.5</sub>-CTFs, (d1) Au<sub>1</sub>-Pd<sub>1</sub>-CTFs, (e1) Au<sub>1</sub>-Pd<sub>1.5</sub>-CTFs, (f1) Au<sub>1</sub>-Pd<sub>2</sub>-CTFs, (g1) Au<sub>1</sub>-Pd<sub>4</sub>-CTFs, (h1) Au<sub>1</sub>-Pd<sub>8</sub>-CTFs, (i1) Pd-CTFs, (j1) after reaction of Au<sub>1</sub>-Pd<sub>1.5</sub>-CTFs and (a2–j2) their particle size distribution histograms.



**Fig. S2** The N<sub>2</sub> sorption isotherms of (a) CTFs, (b) Au-CTFs, (c)  $Au_1$ -Pd<sub>0.25</sub>-CTFs, (d)  $Au_1$ -Pd<sub>0.5</sub>-CTFs, (e)  $Au_1$ -Pd<sub>1</sub>-CTFs, (f)  $Au_1$ -Pd<sub>1.5</sub>-CTFs, (g)  $Au_1$ -Pd<sub>2</sub>-CTFs, (h)  $Au_1$ -Pd<sub>4</sub>-CTFs, (i)  $Au_1$ -Pd<sub>8</sub>-CTFs, and (j) Pd-CTFs.



**Fig. S3** The pore size distributions of (a) CTFs, (b) Au-CTFs, (c) Au<sub>1</sub>-Pd<sub>0.25</sub>-CTFs, (d) Au<sub>1</sub>-Pd<sub>0.5</sub>-CTFs, (e) Au<sub>1</sub>-Pd<sub>1</sub>-CTFs, (f) Au<sub>1</sub>-Pd<sub>1.5</sub>-CTFs, (g) Au<sub>1</sub>-Pd<sub>2</sub>-CTFs, (h) Au<sub>1</sub>-Pd<sub>4</sub>-CTFs, (i) Au<sub>1</sub>-Pd<sub>8</sub>-CTFs, and (j) Pd-CTFs.

![](_page_11_Figure_0.jpeg)

Table S1 Catalytic conversion of  $\beta$ -O-4 lignin model compound 1 over the catalysts <sup>a</sup>

_		Conv.	Product distribution (%)							Selectivity of	TOF
Entry	Catalyst	(%)	2	3	4	5	6	7	Others	product (%)	(h <sup>-1</sup> )
1	Blank	<5	-	-	-	-	-	-	-	-	-
2	CTFs	<5	-	-	-	-	-	-	-	-	-
3	Au-CTFs	5	20	-	-	-	-	-	80	20	1
4	Au <sub>1</sub> -Pd <sub>0.25</sub> -CTFs	20	27	-	11	-	7	-	55	45	5
5	Au <sub>1</sub> -Pd <sub>0.5</sub> -CTFs	76	49	4	16	10	8	1	12	87	19
6	Au <sub>1</sub> -Pd <sub>1</sub> -CTFs	96	47	3	17	17	7	1	8	91	20
7	Au <sub>1</sub> -Pd <sub>1.5</sub> -CTFs	96	49	3	17	15	7	2	7	91	19
8	Au <sub>1</sub> -Pd <sub>2</sub> -CTFs	84	47	5	15	14	7	4	8	88	15
9	Au <sub>1</sub> -Pd <sub>4</sub> -CTFs	78	51	4	19	-	7	2	17	81	13
10	Au <sub>1</sub> -Pd <sub>8</sub> -CTFs	51	52	5	17	-	7	4	15	81	8
11	Pd-CTFs	<5	-	-	-	-	-	-	-	-	<1
12 <sup>b</sup>	Au-CTFs& Pd-CTFs	24	49	4	18	-	8	1	20	79	5
13°	Au <sub>1</sub> -Pd <sub>1</sub> 5-CTFs	11	51	_	32	_	_	_	17	83	2

Reaction conditions: 0.2 mmol of substrate, 40 mg of catalyst, 5 mL of methanol, 160  $^{\circ}$ C, 4 h, 0.5 MPa O<sub>2</sub>. Selectivity of cleavage products was presented as the amount of (2 + 3 + 4 + 5 + 6) in product distribution. Others include some unidentified and undetected compounds that were regarded as non-cleavage products. TOF numbers were calculated on the basis of total loading of metals. <sup>b</sup> 22 mg of Au-CTFs and 18 mg of Pd-CTFs. <sup>c</sup> N<sub>2</sub>.

