



Short Communication

Synthesis of binary Cu–Pd–alginates dry bead and its high catalytic activity for hydroxylation of phenol

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ABSTRACT

A series of binary Cu–Pd–alginate catalysts was prepared and their catalytic activities for phenol hydroxylation were investigated. The binary catalysts were characterized by UV–vis/DRS, FT-IR, ICP-AES, XPS, SEM and EDX measurements. The results of phenol hydroxylation illustrated that the conversions of phenol were associated with the immobilized content of the Cu²⁺ ions, as well the selectivities to dihydroxybenzene were determined by the immobilized content of the Pd²⁺ ions. The highest conversion of phenol catalyzed by Cu–Pd–ALG-30-1 was 53.9%, with selectivities to catechol and hydroquinone being 61.3% and 38.2%, respectively.

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1. Introduction

Dihydroxybenzenes (catechol and hydroquinone) are high value chemicals and catalytic hydroxylation of phenol is the most appropriate way for producing the catechol (CAT) and hydroquinone (HQ) [1,2]. Compared to the homogeneously catalyzed reaction, the heterogeneously catalyzed hydroxylation with solid catalysts has attracted more interest due to favorable properties of the catalysts (eco-friendly nature and catalyst recoverability) [3,4]. Therefore, the search for new heterogeneous catalysts is one of the most important current topics for both industrial and academic researches. Recently, several catalysts have been utilized in this reaction, such as zeolites, heteropolyacids, hydrotalcite-like compounds, Schiff base and mesoporous materials [5–9]. However, complexity, high cost and toxicity in the preparation and utilization process restrict their wider applications. Moreover, the trend to develop new catalysts with high efficiency and catalytic stability is increasing due to the environmental concerns together with economic considerations. Accordingly, researchers have focussed on exploring new catalysts that are easier obtained and more environmentally friendly.

Many studies have revealed that the noble metals (Pd, Pt, Au, etc.) supported on different supports possess high catalytic activities in a number of oxidation reactions and the monometallic catalysts can be modified by adding another metal to improve the dispersion, adsorption and activity in the oxidation of hydrocarbons [10,11]. As a naturally occurring biopolymer, alginates have attracted much attention due to their wide applications, such as metallurgy, chemical

engineering, food industry and so on. Recently the alginates have been utilized as metal supports [12,13]. Sodium alginate can be exchanged by metal cations which can then be coordinated with the –OH of the carboxylate groups to generate ion-crosslinked alginates [14,15]. Our group has reported the Cu–alginate dry beads as an efficient and environmental-friendly catalyst for the direct hydroxylation of phenol under mild reaction conditions [16].

In recent years, many reports have been published in the application of Pd as active center for hydroxylation of benzene to phenol [17,18], but few reports were found on the application of Pd for phenol hydroxylation, even co-catalytic Cu–Pd catalysts. Considering the excellent catalytic activity of the noble metal Pd and trying to explore the catalytic effects of the Cu and Pd co-catalyst in phenol hydroxylation reaction, in the current research, a series of binary Cu–Pd–alginate (Cu–Pd–ALG) catalysts was prepared as illustrated in Scheme 1, and their catalytic activities for phenol hydroxylation were investigated.

