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Short Communication

Hydroxylation of phenol catalyzed by different forms of Cu-alginate with hydrogen peroxide as an oxidant

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ABSTRACT

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1. Introduction

The catalytic hydroxylation reaction has been a topic of concern due to its core role in a variety of chemical processes for producing bulk and fine chemicals. Heterogeneous catalysts are particularly attractive ascribed to their favorable activity, selectivity and easy separation. While researchers have demonstrated that design of suitable heterogeneous catalysts has been an important area in hydroxylation reaction. Recently, several catalysts have been utilized in this reaction, such as zeolites [1–3], heteropolyacids [4], metal oxides [5], hydrotalicite-like compounds [6–8], nanoparticles [9] and mesoporous materials [10–12]. However, complexity, high cost and toxicity in the preparation and utilization process restrict on their wildly application. Consequently, the present research focus is on exploring new catalysts that are cheap, widely abundant and more environmentally friendly.

Alginates are important, naturally occurring biopolymers and the block copolymers of uronic acids, more specifically $(1 \rightarrow 4)$ -linked β -D-mannuronic (M) and α -L-guluronic (G) residues [13,14]. Sodium alginate can be exchanged by metal cations (e.g. Ca²⁺, Ba²⁺ and Fe²⁺) and then be coordinated with the –OH of the carboxylate groups to generate the ion-cross-linked alginates [15–17]. They have been used in several applications including wound dressing and fiber materials [18,19].

Cu (II) alginate has been reported to have excellent activity for the oxidation of organic substances, such as the cycloaddition of alkynes and oxidative of naphthols [20]. However, no reports focused on the

synthesis of biopolymer and metal-cross-linked Cu-alginate catalysts for the phenol hydroxylation.

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Copper alginate (dry beads and powder) catalysts were prepared using four concentrations of copper chloride

dihydrate and sodium alginate. The resulting catalysts were characterized by FT-IR, ICP-AES, SEM, EDX

and nitrogen physisorption measurements. The results of phenol hydroxylation showed that the catalytic

activities of these catalysts are related to the Cu (II) content. The highest conversions of phenol were

52.9% and 62.5% over dry beads and powder, respectively, with a catechol-to-hydroquinone ratio of 3:2.

In the current study, a process was designed to prepare a series of Cu-alginate dry bead and powder catalysts. These catalysts were characterized by inductively coupled plasma atomic emission spectroscopy (ICP-AES), Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), energy dispersive X-ray (EDX) and nitrogen sorption analysis. The catalysts were utilized in phenol hydroxylation with hydrogen peroxide (30 wt.%) as an oxidant. The influences of different forms of catalysts for this reaction were investigated, and the results show that both the Cu-alginate dry beads and the powder have favorable catalytic activities for phenol hydroxylation.

2. Experimental

2.1. Catalyst preparation

Four CuCl₂ solutions with different concentrations (0.1, 0.2, 0.3 and 0.4 mol/L) were prepared in 100 mL of distilled water. Sodium alginate was dissolved in distilled water at a concentration of 4% (w/v) and then dropped into a CuCl₂ solution through a syringe with a 2 mm-diameter needle. The reaction proceeded at 50 °C for 6 h with gentle (200 rpm) or intense (1200 rpm) stirring to form gel beads or powder (Scheme 1), and then these catalysts were separated from the solution and washed with distilled water. After dried at 40 °C for 3 days, the dry beads and powder were obtained. The above catalysts were denoted as Cu-ALG-d-x and Cu-ALG-p-x, where ALG-d and ALG-p represent alginate dry beads and powder, respectively, and x represents the content of Cu (II) (wt.%) in the catalysts.



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Scheme 1. Schematic presentation of the preparation of Cu-alginate.

2.2. Catalyst characterization

FT-IR spectra were recorded on a Nicolet IS10 IR spectrophotometer. The samples were finely ground with KBr and pressed into a self-supporting wafer. The content of Cu (II) in the alginates was determined by a Leeman Prodigy Spec ICP-AES. All determinations were conducted at least in triplicate. The external morphology of the dry beads and powder, and the elemental concentration distribution were examined using a JEOL JSM-5600LV SEM with an EDX system (EDAX-Falcon). The nitrogen adsorption/desorption measurement was performed on a Micromeritics ASAP 2020 M surface area and porosity analyzer.

