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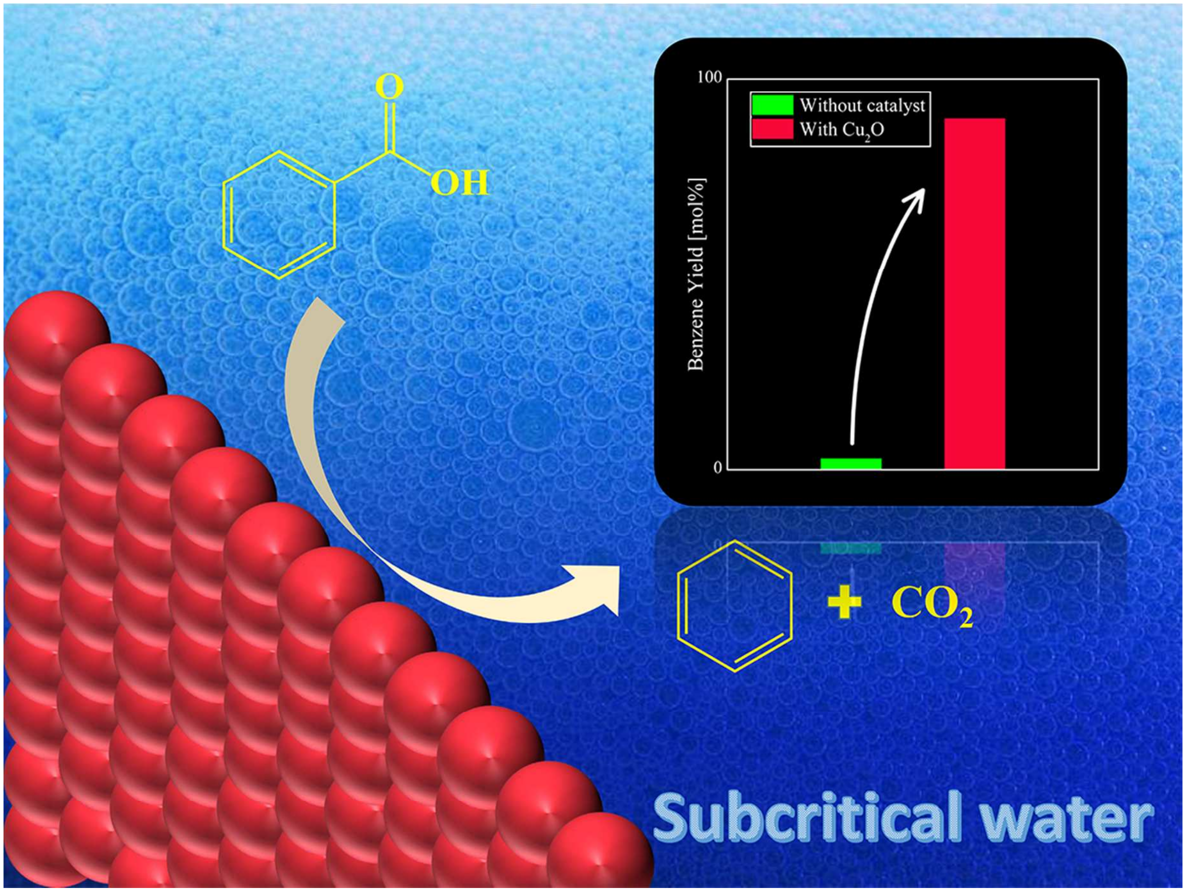

Benzene yield from benzoic acid increased greatly to 90 mol% with 100% selectivity in subcritical water catalyzed by Cu_2O.

