

Effect of promoter copper on the oxidative carbonylation of phenol over the ultrafine embedded catalyst Pd–Cu–O/SiO₂

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Abstract

Effect of the promoter copper on the oxidative carbonylation of phenol to diphenyl carbonate (DPC) over the ultrafine embedded catalyst Pd–Cu–O/SiO₂ was studied. The promoter copper is divided into the heterogeneous Cu(II) contained in the catalyst and the homogeneous Cu²⁺ charged into the reactor directly. The heterogeneous Cu(II) promoter reacts with PdO to form CuPdO₂, changing the chemical environment of Pd atoms. This enables the deactivated Pd(0) atoms to easily transfer electrons to the Cu(II) atoms in the crystal lattice of CuPdO₂ to be reactivated. However, excess Cu(II) hinders the reactants from contacting the active centers, producing negative effects on the yield of DPC. The homogeneous Cu²⁺ can promote the change from Pd(0) to Pd(II) more effectively than the heterogeneous Cu(II) because all the Cu²⁺ in the system can work. However, only the Cu(II) incorporated into the crystal lattice of PdO to form the CuPdO₂ can obtain electrons from Pd(0).

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Diphenyl carbonate (DPC) is an industrially important precursor for the production of the polycarbonate by melt polymerization process [1]. Several methods have been developed for manufacturing DPC. Among them, oxidative carbonylation of phenol with CO and O₂ is one of the most attractive methods [2–6]; it is a one-step process with H₂O being the sole by-product, and the use of highly toxic phosgene can be avoided. Homogeneous palladium compounds with co-catalysts have been reported to be a highly efficient catalytic system for the direct synthesis of DPC. Because of the obvious shortcomings of the homogeneous catalysis, more and more scientists are engaged in the study of heterogeneous catalytic synthesis of DPC [7–11]. All the heterogeneous catalysts reported in the references were prepared by the impregnation methods [7–9] or polymer graft techniques [10,11]. It is well known that the active compo-

nents in the impregnated catalysts are located on the surface of the supports and easily leach out leading to the deactivation of the catalyst. However, the catalysts prepared by polymer graft techniques cannot bear high temperatures and some of their macroscopic natures, such as specific surface area, porosity, are not as good as inorganic supports.

To overcome the drawbacks mentioned above, we have designed a novel heterogeneous catalyst, an ultrafine embedded catalyst Pd–Cu–O/SiO₂ [12,13]. In this catalyst, active species is embedded in the silica particles to form the core/shell structure. The molecules of the reactants penetrate the shell through the pore in it to contact the active species and the products escape from the catalysts via the same way. The silica shell acts as the support and a protective layer for the active component simultaneously, which can decrease the loss of the expensive active species effectively. Moreover, the particles of the embedded catalysts are in nano-size. This can decrease the effect of the diffusion and accelerate the reaction

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rate. The water-in-oil (W/O) microemulsion is the selected reaction medium for the preparation of this ultrafine embedded catalyst.

It is well known that palladium compounds are able to promote the oxidative carbonylation of phenol to produce DPC. But this is not a catalytic reaction and only stoichiometric amounts of DPC is obtained when the Pd compounds is the sole component of the catalyst. It has been reported that Pd(II) is readily reduced to Pd(0) by CO in a phenol solution at 50 °C and then loses its activity [6]. If Pd(0) can be reoxidized to Pd(II), a catalytic cycle would become operative. In these systems, continuous in situ regeneration of Pd(II) from Pd(0) by an oxidant (typically, copper, cobalt or manganese salts) is the key step for the efficient catalytic oxidation.

In the ultrafine embedded catalyst, Pd acts as the catalyst for the oxidative carbonylation of phenol to DPC with the aid of Cu promoters which can be divided into two kinds, heterogeneous and homogeneous, and both of them can reoxidize Pd(0) to Pd(II) efficiently. In this paper, the effect of the two kinds of copper promoters on the catalytic synthesis of DPC by oxidative carbonylation of phenol over the ultrafine embedded catalyst Pd–Cu–O/SiO₂ was studied on the basis of the aforementioned work.

1. Experimental

1.1. Preparation of the ultrafine embedded catalyst Pd–Cu–O/SiO₂ in W/O microemulsion

The ultrafine silica embedded palladium–copper oxide catalyst was prepared using a water-in-oil (W/O) microemulsion consisting of polyoxyethylene (10) nonylphenyl (NP-10), cyclohexane, 1-hexanol and aqua ammonia solution of PdCl₂ and Cu(OAc)₂. The concentrations of NP-10 in cyclohexane and PdCl₂ in aqua ammonia were 0.18 and 0.015 mol l⁻¹, respectively. Tetraethyl orthosilicate (TEOS) as a silica source was added to the microemulsion solution and subjected to hydrolysis at 35 °C for 5 h. The molar ratio of water to surfactant was 31. In order to terminate TEOS hydrolysis, ethanol was added to the solution. Then, the solution was centrifuged to separate the SiO₂ precipitate containing the metallic species. The SiO₂ precipitate thus obtained was thoroughly washed with ethanol, dried at 60 °C in vacuum overnight and calcined in the air at 700 °C for 2 h.

1.2. Catalyst characterization

The X-ray diffraction (XRD) studies were carried out by a Rigaku D/Max-2500 X-ray diffractometer. The X-ray photoelectron spectroscopic studies (XPS) were carried out by a PE PHI-1600 using Mg K α radiation (1253.6 eV, 300 W) at a constant analyzer pass energy of 23.5 eV. All the binding energy was calibrated with respect to the standard C 1s (284.6 eV).