2.3. Catalyst test

Phenol hydroxylation with H_2O_2 was carried out in a three-necked round bottom flask equipped with a reflux condenser. First, 1.0 g (10 mmol) of phenol was dissolved in 30 mL of distilled water, and 0.05 g of catalyst was added.Then, 2.0 mL (20 mmol) of H_2O_2 (30%) was added within 30 min. The solution was stirred for 2 h at 70 °C. The concentration of residual H_2O_2 was determined by the iodometric titration. The products were analyzed by gas chromatography (Agilent GC6890) through an HP-5 column using a flame ionization detector (FID).

The characterization results of the concentrations of phenol, catechol (CAT), hydroquinone (HQ) and p-benzoquinone (BQ) were evaluated using the equations given below. The conversion of phenol was expressed by X_{phenol} :

$$X_{phenol}(\%) = 100 \times (C_{b,phenol} - C_{a,phenol})/C_{b,phenol}$$

where $C_{b, \text{ phenol}}$ and $C_{a, \text{ phenol}}$ are the molar concentrations of phenol before and after the reaction, respectively. The selectivity of the product is shown by S_n :

$$S_p(\%) = 100 \times C_p / (C_{b,phenol} - C_{a,phenol})$$

where C_p was the molar concentration of the product and p = CAT, HQ or BQ. The conversion of H_2O_2 is shown by X_{H2O2} :

$$X_{H2O2}(\%) = 100 \times (C_{b,H2O2} - C_{a,H2O2})/C_{b,H2O2}$$

where $C_{b, H2O2}$ and $C_{a, H2O2}$ are the molar concentrations of H_2O_2 before and after the reaction, respectively.

3. Results and discussion

The gel beads had regular sizes, and their diameters were approximately 3–5 mm, with a certain mechanical strength and elasticity (Fig. S1). After drying, the gel beads shrunk to 1–2 mm and became more compact, and their surfaces became tough. The powder was brown and ground to 80 mesh for phenol hydroxylation.

The FT-IR spectra reveal the changes in the absorption bands for the surface functional group of the sodium alginate before and after reacting with CuCl₂ (Fig. 1). The stretching vibrations of -OH usually form a broad band in the region of $3100-3700 \text{ cm}^{-1}$. In this study, the peak shifted from 3400 to 3426 cm⁻¹ after sodium alginate reacted with CuCl₂ to form the Cu-alginate. The increase in the adsorption peak should be attributed to the attachment of Cu^{2+} on the -OH group. In addition, both the C=O and C-O in the carboxyl group (-COOH) shifted slightly in frequency after cross-linking. The redshifting (from 1639 to 1618 cm⁻¹) of the C=O band could be attributed to the –OH coordination with Cu²⁺, which led to the decrease in the stretching force constant of the carboxyl group [21,22]. In addition, the C–O in the carboxyl group shifted to a higher frequency (from 1386 to 1411 cm⁻¹), which was attributed to the high electron density induced by the copper sorption onto the adjacent hydroxyl group. The stretching vibrations of C-O for both sodium alginate and copper alginate located at 1028 cm⁻¹ indicated that the C-OH on the ring did not participate in the coordination. Compared with Fig. 1A, B and C both have absorption bands at 673 cm^{-1} , which are assigned to the stretching vibration of the Cu = 0 bond.



Fig. 1. FT-IR spectra of sodium alginate (A), Cu-alginate gel beads (B) and Cu-alginate powder (C).

The Cu (II) content of the products before and after phenol hydroxylation was determined by ICP-AES (Table S1). The results showed that the Cu (II) content of the Cu-alginate dry beads and powder increased with the increase in the CuCl₂ concentration. When the CuCl₂ concentration increased from 0.1 to 0.3 mol/L, the Cu (II) content of the dry beads and powder increased significantly (from 9.7% to 15.3% and 11.4% to 17.7%, respectively). However, when the CuCl₂ concentration exceeded 0.3 mol/L, no changes in the Cu (II) content in the Cu-alginate were apparent. This result should be attributed to the saturation of the cross-linked products. To test if metal ions were leaching out from the catalysts, which were analyzed using ICP-AES to detect the Cu (II) content after once hydroxylation reaction. The results showed that a trace amount of Cu was lost (The leaching amount of Cu ions was lower than 3 wt.%.), which accounts for the recoverability and reusability of the Cu-alginate catalysts.

