



Efficient conversion of dimethyl phthalate to phthalide over CuO in aqueous media



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ABSTRACT

An efficient conversion of dimethyl phthalate (DMP) to phthalide (PHT) over CuO in aqueous media was investigated. Among the catalysts we tested, various metals or metal oxides were effective for the conversion of DMP to PHT in water, and CuO showed excellent catalytic activity and gave the best result. The PHT yield of 85% was achieved when Zn acted as a reductant. Mechanism study for the conversion of DMP suggested that an intermediate 2-hydroxymethyl benzoic acid was produced in the process. The present study provides a useful route for the production of PHT from DMP.

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1. Introduction

During the past several decades, the energy crises have led many countries to seek renewable energy resources to reduce the over dependence on fossil fuels [1,2]. After years of over-consumption on unsustainable petroleum, the development of renewable and “green” sources of energy to reduce this use of fossil fuels and reduce CO₂ emissions has become imperative [3–6]. Biomass is a kind of abundant, renewable and relatively non-polluted resource, these qualities make it an excellent candidate for the production of high value-added chemicals. For this reason, the utilization of biomass currently is receiving increasing attention.

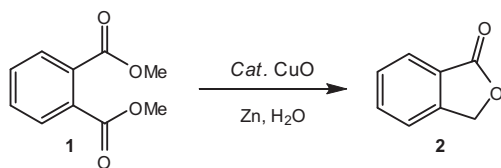
PHT has wide applications in medicine, antiseptics and organic synthesis. It is an intermediate chemical with important uses in, for example, the treatment of circulatory and heart diseases. PHT can also act as a versatile building block in organic synthesis, especially, the PHT is useful in the synthesis of functionalized naphthalenes, anthracenes and naphthalene natural products [7–11]. Due to its beneficial industrial applications, much attention has been paid to the synthesis of PHT. Currently, synthesis of PHT typically involves an industrial process from petroleum-derived phthalimide. DMP, an important biomass compound, can be easily obtained from the plentiful biomass sources, says the celery [12]. Using renewable

biomass compound DMP to obtain PHT is an efficient method which has the potential for the future commercialization. However, to date, very few studies have focused on this field. Franco Piacenti et al. reported the hydrogenation of DMP into the corresponding PHT using a ruthenium hydride complex H₄Ru₄(CO)₈(PBu₃)₄ [13]. Toshiharu Yokayama et al. discussed turning DMP into PHT with a yield of 55% over the ZrO₂ and Cr–ZrO₂ catalyst at a temperature of over 350 °C [14]. Clarke et al. used LiHBt₃ as a catalyst for the reaction and achieved a yield of 34% [15]. However, challenges still lurk in these methods from both academia and industry perspective. For example, the high-pressure gaseous hydrogen, which is often used, is difficult to store and is sometimes unstable; the PHT yield is low; the use of expensive synthesized catalysts and organic solvents are not economic and could be detrimental to the environment; and plus, a longer reaction time. Therefore, the development of an efficient and scalable process to produce PHT from DMP is very important.

Previously, our group and others have reported on a series of experiments concentrated on the conversion of biomass into value-added chemicals using a process involving high-temperature water [5,16–26]. In this process, water is not only an environmentally friendly reaction medium, and it is also an abundant hydrogen resource provided by the oxidation of active metal in water [27]. In addition, we have also reported a highly-efficient production of diols from biomass-derived glycolide or lactic acid over CuO in a high yield with high selectivity [28,29]. On the basis of these findings, if we can extend this concept to the conversion of DMP, PHT

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Scheme 1. Conversion of DMP to PHT in the presence of CuO.

may be produced in a similar manner. Herein, we present a highly efficient conversion of DMP to PHT in the presence of CuO in aqueous media (Scheme 1).

2. Experimental

2.1. Experimental materials

DMP (>99%) as the initial reactant was purchased from J&K. PHT ($\geq 99\%$, chromatographic grade, J&K Scientific Ltd.) was used for quantitative analysis. Zn (200 mesh, Aladdin) was used as the reductant. Ni, Fe, Al, Mn, Mg, CuO, Al_2O_3 , Cu_2O , Fe_2O_3 and Fe_3O_4 (200 mesh, Sinopharm Chemical Reagent Co., Ltd) were also used in the experiment.