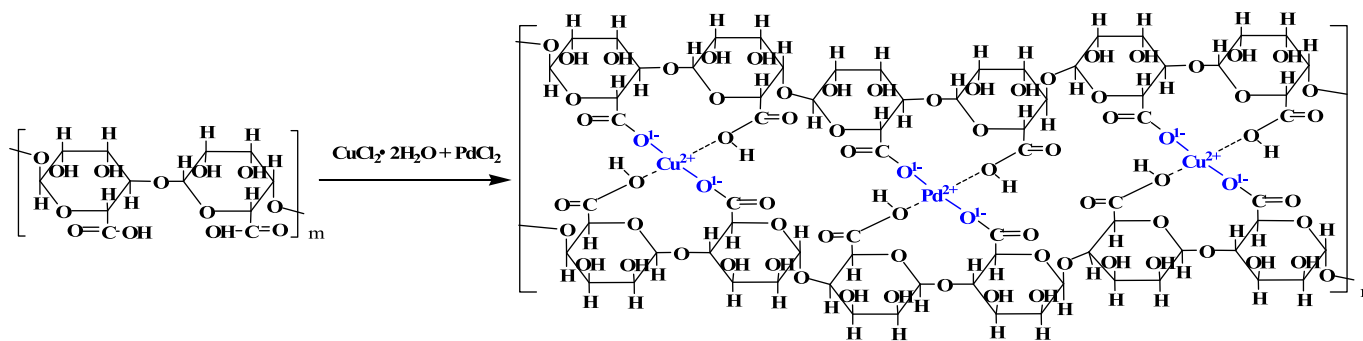
2. Experimental

2.1. Catalyst preparation

Several CuCl₂ and PdCl₂ solutions with a range of concentrations were prepared in 100 mL of distilled water. Sodium alginate was dissolved in distilled water at a concentration of 4% (w/v) and then transferred drop wise into the metal solution using a syringe. The reaction proceeded at 50 °C for 6 h with gentle (200 rpm) stirring to form gel beads, and then these catalysts were separated from the solution and washed with distilled water until the distilled water became colorless. After being dried at 40 °C for 3 days, the dry beads were obtained. The above catalysts were denoted as Cu–Pd–

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Scheme 1. Pathway of the synthesis of Cu-Pd-ALG dry beads catalyst.

ALG-*x*-*y*, where *x* and *y* represent the molar concentration of Cu and Pd in the raw materials.

2.2. Catalyst characterization

UV-vis diffuse reflectance spectra (UV-vis/DRS) were recorded at ambient atmosphere in the wavelength range of 200–800 nm using a Hitachi U-4100 spectrometer. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet IS10 IR spectrophotometer. The contents of Cu and Pd in the alginates were determined by a Leeman Prodigy Spec inductively coupled plasma atomic emission spectroscopy (ICP-AES). All determinations were conducted at least in triplicate. X-ray photoelectron spectroscopy (XPS) was performed in Thermo ESCALAB 250 spectrometer. The external morphology of the dry beads and the elemental concentration distribution were examined using a JEOL JSM-5600LV SEM with an EDX system (EDAX-Falcon).

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 drop wise 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 $C_{b, phenol}$ and $C_{a, phenol}$ are the molar concentrations of phenol before and after the reaction, respectively. The selectivity of the product is shown by S_p :

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

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

$$X_{H_2O_2}(\%) = 100 \times (C_{b, H_2O_2} - C_{a, H_2O_2}) / C_{b, H_2O_2}$$

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

3. Results and discussion

UV-vis/DRS spectroscopy was used to confirm the existence of the Cu^{2+} and Pd^{2+} ions in the structure of the crosslinked catalysts. The UV-vis/DRS spectra of the Cu-Pd-ALG are presented in Fig. 1. The broad band at around 500–700 nm was assigned to electronic d-d transitions in the Cu^{2+} ions [19]. As well, the absorption band at 287 nm was attributed to Pd-O charge transfer transition (the chemical state of Cu and Pd in the Cu-Pd-ALG-30-3 were confirmed by XPS, see Fig. S1) [20]. All the above indicated that the Cu^{2+} and Pd^{2+} ions had crosslinked with the alginate successfully.

The FT-IR spectra of sodium alginate and Cu-Pd-ALG are shown in Fig. 2. The stretching vibration of -OH in sodium alginate forms a broad band at 3400 cm^{-1} , and after reaction with $CuCl_2$ and $PdCl_2$, the peak shifted from 3400 to 3437 cm^{-1} . The blue shift of the adsorption peak should be attributed to the attachment of the Cu^{2+} and Pd^{2+} ions on the -OH group. In addition, both the C=O and C-O in the carboxyl group (-COOH) shifted slightly in frequency after crosslinking. The red-shifting (from 1639 to 1630 cm^{-1}) of the asymmetrical stretching vibration absorption band of carboxyl group could be attributed to the -OH coordination with Cu^{2+} and Pd^{2+} , which led to decrease in the stretching force constant of the carboxyl group [21]. In addition, the C-O bond in the carboxyl group shifted to a higher frequency (from 1386 to 1406 cm^{-1}), which was mainly attributed to the coordination of Cu or Pd ions to the carboxylate ion ($-COO^-$), as well the high electron density induced by the metal ions sorption onto the adjacent hydroxyl group. The stretching vibrations of C-O for both sodium alginate and Cu-Pd-ALG located at 1025 cm^{-1} indicated that the C-OH on the ring did not participate in the coordination.

