

## Supporting Information

### **Bio-oil upgrading at ambient pressure and temperature using zero valent metals**

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The following is included as supporting information for this work:

**Additional remarks S1.** Experimental details for measurements and characterization

**Table S1.** Catalytic effects of Zn and its cations

**Table S2** Comparison between the results in this work with other results for bio-oil upgrading reported in literature

**Fig. S1.** (A) Survey XPS spectra of Zn powder before reaction; (B) Survey XPS spectra of in the solid residue; and (C) Zn 3p spectra of the Zn powder before reaction and solid residue

**Fig. S2**  $^{13}\text{C}$ -NMR spectrum of the raw and upgraded bio-oil

### **Determination of the Zn contents in the bio-oils**

The Zn contents of the raw and upgraded bio-oils were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Optima 7300 DV, Perkin Elmer Co., U.S.A.) after digested by the concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30%, v/v) at 493 K.

For the upgraded bio-oil, after reaction with Zn for 300 min, the mixture was separated by centrifugation at 2000 rpm for 15 min. After solid-liquid separation, a liquid sample (upgraded bio-oil) of 1.000 gram was placed in a Kjeldahl bottle, followed by the addition of concentrated sulfuric acid (5.0 mL, 98%). Then the bottle was put in an oil-bath. The temperature was elevated to 493 K, and maintained there for 30 min. Thereafter, 30% of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) was added to the bottle till the digested solution became colorless and transparent. After cooled to room temperature, the digested solution was made up to 100 mL using deionized water. The concentrations of Zn in the solution were determined using ICP-AES, and the Zn contents in the magnetic carbon support Cu NPs were calculated correspondingly. For the raw bio-oil, the method is the same except for the centrifugation process.

### **Analysis of the chemical state of the Zn in the solid residue**

After reaction with Zn for 300 min, the mixture was separated by centrifugation at 2000 rpm for 15 min. After solid-liquid separation, the solid residue was washed with THF several times to remove the impurity adsorbed on the surface of the solid residue. Then the solid was vacuum dried at ambient temperature (about 6 °C in the

experiment) for 6 hours.

The obtained solid was characterized using X-ray photoelectron spectroscopy (XPS) to analyze the chemical state of Zn in the solid residue after reaction. The XPS spectra were obtained using an X-ray photoelectron spectrometer (ESCALAB250, Thermo-VG Scientific, U.K.) with monochromatized Al K $\alpha$  radiation (1486.92 eV). The XPS Characterizations were carried out in a Constant Analyzer Energy (CAE) mode with 70 eV pass energy for survey spectra and 20 eV for high resolution spectra.

### **Phase separation of the upgraded bio-oil**

First, the upgraded bio-oil is centrifuged to removal the solid residue. Then some NaCl powder and THF (0.1g of NaCl and 1 mL of THF to 5 mL of upgraded bio-oil) was added to the bio-oil and shaken for 5 min. Thereafter, the mixture was standing for 15 min to make phase separated. The upper layer is organic phase, the main part for the bio-oil to be used as a fuel or chemicals source. The Zn concentration of the organic phase was determined by ICP-AES as 2.6 mg kg<sup>-1</sup>. Besides, the Na concentration was also determined by the ICP-AES to find if some Na<sup>+</sup> is newly introduced to the bio-oil, and the results show that the Na concentration in the organic phase of upgraded bio-oil is 183.8 mg kg<sup>-1</sup>, while the Na concentration of total raw bio-oil is 214.6 mg kg<sup>-1</sup>, indicating that the introduction of Na in this process can also be significantly reduced.

