## **Electronic Supplementary Information**

## An Efficient Production of Benzene from Benzoic Acid in Subcritical Water Using a Copper (I) Oxide Catalyst

Qingxin Zheng, Masato Morimoto\*, and Toshimasa Takanohashi\*\*

Advanced Fuel Group, Energy Technology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba 305-8569, Japan.

\*, \*\* Corresponding authors: \* m.morimoto@aist.go.jp and \*\* toshi-takanohashi@aist.go.jp

## **Experimental section**

**Chemical reagents.** Benzoic acid ( $C_6H_6COOH$ , 99.5%, powder, Wako Pure Chemical Industries, Ltd.) and copper (I) oxide ( $Cu_2O$ , 99.5%, powder, Wako Pure Chemical Industries, Ltd.) were used as the reactant and catalyst, respectively. Organic solvents such as dichloromethane ( $CH_2Cl_2$ , 99.5%, Wako Pure Chemical Industries, Ltd.), hexane ( $C_6H_{14}$ , 96.0%, Wako Pure Chemical Industries, Ltd.), and decane ( $C_{10}H_{22}$ , 99.0%, Wako Pure Chemical Industries, Ltd.) were used for product recovery and analyses.

**Apparatus.** The apparatus consisted of a cylinder-shaped autoclave and a rocking electric furnace, as shown in Fig. S1. The autoclave was made by SUS316 alloy with an internal volume of 50 cm<sup>3</sup>, a length of 345mm and a thickness of 8.3mm. The autoclave was equipped with a pressure gauge amplifier and a thermocouple to monitor the inner pressure and temperature, respectively. The use of the rocking furnace is to assist mixing of reactants.

**Experimental procedure.** In a typical experiment,  $0.86g Cu_2O$ , 1.47g benzoic acid, and 29.23g distilled water were fed into the autoclave and the interior air was replaced with nitrogen. The autoclave was inserted into a furnace heated to the desired temperature. The temperature and pressure inside the autoclave were recorded during each reaction. The time required to reach 350°C was about 26 min and the pressure increased from the initial pressure of 0.1 MPa to autogenous pressures. After the desired reaction time, the autoclave was removed from the furnace and allowed to cool to room temperature.

The gaseous product (carbon dioxide) was collected in a gasbag by washing with nitrogen. The other products, which were oil and water phases, and solid catalyst, were recovered by inverting the autoclave and washing with an organic solvent (dichloromethane, hexane or decane). After a centrifugation at 6000 rpm for 15 min, the solid catalyst was separated from the solution and then dried at 80°C for 24 h in a vacuum oven. The remaining solutions, composed of oil phase fraction which was dissolved in organic solvent and water phase fraction, were separated further using a separation funnel. Benzene was obtained from the organic solvent. All the experiments were repeated more than twice.

The process to replace the interior air by nitrogen was as following: (P1) A line for gas exchange (Line 1, orange part in Fig. S2) was connected to Valve A; (P2) Valves A, B, and C were closed; (P3) The pressure of  $N_2$  gas bottle was kept at 2 MPa; (P4) Valves A and B were opened to insert  $N_2$  gas to the autoclave; (P5) Valve B was closed and Valve C was opened to purge the pressurized interior gas; (P6) Valve C was closed and Valve B was opened; (P7) Procedures P5 and P6 were repeated more than five times to replace the air in autoclave to nitrogen almost completely; (P8) Valve A was closed; (P9) Line 1 was disconnected. The process to collect the gaseous product was as following: (Q1) A line for gas collection (Line 2, blue part in Fig. S2) was connected to Valve A; (Q2) Valves A and D were opened slowly to recover the interior gas with a high pressure after experiment; (Q3) Valves A and D were closed, and Line 2 was disconnected; (Q4) Procedures P1 to P4 and P8 to P9 were done; (Q5) Procedures Q1 to Q4 were repeated for twice to collect almost all the gaseous product into the gasbag; (Q6) Procedures Q1 to Q3 were done as the end.

**Analyses.** The volume and composition of the product gas were measured in a cylinder and a gas chromatograph (GC, GC-3200, GL Science Inc.), respectively. The compound in the oil phase was identified by gas chromatography-mass spectrometry (GC-MS, HP 6890 series GC system with 5973 mass selective detector, Hewlett Packard) and its amount

was determined using a gas chromatograph-flame ionization detector (GC-FID, HP 6890 series GC system, Hewlett Packard). The pH of the water phase was determined using pH test strips and the concentration of copper was measured with an inductively coupled plasma atomic emission spectrometer (ICP-AES, performed by Nippon Steel & Sumikin Eco-Tech Corp.). The crystal structure of the catalyst was analyzed using an X-ray diffractometer (XRD, M03XHF22, Bruker-AXS) and the morphology of the catalyst particles was examined using a scanning electron microscope (SEM, SU1510, Hitachi). The nitrogen isotherm of the catalyst was measured at 77K using a volumetric gas adsorption instrument (BELSORP-max, BEL Japan. Inc.) and the BET surface area was calculated from the isotherm. The copper oxidation state of the catalyst surface was examined by X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe).

Table S1. Yields of Benzene as a Function of Temperature.

entry	temperature	holding time	yield	number of
	(°C)	(min)	(mol %)	replicates
1	350	90	$90.7\pm0.1$	2
2	350	60	$87.4\pm0.3$	3
3	350	10	$74.7\pm0.4$	2
4	350	0	$65.4 \pm 0.1$	2
5	300	0	$3.0 \pm 0.1$	2
6	210	0	$0.1 \pm 0.0$	2

Here the ratio of Cu<sub>2</sub>O to benzoic acid was 50 mol% and that of benzoic acid to water was 5 wt%.



Figure S1. Schematic diagram of the apparatus.



Figure S2. Processes to replace the interior air by nitrogen (Line 1) and collect the gaseous product (Line 2).





**Figure S3.** GC-MS spectra of products dissolved in dichloromethane (top), hexane (middle), and decane (bottom). Each inner figure is the mass spectrum of the indicated peak.



Figure S4. Nitrogen isotherm of the Cu<sub>2</sub>O catalyst at 77K.



Figure S5. SEM micrographs of the Cu<sub>2</sub>O catalyst (a) before and (b) after the reaction from benzoic acid to benzene.



Figure S6. XRD diffractograms of the Cu<sub>2</sub>O catalyst before and after the reaction from benzoic acid to benzene.



Figure S7. XPS patterns of the Cu<sub>2</sub>O catalyst after the reaction from benzoic acid to benzene.