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

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Qingxin Zheng, Masato Morimoto*, and Toshimasa Takanohashi*

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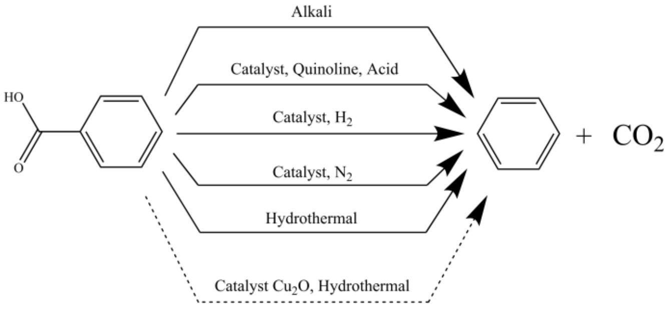
A method combining subcritical water technology and a commercially available copper (I) oxide catalyst has been performed for the production of benzene from benzoic acid. The benzene yield reached 91 mol% with 100% selectivity at 350°C and ~25 MPa in 90 min. This is the first time to realize the reaction from benzoic acid to benzene environmental-friendly, efficient and economical. The proposed reaction mechanism indicates that Cu_2O was an effective and stable catalyst, and the process was driven by the unique properties of subcritical water: high ion product, the high solubility of products and high diffusivity.

Produce of benzene from benzoic acid is one of the most basic reactions in organic chemistry.[1] In the past more than 100 years, various methods have been proposed, as shown in Scheme. 1. Initially, benzoic acid was heated with a large amount of alkali, such as soda-lime,[2] which proved environmentally harmful. A copper-quinolone system latter was employed and the reaction rate was enhanced by the addition of an acid.[1, 3] Then Maier et al.[4] obtained benzene yields of 96% on an alumina-supported nickel catalyst at 180°C and 95% yield on a silica gel-supported palladium catalyst at 370°C, in the presence of excess hydrogen. Afterwards in a nitrogen atmosphere, Takemura et al.[3] acquired benzene yield of 86.2% on a moist cerium cation-exchanged hydrogen Y type zeolite (CeHY) at 370°C after 60 min. While some methods above achieved high conversion rates, their use of alkali, acid, organic solvents, hydrogen or expensive catalysts are obvious drawbacks with regard to environment, cost and natural resource availability. Recently, hydrothermal methods using subcritical water (SbCW) or supercritical water (SCW) have also been applied for the production of benzene from benzoic acid. Hydrothermal method is inherently environmentally benign,[5-7] however, the relatively high stability of benzoic acid in water greatly limits the efficiency of the reaction and all the past relevant research shows that the yield of benzene obtained from benzoic acid by hydrothermal method is quite low.[8-12] For example, when benzoic acid was heated at 350°C in SbCW for 500 min, the benzene yield was less than 10%.[12] Therefore, it is significant and challenging to explore a novel method to realize the reaction from benzoic acid to benzene involving an environmental-friendly, efficient and economical system.

The current report describes the combination of SbCW technology with a commercially available catalyst, Cu_2O, for the production of benzene from benzoic acid (dotted arrow in Scheme. 1). Despite its simplicity, this idea had not been evaluated previously. Drastic improvements in reaction performance were observed and a reaction mechanism was proposed herein based on examination of various influential factors. The development of an environmentally benign, efficient and economical method is highly desirable.

The experimental procedure is described in the ESI and Table 1 summarizes the conditions and results. The first factor evaluated was product selectivity. Previous research has shown that benzoic acid under hydrothermal conditions can result in the production of benzene, phenol, biphenyl, and benzophenone.[10, 12] In the current study, processing benzoic acid at 350°C and 24-28 MPa (entry 5) resulted in benzene as the sole product, based on the chromatogram of dichloromethane-recovered products shown in Fig. 1 and the GC-MS spectra of products dissolved in dichloromethane, hexane, and decane, respectively, shown in Fig. S3. Thus, the method described herein exhibited 100% selectivity in the conversion of benzoic acid to benzene and carbon dioxide. Since no undesired products were obtained, the molar yields of benzene shown in Table 1 were determined from those of carbon dioxide, which are stoichiometrically equivalent.