The external morphology of the powder and dry beads was examined by SEM (Fig. 2). As shown in Fig. 2A and B, the powder particles were present in a bulky form, and their sizes were at the micron-scale level. Some floccules and stratified structures were found on the surface of the blocks. Fig. 2C and D showed that the dry beads had a rough surface, on which some sagging was noted. Compared with the gel beads, the dry beads were more compact, which enhanced the mechanical stability of the dry beads. The SEM images of the Cu-alginate dry beads after reacting three times were shown in Fig. 2E and F. From these figures, it could be determined that after washing with ethanol, the surface of the dry beads was covered by tarry by-products of the hydroxylation reaction, which reduced the accessibility of the active sites for H_2O_2 and phenol [23]. This should be one of the reasons that caused the activities' reducing of the catalyst.

Besides, the elemental concentration distribution and the quantitative analyses of the dry beads can be analyzed using the analysis of SEM/EDX. The Cu ions distribution mapping of EDX analysis for the catalyst before and after hydroxylation is illustrated in Fig. 3A and B. The bright white points in Fig. 3A and B represented the signal of copper element on the surface of the dry beads. The result showed



Fig. 2. SEM images of Cu-alginate powder (A and B), Cu-alginate dry beads before (C and D) and after (E and F) phenol hydroxylation.



Fig. 3. Mapping EDAX analysis of Cu element for Cu-ALG dry beads before (A) and after (B) phenol hydroxylation reaction.

that after hydroxylation and without any washing, the amount of Cu ions on the surface of the catalyst reduced a lot. Combined with the results of the ICP-AES, the reduction of the Cu ions should be attributed to the coverage of the catalysts' surface.

The spectrum of dry beads by using elemental microprobe analysis of EDX is illustrated in Fig. S2. From these figures, it could be found that the wt.% of Cu ions on the dry beads surface increased from 27.37% to 35.69% with the concentration of CuCl₂ increasing from 0.1 to 0.4 mol/L, which indicated that the active sites increased with the CuCl₂ concentration increasing [24].

To investigate the specific surface area and porosity of the Cu-alginate dry beads and powder, a BET test was performed. The results of nitrogen sorption ($<1 \text{ cm}^3/\text{g}$) and surface area ($<1 \text{ m}^2/\text{g}$), calculated by the BET method, indicated that the dry beads and powder have no pores with those small dimensions [25]. Thus, the sags on the surface were likely caused by the depressions of the surface, which occurred during the drying phase.

Phenol hydroxylation catalyzed by copper has long been a subject of study. However, no reports have been published with Cu-alginate as the catalyst for this reaction. The catalytic performance of various Cu-alginate catalysts in phenol hydroxylation was listed in Table 1. The result of a blank experiment under the same reaction conditions showed that in the absence of the catalyst, H₂O₂ alone was unable to oxidize phenol to a significant extent (only 5.3%, entry 1). After the catalyst was added, an obvious increase in conversion was observed. For both the dry beads and powder, the conversion increased as the Cu (II) content increases (entries 2–9). Additionally, the turnover frequency (TOF: moles of reacted substrate over moles of Cu per hour) was also employed to evaluate the reaction rate. With regard to the dry beads, when the Cu (II) content increased from 9.7% to 15.3% (entries 2-4), the TOF value changed little, while the phenol conversion and H₂O₂ conversion increased from 33.1% to 52.7% and 88.2% to 96.7%, respectively, which is higher than the value reported in the literature [26,27]. It is believed that a large number of copper active sites increased the

Table 1	
Catalytic performance of Cu-alginate fo	or phenol hydroxylation.