**Table S1.** Catalytic effects of Zn and its cations

Entry	Solvent	ZVMs	Acid	Time (min)	Benzaldehyde conversion (%)	Benzalcohol selectivity (%)	Toluene selectivity (%)
1	THF	Zn	CH <sub>3</sub> COOH	60	95	>99	<1
2	THF	Zn	- <sup>a</sup>	60	trace <sup>b</sup>	trace	Trace
3	THF	Zn <sup>2+</sup> +H <sub>2</sub> <sup>c</sup>	CH <sub>3</sub> COOH	60	Trace	trace	Trace

<sup>a</sup> no any acid is added in this experiment. <sup>b</sup> means not detectable. <sup>c</sup> under ambient pressure and temperature, and the Zn<sup>2+</sup> source is Zn(CH<sub>3</sub>COO)<sub>2</sub>.

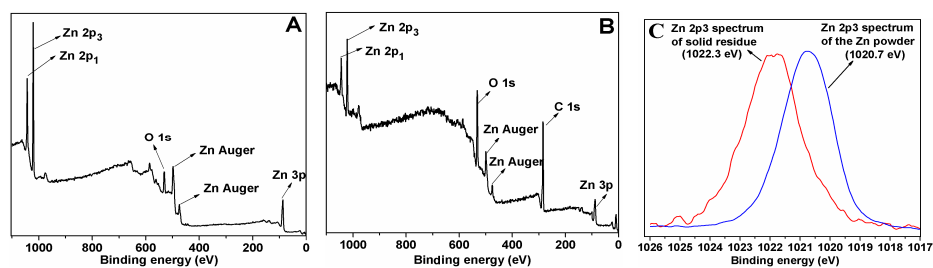
From the result of Entry 2, it can be seen that the metal Zn itself cannot act as reductant or catalyst to convert benzaldehyde into benzalcohol. While the results in entry 3 show that the Zn<sup>2+</sup> cannot act as a catalyst to activate the hydrogen gas to form hydrogenation product with benzaldehyde at ambient pressure and temperature. Thus, it is concluded that there are no catalytic effects of both metal Zn and Zn cations at ambient pressure and temperature for the model reaction.