Entry	Radical scavenger	Equivalent	Conv. (%)
1	-	-	91
2	TEMPO	0.4	93
3	BHT	0.4	91
4	BHT	1.2	93

Table S2 Radical trapping experiments for the conversion of lignin model 1<sup>a</sup>

<sup>a</sup> Reaction conditions: 0.2 mmol of substrate, 40 mg of Au<sub>1</sub>-Pd<sub>1.5</sub>-CTFs, 5 mL of methanol, 160  $^{\circ}$ C, 2 h, 0.5 MPa O<sub>2</sub>. The equivalent relates to the molar ratio of the added radical scavenger to the substrate.

![](_page_12_Figure_3.jpeg)

Fig. S4 Yields of identified monomer products after the catalytic cleavage of organosolv lignin.

![](_page_13_Figure_0.jpeg)

Fig. S5 The reaction time profile. Reaction conditions: 0.2 mmol of substrate, 40 mg of Au<sub>1</sub>-Pd<sub>1.5</sub>-CTFs, 5 mL of methanol, 150  $^{\circ}$ C, and 0.5 MPa O<sub>2</sub>.

![](_page_14_Figure_0.jpeg)

**Fig. S6** The linear fit of  $\ln(C_t/C_0)$  against the reaction time of (a) 2-phenoxy-1-phenylethanol, (b)  $C_{\alpha}$ -deuterium-labeling 2-phenoxy-1-phenylethanol and (c) 2-phenoxyacetophenone,  $C_t/C_0$  was defined as the ratio of the concentration at t and initial of the substrate. Reaction conditions: 0.2 mmol of substrate, 40 mg of Au<sub>1</sub>-Pd<sub>1.5</sub>-CTFs, 5 mL of methanol, 150 °C, 0.5 MPa of O<sub>2</sub>.

![](_page_15_Picture_0.jpeg)

**Fig. S7** The color change of 2-phenoxyacetophenone reaction solution (left) after adding the KI aqueous (middle) and titration by  $Na_2S_2O_3$  (right). The color of the solution changed from pale yellow to brown with  $\Gamma$  oxidizing to  $I_2$ , indicating the presence of peroxide.

![](_page_16_Figure_0.jpeg)

Fig. S8 The detection of possible intermediates.

![](_page_17_Figure_0.jpeg)

**Fig. S9** The linear fit of  $ln(C_t/C_0)$  against the reaction time of (a) 2-phenoxyacetophenone and (b)  $C_{\alpha}$ -deuterium-labeling 2-phenoxyacetophenone,  $C_t/C_0$  was defined as the ratio of the concentration at t and initial of the substrate. Reaction conditions: 0.2 mmol of substrate, 40 mg of Au<sub>1</sub>-Pd<sub>1.5</sub>-CTFs, 5 mL of methanol, 120 °C, 0.5 MPa of O<sub>2</sub>.

-	Catalyst	Conv.		Pro	Selectivity					
Entry		(%)	2	3	4	5	6	8	others	product (%)
1	CTFs	54	41	9	13	12	4	18	3	79
2	Au-CTFs	69	47	12	12	8	7	1	13	86
3	Au <sub>1</sub> -Pd <sub>0.5</sub> -CTFs	69	46	14	12	15	5	2	6	92
4	Au <sub>1</sub> -Pd <sub>1</sub> -CTFs	74	45	13	12	12	5	1	12	87
5	Au <sub>1</sub> -Pd <sub>1.5</sub> -CTFs	69	47	14	12	12	5	2	8	90
6	Au <sub>1</sub> -Pd <sub>2</sub> -CTFs	75	41	11	12	17	4	2	13	85
7	Pd-CTFs	72	48	12	11	9	5	2	13	85