Entry	Catalyst	X _{phenol} (%) ^a	Х	Selectivity/% ^c			TOF
			н202 (%) ^b	CAT	HQ	BQ	$(h^{-1})^{d}$
1	Blank	5.3	61.4	59.1	38.8	2.1	-
2	Cu-ALG-d-9.7	33.1	88.2	58.9	38.2	2.9	2.10
3	Cu-ALG-d-14.1	48.6	94.0	57.1	40.0	2.9	2.13
4	Cu-ALG-d-15.3	52.7	96.7	59.5	38.4	2.1	2.14
5	Cu-ALG-d-15.5	52.9	96.8	57.4	40.6	2.0	2.13
6	Cu-ALG-p-11.4	39.2	90.2	57.1	40.2	2.7	2.12
7	Cu-ALG-p-14.9	51.4	95.3	57.3	40.3	2.4	2.14
8	Cu-ALG-p-17.7	61.2	99.4	56.5	41.4	2.1	2.15
9	Cu-ALG-p-18.1	62.5	100.0	57.4	40.4	2.2	2.15

^a All reactions were performed under the following conditions: phenol 1.0 g, catalyst 50 mg, phenol/H₂O₂ molar ratio 1:2, solvent (water) 30 mL, temperature 70 °C, time 2 h. ^b X_{H2O2} (%) = 100×($C_{b, H2O2} - C_{a, H2O2}$)/C_b, H2O2.

^c Product distribution given on a tar-free basis.

^d TOF: moles of substrate converted per mole of metal (in the catalyst) per hour.



Fig. 4. Catalytic performance of Cu-ALG-d-15.3 in the phenol hydroxylation reaction.

decomposition rate of H₂O₂ [24]. Moreover, the molar ratio of catechol to hydroquinone nearly reaches a constant being 3:2 and the distribution of CAT and HQ in the products is similar to the value reported in the literature [28,29]. The conversion changed little when the loaded Cu (II) reached 15.5% (entry 5), which was likely attributed to the saturation of Cu-ALG-d. This result was consistent with the results of the ICP-AES.

In the case of dry beads, the conversions of phenol catalyzed by the powder have the same trends (entries 6-9). Considering that they were prepared from the same concentration of CuCl₂, the powder carried more Cu (II) and possessed higher catalytic activity than the dry beads. Therefore, the activity of Cu-alginate catalysts depends on the immobilized content of Cu (II) ions.

Because of their superior mechanical stability, the Cu-alginate dry bead catalyst had been used to investigate their reusability [29]. The Cu-ALG-d-15.3, which has favorable catalytic activity, was used 3 times for phenol hydroxylation (Fig. 4). All the 3 runs were under the same condition: the amount ratio of phenol to catalyst was 20:1 and the molar ratio of phenol to H_2O_2 was 1:2. After each run, the spent catalyst was recovered by filtration, washed thoroughly with ethanol and dried. The weighed masses of the Cu-ALG-d-15.3 catalyst were 50, 44, and 37 mg, and the used amount of phenol were 1.0, 0.88 $(44 \times 10/50)$ and 0.74 $(37 \times 10/50)$ g, as well the used H₂O₂ were 2.0, 1.76 ($44 \times 20/50$) and 1.48 ($37 \times 20/50$) mL, corresponding to the conversions of phenol were 52.7%, 48.7%, and 46.5%, for the 1st, 2nd and 3rd runs, respectively. The selectivities of catechol to hydroquinone were all 3:2. Combining the results of the SEM, the activity of the Cu-alginate catalyst decreased slightly after three consecutive phenol hydroxylation cycles, which is possibly due to the surface's coverage by tar [10,30].

4. Conclusion

A series of ion-cross-linked Cu-alginate dry beads and powder were synthesized through ion exchange, followed by the coordination of alginate and Cu (II) ions. The catalysts exhibited outstanding catalytic performance for phenol hydroxylation with H₂O₂ as an oxidant in water. The catalytic activities were associated with the immobilized content of the Cu (II) ions. The results of the experiment tested the reusability of Cu-ALG-d-15.3 indicate that after simple treatment, the catalyst retained the majority of its initial activity.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10. 1016/j.catcom.2012.04.008.

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