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Highly selective hydrothermal production of cyclohexanol from biomass-derived cyclohexanone over Cu powder

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ABSTRACT

An efficient conversion of biomass-derived cyclohexanone to cyclohexanol by in situ-formed hydrogen over Cu catalyst under hydrothermal conditions was reported at first. Among the catalysts tested, Cu exhibited high catalytic activity for the conversion of cyclohexanone, and the highest yield of 100% was obtained when Zn acted as reductant. The experiment was carried out by using gaseous hydrogen as the external hydrogen source indicated that the yield of 75.1% was lower than in situ-formed hydrogen by oxidation of Zn in water. The present study provides an efficient route by environmentally benign, commercially available Cu powder as a catalyst for cyclohexanone conversion to cyclohexanol.

1. Introduction

Cyclohexanol has been considered as very important intermediate and is widely used in the synthesis of hexane diacid and hexanolactam. Moreover, cyclohexanol could also be used in pharmaceuticals, plasticisers, surfactant, paint, industry solvent and so on. Due to its importance, much attention has been paid to developing efficient methods for the production of cyclohexanol in recent years. Among these processes, catalytic hydrogenation of cyclohexanone to cyclohexanol is an attractive route since the reaction proceeds under mild conditions.

We all know that the hydrogenation of ketones to alcohols is an important reaction in organic chemistry [1,2]. Cyclohexanone is a significant by-product in the degradation process of lignocellulose. Lignocellulose is an important biomass which makes up a high proportion of biomass [3]. Besides, biomass and biomass-derived compounds as a promising renewable resource instead of fossil fuel is attracting more and more attention because they can provides not only clean energy but also raw material for chemical industry [4–7]. Therefore, the conversion of biomass-derived cyclohexanone to produce cyclohexanol will be more meaningful.

Currently, catalytic hydrogenation of cyclohexanone to cyclohexanol attracts more and more attention due to its promising use in the field of green chemistry [8–10]. Bhar et al. reported the hydrogenation of ketones to the corresponding alcohols by aluminum powder (5 eq.) in the presence of sodium hydroxide in MeOH:H_2O = 2:1, the yield of cyclohexanol was only 19% [8]. Campbell et al. used Meerwein-Pondorf-Verley reduction by aluminum complexes in toluene at room temperature, after 2 h, the yield of cyclohexanol reached 96% [9]. Fujihara et al. used copper complexes as catalyst and Ph_2SiH_2 as hydrogen source in toluene at room temperature, the catalytic activity was good. However, they used complicated and toxic complexes, and the hydrogen source was expensive [10]. Other noble metal, such as Ir, [11] Rh, [12] Ru, [13] can also showed high catalytic activity in the conversion of cyclohexanone and obtained good results. However, these previous works still have some obvious defects, such as expensive prepared noble metal catalysts, [11–13] organic solvents [8–10] [12,13] and longer reaction times (6–12 h).[11] Therefore, one of the great challenges is to develop a useful conversion process of cyclohexanone in the presence of high-efficiency commercial catalysts. As a solvent, water has some merits that other organic solvent doesn't have, such as cheap, non-toxic, non-flammable, non-explosive

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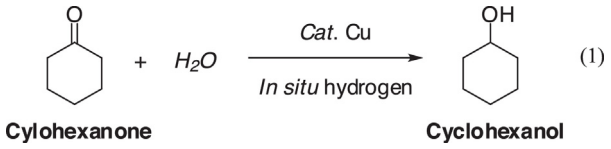
and environmental friendly [14]. If water could be widely used as a solvent for organic reaction, it would bring about enormous achievement in environmental, economic and safety aspects [15].

In previous works, we and other groups had developed many methods to convert biomass and biomass-derived compounds to value-added chemicals in high-temperature water [16–18]. For example, we developed an efficient process for the selective conversion of glucose to lactic acid under alkaline hydrothermal conditions with the highest yield of 25% [19]. Recently, we reported a method for the formation of ethylene glycol from glycolide over CuO in water, and high yield of 94% was achieved [16]. Also we also developed catalytic conversion of ethyl lactate to 1,2-propanediol in the presence of CuO with the yield of 93% [20].

Based on the studies above, we herein present a highly efficient hydrothermal conversion of biomass-derived cyclohexanone to cyclohexanol with high yield and high selectivity using *in situ*-formed hydrogen in water in the presence of Cu catalyst. A mechanism of cyclohexanone conversion was also proposed (Eq. 1).



2. Experimental

2.1. Experimental materials

Cyclohexanone (≥ 99.5%) as the initial reactants was purchased from J&K Scientific Ltd. Cyclohexanol (≥ 98.5%) was used for quantitative analysis. Zn (200 mesh, Sinopharm Chemical Reagent Co., Ltd) was used as the reductant. Fe, Fe_2O_3, Fe_3O_4, Cu, CuO, Cu_2O, Ni, NiO, Co, SiO_2, ZrO_2, Al_2O_3, TiO_2, Pd/C, active carbon (AR, 200mesh, Sinopharm Chemical Reagent Co., Ltd) and Mn (AR, 200 mesh, Aladdin) and Sn (AR, 200 mesh, Sigma–Aldrich) were also used in the experiments. And two catalysts, $Cu(OH)PO_4$ and $CuFe_2O_4$,were prepared by ourselves according to the recent publication [21].