Scheme 1. Illustration of Benzene Production from Benzoic Acid by Different Methods.

Table 1. Influence of Catalyst Concentration, Benzoic Acid Concentration, Temperature, Pressure and Holding Time on the Formation of Benzene from Benzoic Acid.

entry	Cu_2O/benzoic acid (mol %)	benzoic acid/water (wt %)	temperature (°C)	holding time (min)	pressure (MPa)	yield (mol %)	number of replicates
1	100	1.0	350	60	--	86.3 ± 0.6	2
2	50	1.0	350	60	19.4-21.0	45.8 ± 0.2	2
3	10	1.0	350	60	--	3.0 ± 0.1	2
4	0	1.0	350	60	--	2.4 ± 0.1	2
5	50	5.0	350	60	24.4-27.7	87.4 ± 0.3	3
6	50	5.0	350	60	18.4-19.7	48.2 ± 0.2	2
7	50	1.0	210	60	1.8-2.0	0.5 ± 0.2	2
8	50	1.0	210	60	18.0-19.8	0.2 ± 0.1	2

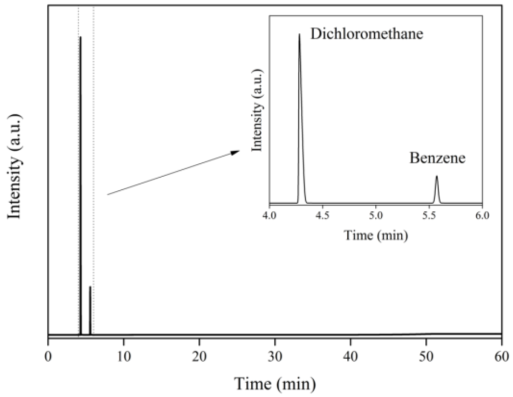


Figure 1. Chromatogram obtained by GC/FID analysis of the obtained products. The inset shows an enlarged region of the chromatogram.

The necessity and stability of the Cu_2O catalyst were also examined. Entry 4 shows that without any catalyst the decarboxylation of benzoic acid at 350°C and 60 min gave only trace amounts of benzene, with a 2.4 mol% yield. This is in agreement with the 5 mol% yield obtained in previous research using identical conditions.[12] This result shows that benzoic acid is almost inert when subjected to direct decarboxylation in SbCW. In contrast, entries 1-4 show that benzene yield increases linearly with the amount of Cu_2O added to the reaction mixture. Under the conditions listed in entry 5, the benzene yield reached 87.4 mol%, which is much higher than that obtained using only SbCW or SCW, and even higher than that reported yields using a CeHY catalyst in a nitrogen atmosphere.[3] Thus, Cu_2O is an excellent catalyst for the hydrothermal synthesis of benzene from benzoic acid. Note that a relatively large amount of catalyst was used because the commercially available Cu_2O particles had a very low specific surface area of 0.7 m^2/g, as shown in Fig. S4. The use of Cu_2O particles with a higher specific surface area would decrease the amount of catalyst required.

The catalyst was almost completely recovered after the experiment (99%). By using ICP, the fraction of Cu_2O leached into water was determined to be as small as 0.08%. Fig. S5 shows SEM micrographs of Cu_2O particles before and after the experiment. It appears that particle size increased slightly during the reaction, possibly due to partial dissolution in SbCW. Figs. S6 and S7 show the XRD diffractograms and XPS spectra of catalyst, respectively, indicating that there were no changes in the crystal structure or valence state of both copper and oxygen. These data indicate that the Cu_2O catalyst is stable in SbCW.

Temperature was an important factor in this reaction. When the reaction was performed at 210°C and ~2 or 19 MPa for 60 min (entries 7 and 8, respectively), benzene yields were less than 1 mol%. The temperature claimed in the patent of Pfirmann and Schubert[13] (210°C) had no effect even at high pressure. The yield at 350°C, however, was 45.8%. Thus, the reaction described herein requires high temperatures for optimum efficiency.