The external morphology of the Cu-Pd-ALG-30-1 dry beads was examined by SEM (Fig. 3). Fig. 3A shows that the dry beads had a

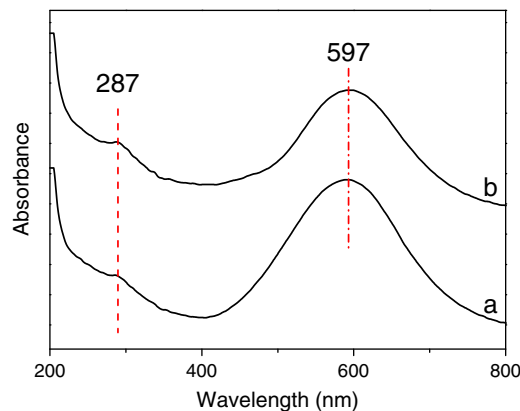


Fig. 1. UV-vis/DRS spectra of Cu-Pd-ALG-30-3 (a) and Cu-Pd-ALG-30-1 (b).

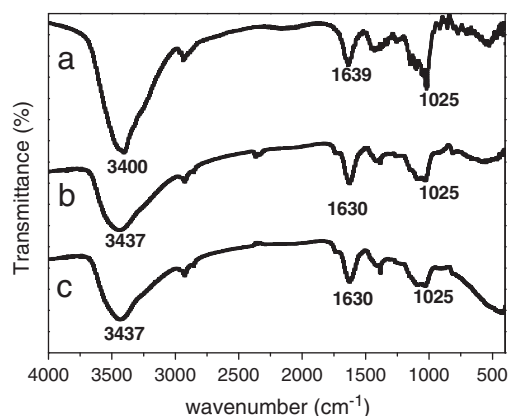


Fig. 2. FT-IR spectra of sodium alginate (a), Cu-Pd-ALG-30-3 (b) and Cu-Pd-ALG-30-1 (c).

rough surface, on which some saggings are noted. The diameter of the dry beads ranged from 1–2 mm. As shown in Fig. 3B, some floccules and stratified structures were found on the surface of the dry beads.

The spectra of Cu-Pd-ALG dry beads by using elemental microprobe analysis of EDX are illustrated in Fig. S2. The results indicated that no Na⁺ ions existed on the dry beads surface. Also when the molar ratio of Cu/Pd decreased from 30:1 to 30:3, the wt.% of Cu²⁺ and Pd²⁺ ions on the dry beads surface changed from 67.76% to 59.34% and 0.75% to 3.15%, respectively.

The Cu²⁺ and Pd²⁺ contents of the dry whole beads before and after phenol hydroxylation were determined by ICP-AES (Table 1). The results illustrated that the Cu²⁺ content of the Cu-Pd-ALG dry beads increased with the increasing of the concentration of CuCl₂ in