2.2. Experimental procedure

All the experiments were performed in a Teflon-lined steel batch reactor whose internal volume is 30 mL. Cyclohexanone (0.193 mmol, 20 μL) was used for all experiments in this study. The procedure for the synthesis of cyclohexanol was as follows. First of all, desired cyclohexanone, deionized water, reactant and catalyst were loaded into reactor. Then, after filling in with nitrogen to remove air, the reactor was putted into a drying oven. After a certain period of time, we took out the reactor from drying oven immediately. Due to the oven setting, it would take 20 minutes to be preheated to the desired temperature, so we prolonged 20 minutes to reaction times. The reactor was cooled by an air fan. Finally, liquid sample was collected and filtered by 0.45 μm Syringe Filter. Solid sample was collected and washed by deionized water for several times and dried in drying oven at 60 °C for 24 h. The samples would be analysed later. The schematic diagram of reactor and drying oven was shown in Fig. SI-1.

2.3. Product analysis

After the reaction, liquid samples were confirmed with GC-MS (Agilent 7890A GC system, 5975 C inert MSD with Triple-Axis Detector) equipped with an HP Innowax polyethylene glycol capillary column (30 m × 250 μm × 0.5 μm). The qualification of cyclohexanol was confirmed with GC-FID (Agilent 7890A GC system, 5975 C inert MSD with Triple-Axis Detector) equipped with an HP Innowax polyethylene glycol capillary column (30 m × 250 μm × 0.5 μm). The solid samples were analysed with X-ray diffraction (Shimadzu, Lab-XRD-6100). The total organic carbon concentration was confirmed by a TOC Analyzer (Shimadzu TOC-V).

The yield of cyclohexanol was calculated on the basis of the following equation:

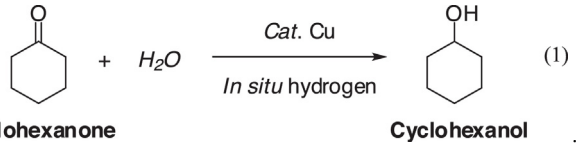
$$\text{The yield}(\%) = \frac{\text{The mole of cyclohexanol obtained}}{\text{The mole of cyclohexanone}}$$

3. Results and discussion

3.1. Catalyst screening

Initially, a series of experiments were carried out to investigate the feasibility of converting cyclohexanone to cyclohexanol in the presence of 5 mmol metal or metal oxides and 25 mmol Zn with 25% water filling (7.5 mL H_2O) at 250 °C for 150 min. The results are summarized in Table 1. The conversion of cyclohexanone was higher and cyclohexanol yield of 92.2% was achieved in the presence of both Cu and Zn (entry 1). It is obvious that the unique peak of desired cyclohexanol and 100.1 of its mass-to-charge ratio (m/z) can be observed by GC-MS spectrum as shown in Fig. 1(a). From Fig. 1(b), the peak of cyclohexanone is getting smaller and smaller until disappearing completely while the peak of cyclohexanol becomes bigger gradually as the time increased from 0 to 150 min, indicating that cyclohexanone was converted completely. Various Cu complexes, such as CuO, Cu_2O, $Cu_2(OH)PO_4$ and $CuFe_2O_4$, were investigated and gave desired products in moderate to high yields, but the yields were not superior to that obtained with Cu catalyst (entries 2–5). Co, Sn, Ni and NiO were also effective for the conversion of cyclohexanone to afford good yields (entries 6–9). However, other metals or metal oxides, such as Fe, Fe_2O_3,

Table 1
Catalyst screening on the yield of cyclohexanol.[a]



Entry	Reductant	Catalyst	Cyclohexanol (%)
1	Zn	Cu	92.2
2	Zn	Cu_2O	71.2
3	Zn	CuO	70.5
4	Zn	$Cu_2(OH)PO_4$	47.4
5	Zn	$CuFe_2O_4$	57.6
6	Zn	Co	86.7
7	Zn	Sn	64.0
8[b]	Zn	Ni	70.8
9	Zn	NiO	75.4
10	Zn	Fe	18.2
11	Zn	Fe_2O_3	15.4
12	Zn	Fe_3O_4	5.3
13	Zn	SiO_2	8.7
14	Zn	ZrO_2	14.4
15	Zn	Al_2O_3	17.8
16	Zn	TiO_2	11.1
17	Zn	Pd/C	5.0
18	Zn	Mn	16.2
19	Zn	active carbon	9.7
20	Zn	–	11.5
21	–	Cu	0
22	–	–	0

[a] Reaction conditions: [cyclohexanone (0.193 mmol, 20 μL), 25 mmol Zn, 5 mmol catalyst, 25% water filling (7.5 mL H_2O), 250 °C, 150 min].
[b] Byproduct phenol of 17.0% was obtained with the conversion of 87.8%.