The influence of pressure is evident from entries 5 and 6, which were obtained at 350°C and ~26 and ~19 MPa, respectively. Benzene yield increased from 48 to 87% with the increased pressure, indicating that higher pressure was preferable; i.e., a higher density of water was beneficial to the overall reaction. This result agrees with previous reports that, when run at 400°C, the decarboxylation rate is a function of water density.[11] The effect of water density is due to the unique properties of subcritical water, such as the concentrations of hydronium/hydroxyl ions (H_3O^+/OH^-) and the solubility of organic compounds.

The ion product of water (K_w) reflects the degree of water ionization and increases with increasing density in hydrothermal conditions. The densities of water at 350°C and 26 and 19 MPa were 630 and 594 Kg/m^3 with K_w^* values of 1.8×10^{-12} and 8.1×10^{-13}, respectively.[14] This corresponds to higher levels of H_3O^+/OH^- at higher pressures. Our results suggest that the decarboxylation of benzoic acid prefers higher ion concentrations, since higher pressures yielded greater degrees of conversion (entries 5 and 6). The solubility of benzene in SbCW may be another important factor affected by pressure. The water–benzene mixture at 350°C exists as a single phase at pressures greater than 20 MPa, but separates into two phases at pressures ≤ 20 MPa.[15] Therefore, it is possible that the higher solubility of benzene under high-pressure conditions (entry 5) contributed to the observed higher conversion. The high diffusivity of SbCW may also facilitate a rapid reaction.

Fig. 2 shows the benzene yields as a function of temperature and reaction time using 50 mol% of Cu_2O to benzoic acid and 5 wt% of benzoic acid to water (see entry 5). The pressure observed during the experiment increased with increasing reaction time because the number of product molecules (benzene and carbon dioxide) was twice that of the reactants (benzoic acid). The benzene yield increased with increasing reaction time, reaching as much as 91 mol% at 90 min. This yield is considerably higher than any other attained in previous reports with no use of hydrogen.

Based on past research on copper-quinoline decarboxylation,[16] subcritical water technology, and the results of the current study, a mechanism is proposed for the synthesis of benzene from benzoic acid with Cu_2O in SbCW, shown in Scheme. 2. The mechanism involves the following steps: (1) benzoic acid is ionized with water

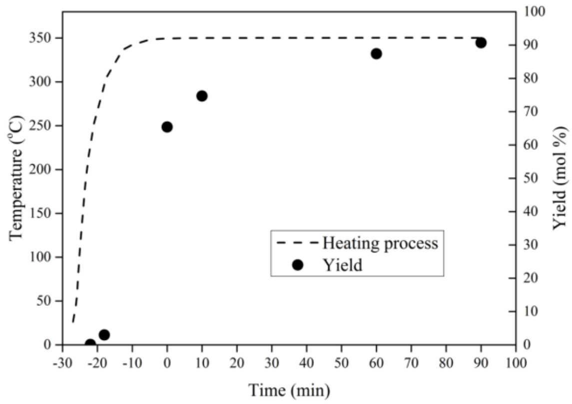
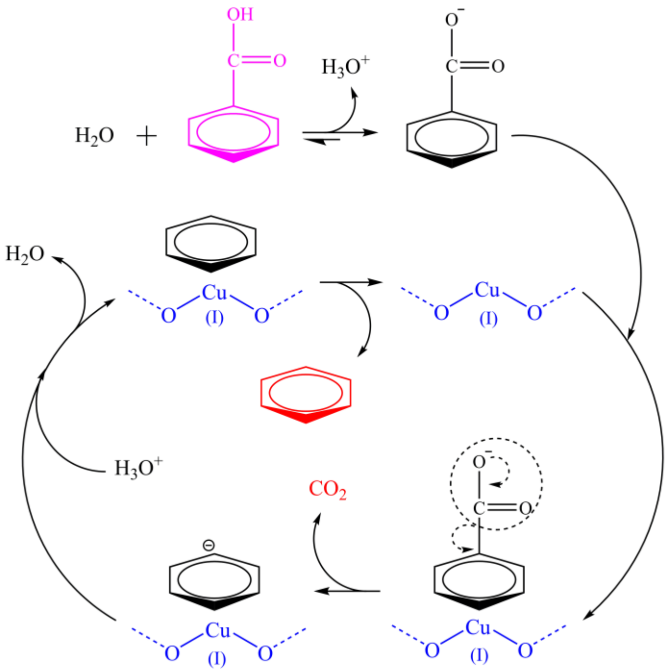