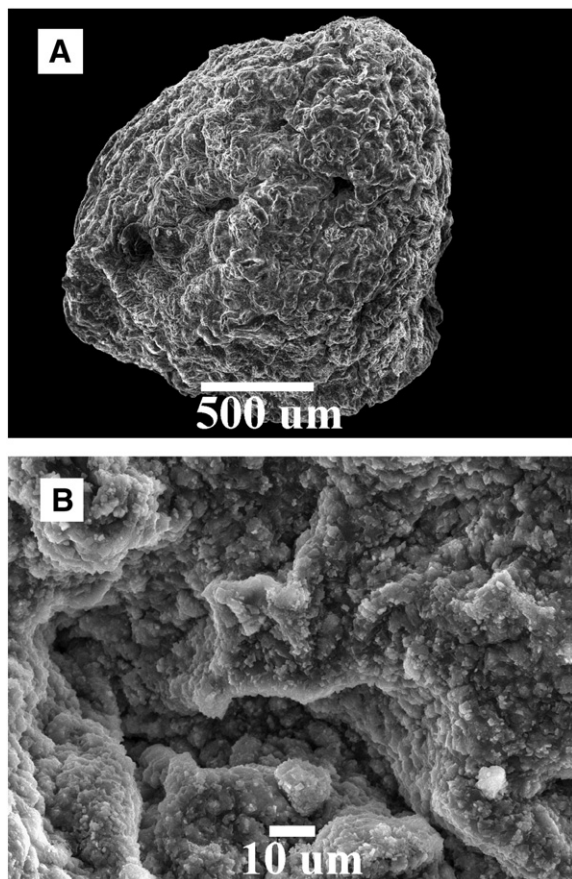


Fig. 3. SEM images of Cu-Pd-ALG-30-1.

Table 1

The contents of Cu and Pd in alginate dry beads.

Entry	Molar ratio of Cu:Pd (raw materials)	CuCl ₂ /mmol/L	PdCl ₂ /mmol/L	Cu content (BR ^a)/%	Pd content (BR)/%	Cu content (AR)/%	Pd content (AR)/%
1	24:6	240	60	12.83	2.13	12.75	2.11
2	27:3	270	30	12.92	1.39	12.79	1.38
3	28:2	280	20	13.55	1.24	13.42	1.23
4	29:1	290	10	13.94	0.91	13.79	0.90
5	30:1	300	10	14.76	0.87	14.61	0.87
6	30:2	300	20	14.44	1.35	14.31	1.34
7	30:3	300	30	14.41	1.36	14.32	1.35
8	–	300	–	15.31	–	15.22	–

^a BR means before reaction and AR means after reaction.

the raw material. Consulting entries 1 to 5, when the CuCl₂ concentration increased from 240 to 300 mmol/L, the Cu²⁺ contents of the dry beads increased from 12.83% to 14.76%; when the concentration of PdCl₂ decreased from 60 to 10 mmol/L, the Pd²⁺ content decreased from 2.13% to 0.87%. Consulting entries 5 to 7, when the concentration of CuCl₂ was kept at 300 mmol/L, increasing the concentration of PdCl₂, the content of Cu²⁺ in the catalyst decreased, which should be resulted by that the Pd²⁺ ions crosslinked with the alginate instead of some Cu²⁺ ions. However, when the PdCl₂ concentration exceeded 20 mmol/L, the change of the Pd²⁺ content in the catalyst was neglectable. This result illustrated that high concentration of Cu²⁺ and Pd²⁺ ions could lead to the saturation of the metals ions crosslinked on the alginate [13,16]. To test if metal ions were leaching out from the catalysts, which were analyzed using ICP-AES to detect the metal ions after hydroxylation. The results showed that a trace amount of Cu²⁺ and Pd²⁺ were lost (both the leaching amount of Cu²⁺ and Pd²⁺ ions were lower than 1 wt.%).

Phenol hydroxylation catalyzed by copper has long been a subject of study. In a previous study, our group investigated the activities of Cu-ALG catalysts for hydroxylation of phenol [16]. And on the basis, the current study concerns binary Cu-Pd-ALG dry beads as the phenol hydroxylation catalyst. The catalytic performance of Cu-Pd-ALG dry beads catalyst in phenol hydroxylation is listed in Table 2. The blank experiment gave only 5.3% of conversion of phenol without catalyst (entry 1). After the catalyst was added, a remarkable increase in conversion was observed. The conversion of phenol increased with the increasing of the Cu²⁺ content (entries 2–6). When the Cu²⁺ content increased from 12.83% to 14.76%, the conversions of phenol and H₂O₂ increased from 44.4% to 53.9% and 92.0% to 97.2%, respectively, which were higher than the values reported in the literature [16,22]. It is believed that a large number of copper active sites increased the decomposition rate of H₂O₂. Moreover, the ratios of CAT to HQ remain

Table 2

Hydroxylation of phenol catalyzed by Cu-Pd-ALG dry bead catalysts.