Table S3 Catalytic conversion of ketone compound 7 over the catalysts <sup>a</sup>

<sup>a</sup> Reaction conditions: 0.2 mmol of substrate, 40 mg of catalyst, 5 mL of methanol, 120  $^{\circ}$ C, 2 h, 0.5 MPa O<sub>2</sub>. Selectivity of cleavage products was presented as the amount of (2 + 3 + 4 + 5 + 6) in product distribution. Others include some unidentified and undetected compounds that were regarded as non-cleavage products.

![](_page_19_Figure_0.jpeg)

**Fig. S10** The linear fit of  $\ln(C_t/C_0)$  against the reaction time of 2-phenoxyacetophenone over the catalysts (a) CTFs, (b) Au-CTFs, (c) Au<sub>1</sub>-Pd<sub>1.5</sub>-CTFs and (d) Pd-CTFs,  $C_t/C_0$  was defined as the ratio of the concentration at t and initial of the substrate. Reaction conditions: 0.2 mmol of substrate, 40 mg of catalyst, 5 mL of methanol, 120 °C, 0.5 MPa of O<sub>2</sub>.

## NMR spectra of the compounds

![](_page_20_Figure_1.jpeg)

![](_page_21_Figure_0.jpeg)

![](_page_22_Figure_0.jpeg)

![](_page_22_Figure_1.jpeg)

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 fl (ppm) - 1600 - 1400 - 1200 - 1000 - 800 - 600 - 400 - 200 - -200 - -200

30 20 10 0 -10

![](_page_23_Figure_0.jpeg)

![](_page_23_Figure_1.jpeg)

![](_page_24_Figure_0.jpeg)

![](_page_24_Figure_1.jpeg)

![](_page_25_Figure_0.jpeg)

![](_page_26_Figure_0.jpeg)

![](_page_26_Figure_1.jpeg)

![](_page_27_Figure_0.jpeg)

![](_page_28_Figure_0.jpeg)

![](_page_28_Figure_1.jpeg)

![](_page_28_Figure_2.jpeg)

![](_page_29_Figure_0.jpeg)

![](_page_29_Figure_1.jpeg)

<sup>13</sup>C NMR

![](_page_29_Figure_3.jpeg)

![](_page_30_Figure_0.jpeg)

![](_page_30_Figure_1.jpeg)

![](_page_31_Figure_0.jpeg)

![](_page_31_Figure_1.jpeg)

![](_page_31_Figure_2.jpeg)

![](_page_32_Figure_0.jpeg)

![](_page_32_Figure_1.jpeg)

![](_page_33_Figure_0.jpeg)

![](_page_34_Figure_0.jpeg)

![](_page_34_Figure_1.jpeg)

1. P. Kuhn, M. Antonietti and A. Thomas, Angew. Chem., Int. Ed., 2008, 47, 3450–3453.

M. Sankar, E. Nowicka, R. Tiruvalam, Q. He, S. H. Taylor, C. J. Kiely, D. Bethell,
 D. W. Knight and G. J. Hutchings, *Chem. Eur. J.*, 2011, **17**, 6524–6532.

3. M. Wang, L. H. Li, J. M. Lu, H. J. Li, X. C. Zhang, H. F. Liu, N. C. Luo and F. Wang, *Green Chem.*, 2017, **19**, 702–706.

4. M. Wang, J. Lu, X. Zhang, L. Li, H. Li, N. Luo and F. Wang, *ACS Catal.*, 2016, **6**, 6086–6090.

5. J. Zhang, Y. Liu, S. Chiba and T. P. Loh, *Chem. Commun.*, 2013, **49**, 11439–11441.

6. C. S. Lancefield, O. S. Ojo, F. Tran and N. J. Westwood, *Angew. Chem., Int. Ed.*, 2015, **54**, 258–262.