Figure 2. Yields of benzene as a function of temperature.



Scheme 2. Proposed Mechanism for the Reaction from Benzoic Acid to Benzene Catalyzed by Copper (I) Oxide in Subcritical Water.

to $C_6H_5COO^-$, (2) the $C_6H_5COO^-$ ion is adsorbed onto the surface of Cu_2O, (3) a π- electron of the aromatic ring is withdrawn by the positive charge on copper, resulting in an electron transfer from the carboxyl ion to the aromatic ring, (4) a molecule of carbon dioxide is released, (5) the negative charge on the aromatic ring is protonated by H_3O^+ and benzene is formed with a molecule of water, (6) benzene is removed from the surface of Cu_2O by water. These six steps therefore control the reaction and are subject to the various influential factors discussed above. The ionic reaction on the surface of Cu_2O with no thermal decomposition resulted in 100% selectivity for the production of benzene. The surface of Cu_2O is required for the charge transfer in step 3. This is evidenced by the increased conversion of benzoic acid with increasing amounts of catalyst. The pressure of system affected both K_w and the solubility of benzene in SbCW. The degree of ionization in step 1 is directly influenced by K_w and the high concentration of H_3O^+ ions increases the probability of protonation in step 5. In addition, high-pressure SbCW afforded complete dissolution of benzene in step 6, which enabled removal of the product from the catalyst surface. This step was accelerated by the high diffusivity of SbCW, which would also increase the diffusion rates of steps 2, 4, and 6. Therefore, high-pressure conditions yielded greater degrees of conversion. Thus, the method described herein makes use of all of the advantages of SbCW: high H_3O^+/OH^- concentrations, high diffusivity, and enhanced solubility of organic compounds.

We present a novel method for the production of benzene from benzoic acid using a Cu_2O catalyst in subcritical water at ~350°C and ~25 MPa. Without alkali, acid, organic solvents, hydrogen or expensive catalysts, conversion yields reached >90 mol% in 90min with 100% selectivity. Based on the influence of factors, a mechanism has been proposed to explain the reaction process, indicating that Cu_2O was an effective and stable catalyst for the reaction, and the process was driven by the unique properties of SbCW: a high concentration of hydronium/hydroxyl ions (high ion product), the high solubility of products and high diffusivity. This is the first time to realize the reaction from benzoic acid to benzene in a really "green" method: environmentally friendly, efficient and economical. This method is applicable for the sustainable production of benzene and enlightening for the development of hydrothermal method in the current organic chemistry.

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Advanced Fuel Group, Energy Technology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba 305-8569, Japan.
Email: m.morimoto@aist.go.jp (M. Morimoto);
toshi-takanohashi@aist.go.jp (T. Takanohashi).

† Electronic Supplementary Information (ESI) available: Experimental section, yields of benzene as a function of temperature, a schematic diagram of the reaction apparatus, processes to replace the interior air by nitrogen and collect the gaseous product, GC-MS data, adsorption-desorption isotherm, SEM micrographs, XRD diffractograms, and XPS spectra. See DOI: 10.1039/c000000x/

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