Entry	Catalyst	X _{phenol} (%) ^a	X _{H₂O₂} (%) ^b	Selectivity/% ^c			TOF (h ⁻¹) ^d
				CAT	HQ	BQ	
1	Blank	5.3	61.4	51.9	38.8	2.1	–
2	Cu-Pd-ALG-24-6	44.4	92.0	61.9	37.9	0.2	2.21
3	Cu-Pd-ALG-27-3	47.8	92.2	62.4	37.3	0.3	2.36
4	Cu-Pd-ALG-28-2	48.2	93.1	61.7	37.9	0.4	2.28
5	Cu-Pd-ALG-29-1	50.6	93.8	61.4	38.1	0.5	2.32
6	Cu-Pd-ALG-30-1	53.9	97.2	61.3	38.2	0.5	2.34
7	Cu-Pd-ALG-30-2	51.8	94.7	61.4	38.2	0.4	2.29
8	Cu-Pd-ALG-30-3	51.4	94.2	61.1	38.5	0.4	2.28
9	Cu-ALG-30	52.7	96.7	59.5	38.3	2.2	2.14

^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 Cu (in the catalyst) per hour.

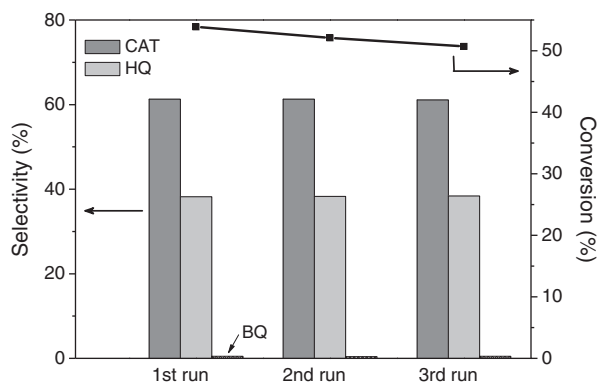


Fig. 4. Catalytic performance of Cu–Pd–ALG–30–1 in phenol hydroxylation. All reactions were performed under the following conditions: phenol/catalyst amount ratio 20:1, phenol/H₂O₂ molar ratio 1:2, solvent (water) 30 mL, temperature 70 °C, and time 2 h. Product distribution given on a tar-free basis.

constant (approximately 1.6:1) under different reaction conditions and the distribution of CAT and HQ in the products is similar to the value reported in the literature [23]. Additionally, regarding Cu²⁺ ions as the active sites in this reaction, the turnover frequency (TOF: moles of reacted substrate over moles of Cu per hour) was also employed to evaluate the reaction rate. Although no obvious changes have been found in the conversion of phenol with the changing of the content of Cu²⁺ ions, a conclusion could be obtained that the TOF values of the Cu–Pd–ALG were higher than the Cu–ALG catalyst. An interesting finding is that the introduction of Pd can greatly reduce the formation of byproducts. Given on a tar-free basis, the selectivity to benzoquinone (BQ) decreased to less than 0.5% (entries 2–8). When the content of Pd²⁺ in catalyst increased, the selectivity to BQ decreased. Considering the economic benefits and the catalytic activity of the binary catalysts, the recyclability of the Cu–Pd–ALG–30–1 was investigated by subjecting the catalyst systems to three cycles of re-using (Fig. 4). Under the same condition, the conversion of phenol decreased from 53.9% to 50.7%, however the CAT/HQ ratio showed very little change, which illustrated excellent stability of the catalyst.

4. Conclusion

A series of ion-crosslinked Cu–Pd–ALG dry beads catalysts has been prepared and their outstanding catalytic performance for phenol hydroxylation with H₂O₂ as an oxidant in water was reported. The binary Cu–Pd–ALG dry bead catalysts have better catalytic activities than Cu–ALG catalyst. The conversion of phenol was associated with the immobilized content of the Cu²⁺ ions, and the introduction of Pd²⁺ ions can reduce the selectivity to BQ effectively.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.catcom.2012.08.015>.

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