2.2. Experimental procedure

All experiments were carried out in a Teflon-lined stainless steel batch reactor with an internal volume of 30 mL. 0.5 mmol DMP was used in all experiments. The typical procedure for the synthesis of PHT was as follows. First, desired DMP, reductant, catalyst and ultrapure water were loaded into the reactor. Then, the nitrogen was charged into the reactor in order to exclude the effect of air and then the sealed reactor was put into a drying oven, it will take about 20 min to be preheated to the desired temperature. After a desired reaction time, the reactor was quickly moved out from the drying oven to cool down. Liquid sample was collected and extracted by 10 mL ethyl acetate, then filtered with 0.45 μm Syringe Filter. Solid sample was collected and washed with deionized water and ethanol several times to remove impurities and dried in the oven at 50 °C for 24 h. The schematic of the reactor system was shown in Fig. SI-1.

2.3. Product analysis

After the reaction, the solution samples were collected and filtered for GC–MS analysis (Agilent GC7890A-MS5975C) equipped with an HP-5 polyethylene glycol capillary column with dimensions of 30 m \times 250 μm \times 0.25 μm , and GC–FID. Details on the conditions of GC–MS/FID analyses are available elsewhere [15]. The total residual organic carbon concentration in liquid samples was also measured with a TOC analyzer (Shimadzu TOC-V). The gas product was detected by thermal conductivity detector (TCD, Agilent Technologies). Thin layer chromatography (TLC) was performed on aluminum-precoated plates of silica gel 60 with an HSGF254 indicator and visualized under UV light or developed by immersion in the solution of 0.6% KMnO_4 and 6% K_2CO_3 in water. Solid samples were collected and analyzed by X-ray diffractometer (Shimadzu XRD-6100) to determine the composition and phase purity. The yield of PHT is calculated as the following equation:

$$\text{The yield (\%)} = \frac{\text{the amount of PHT obtained}}{\text{the amount of PHT in theory}} \times 100\%$$

Table 1
Effect of catalysts on the yield of PHT.^a

Entry	Reductant	Catalyst	Yield of PHT (%)
1	–	–	0
2	Zn	–	24
3	–	Cu	0
4	–	CuO	0
5	Zn	Fe	47
6	Zn	Cu	61
7	Zn	Co	43
8	Zn	CuO	85
9	Zn	Cu_2O	55
10	Zn	Fe_2O_3	0
11	Zn	Fe_3O_4	26
12	Zn	TiO_2	57
13	Zn	MnO_2	58
14	Zn	ZrO_2	42
15	Zn	CuFe_2O_4	12
16	Zn	Pd/C	24
17	Zn	Ni	15

^a Reaction conditions: DMP 0.5 mmol, reductant 25 mmol, catalyst 5 mmol, 250 °C, 2 h, water filling 25%.

3. Results and discussion

3.1. Catalyst screening

Initially, we investigate the influence of metal or metal oxides on the production of DMP to PHT. The reaction of DMP was conducted in the presence of 5 mmol Cu and 25 mmol Zn at 250 °C for 120 min. The result showed that the reaction proceeded efficiently and produced the desired PHT at a 61% yield, as determined by GC–FID NMR and GC–MS (Figs. SI-2 and SI-3). Next, we screened a series of metal or metal oxides to determine the most suitable one. The results are summarized in Table 1. The reaction did not proceed at all in the absence of both reductant and catalyst or in the presence of the catalysts only (entries 1, 3–4). The reaction with 25 mmol Zn but without the addition of any catalyst, gave the desired PHT at a 24% yield (entry 2), this result could be reckoned as an evidence of the importance of the combined use of the reductant and catalyst. Among the various catalysts we investigated (entries 5–17), the use of CuO improved the transformation efficiency and afforded PHT at a better yield (entries 8). However, the use of Fe_3O_4 is completely ineffective (entry 11). CuFe_2O_4 and Ni gave lower yield (entries 15, 17).

As the XRD patterns of solid residues after the reaction shown in Fig. SI-4(a), the Cu still exists while Zn has been oxidized into ZnO, it is obviously that the Cu acted as a catalyst and Zn acted as a reductant in the reaction process. According to the result of Fig. SI-4(b), unexpectedly, the Cu instead of CuO is observed in the solid sample. Our previous work [28] had confirmed that CuO could be reduced completely into Cu by *in situ*-formed hydrogen by the oxidation of Zn in water. We measured the Cu ion concentration in the solution by ICP and only a small amount of Cu ions (<1 ppm) in the liquid sample was found. This result suggested that Cu was most likely present in the solid residual.

Next, we investigated the effect of the amount of CuO on the yield of PHT. The reaction was conducted in the presence of 25 mmol Zn with 25% water filling at 250 °C for 120 min. The results are shown in Fig. 2(a). The yield of PHT increased significantly at first as the amount of CuO increased from 0 to 5 mmol, and the maximum value of 85% PHT was achieved at 5 mmol CuO. The yield decreased when the amount of CuO was further increased. These results may be led from that more CuO would lead to the decomposition of PHT to more by-products, which might result in a decrease in PHT selectivity.

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