**Table S2** Comparison between the results in this work with other results for bio-oil upgrading reported in literature

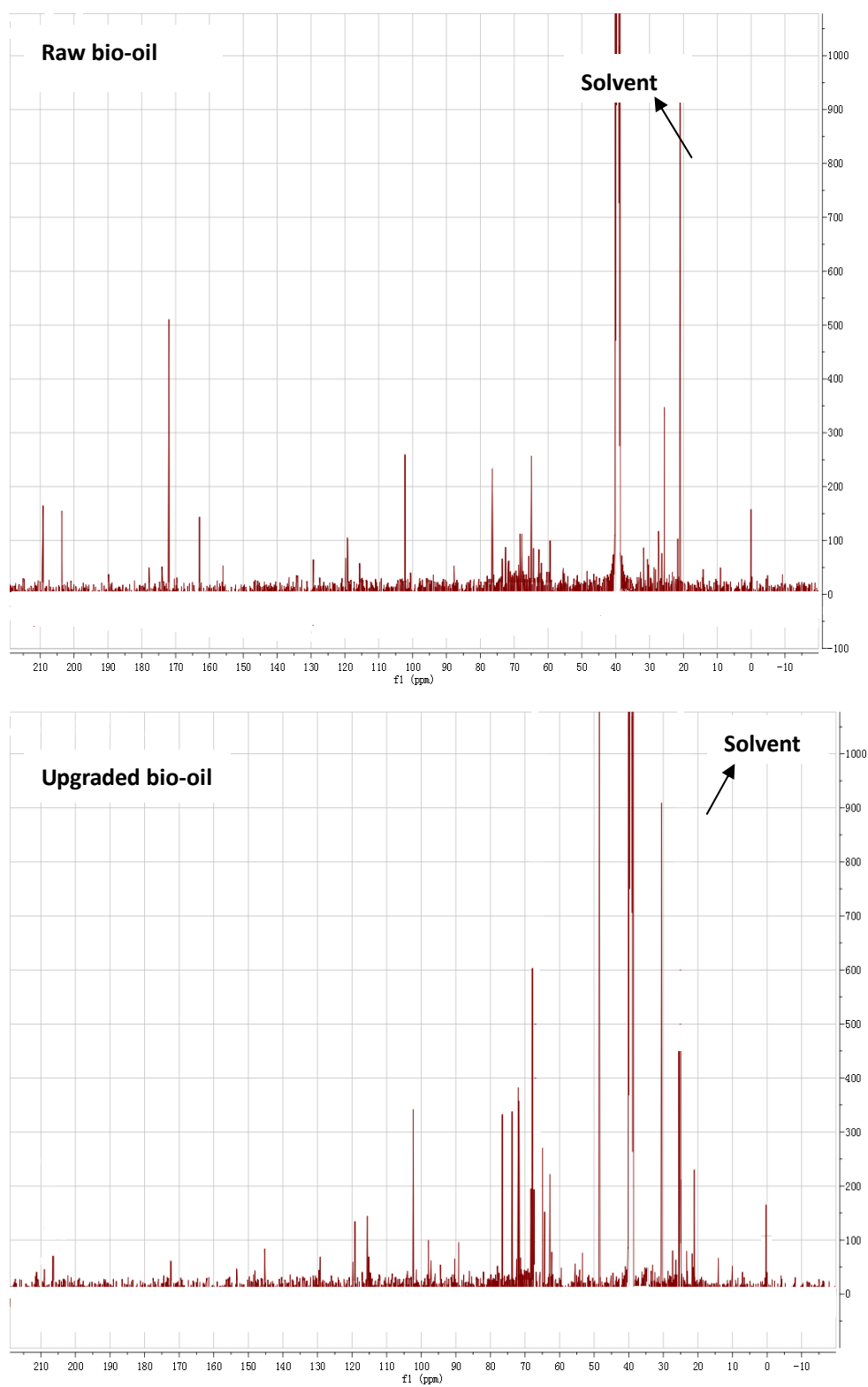
Methods	Experimental conditions	Catalyst	Results	Ref.
1	Hydrogenation T = 145 °C, P (H <sub>2</sub> ) = 10 atm	Ru-based Shvo catalyst	Carbonyl compounds were almost totally hydrogenated.	1
2	Hydrogenation T=125–175 °C P(H <sub>2</sub> )=6.9 MPa	Ru/C	The various aldehydes; acids; sugars in the bio-oil was converted to alcohols.	2
3	Hydrogenation ambient pressure temperature, Zn	Without catalyst	pH increases from 3.53 to 4.85, and the carbonyl compounds are significantly reduced.	<b>This work</b>
4	Aqueous-phase reforming T=265 °C P=5.5 MPa	Pt/Al <sub>2</sub> O <sub>3</sub> Pt/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	Hydrogen gas and alkane were produced with selectivities of 60% and 45%, respectively.	2
5	Steam reforming T=500-800 °C steam/carbon=17	NiO/MgO	Maximum hydrogen gas yield was 56.3%.	3
6	Catalytic cracking T=350-450 °C	Zeolite catalyst, ZSM-5	Highest yield of organic liquid product is 91.2%.	4
7	Catalytic cracking T=700 °C	Pt/CeZrO <sub>x</sub> Ru/CeZrO <sub>x</sub>	The hydrogen gas yield is 18 mmol of H <sub>2</sub> per gram of bio-oil	5

## References

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**Fig. S1.** (A) Survey XPS spectra of Zn powder before reaction; (B) Survey XPS spectra of in the solid residue, the result shows that after reaction, the solid residue is mainly comprised of Zn, O and C, which can be attributed to the reaction products of Zn with the bio-oil species; and (C) Zn 3p spectra of the Zn powder before reaction and solid residue, the result shows that, after reaction, the Zn is mainly in its oxidation state (i.e., Zn(II))



**Fig. S2.**  $^{13}\text{C}$ -NMR spectrum of the raw and upgraded bio-oil