1.3. Catalyst evaluation

DPC synthesis by oxidative carbonylation of phenol was carried out in a 100 ml stainless steel autoclave, provided with a magnetic stirrer. Typical reaction conditions were as follows: $T = 80\text{ }^{\circ}\text{C}$, $P = 3.9\text{ MPa}$ (CO/O₂ = 12/1 molar ratio), phenol = 28 mmol, Pd/Cu(OAc)₂/hydroquinone (H₂BQ)/tetrabutylammonium bromide (TBAB) = 1/4.5/60/60 molar ratio, Pd (in the catalyst) = 0.047 mmol, 4A molecular sieve as drying agent, reaction time 4 h. In a typical experiment, the catalyst and co-catalyst along with phenol and the solvent (dichloromethane, CH₂Cl₂), 4A molecular sieve were introduced into the autoclave. Then the autoclave was pressurized with the mixture of carbon monoxide and oxygen. At the end of the reaction the autoclave was cooled to room temperature and vented.

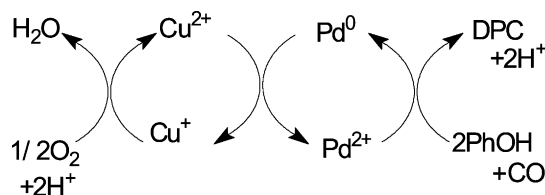
The reaction products were identified and quantified by a capillary gas chromatograph with an FID detector (SP-3420 Gas Chromatograph of BAIF, PEG 20M column, 30 m, 0.25 mm).

2. Results and discussions

The process of oxidative carbonylation of phenol to DPC was first presented by Hallgren et al. [14]. The reaction mechanism is shown in Scheme 1. During the reaction, phenol and CO are catalyzed by Pd(II) to form DPC, while Pd(II) is readily reduced to Pd(0) by CO and loses the catalytic activity. Fortunately, Pd(0) can be in situ reoxidized to Pd(II) by the redox agent, such as copper compounds, to restore the activity. The effect of Cu promoters on the synthesis of DPC was studied in the following chapters. It was found that the Cu promoters are divided into the heterogeneous one that existed in the ultrafine embedded catalyst Pd–Cu–O/SiO₂, denoted as Cu(II), and the homogeneous one that charged into the system during the reaction, denoted as Cu²⁺. Both of them are indispensable for the oxidative carbonylation of phenol to DPC.

2.1. Effect of heterogeneous Cu(II) promoter on the synthesis of DPC

Effect of the Cu(II) content in the ultrafine embedded catalyst Pd–Cu–O/SiO₂ on the oxidative carbonylation of phenol to DPC was studied and the results are shown in Fig. 1. The



Scheme 1. Mechanism of oxidative carbonylation of phenol to DPC over the Pd–Cu catalytic system.

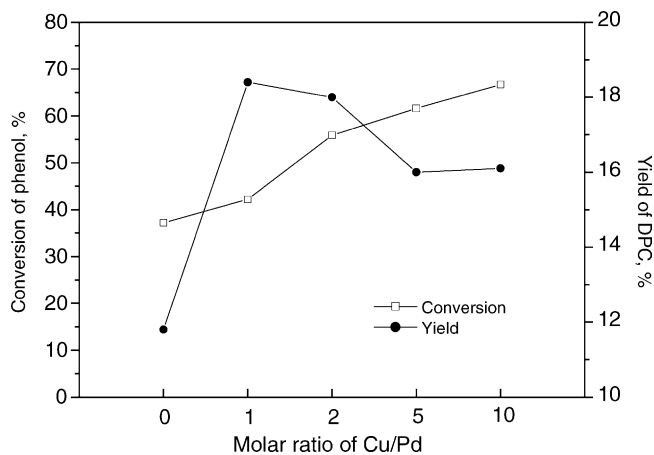


Fig. 1. Effect of the amount of promoter Cu(II) on the synthesis of DPC reaction conditions: phenol, 28 mmol; [Pd], 0.047 mmol; Cu(OAc)₂, 0.21 mmol; TBAB, 2.7 mmol; H₂BQ, 2.7 mmol; MS 4A, 4.0 g; CH₂Cl₂, 20 ml; CO, 3.6 MPa; O₂, 0.3 MPa; reaction temperature, 80 °C; reaction time, 4 h.

catalysts used in the experiments had the same Pd content, while the molar ratios of Cu/Pd were varied. Cu(II) can promote the conversion of phenol because the value increases monotonously with the ratio of Cu/Pd. However, the yield of DPC changes in a manner different from the phenol conversion. The yield of DPC was 11.8% when there was no Cu(II) promoter added. The yield of DPC was 18.4% when the molar ratio of Cu(II)/Pd was unity. The results indicated that the existence of Cu(II) helps to increase the conversion of phenol and the yield of DPC. But the excessive Cu(II) would adversely affected the synthesis of DPC.

To investigate the role of the Cu(II), the ultrafine embedded catalysts Pd–Cu–O/SiO₂ with different Cu(II) contents were characterized by XRD. The results are shown in Fig. 2. The pattern shows a weak diffraction peak corresponding to PdO when the Cu(II) content is null (as shown in Fig. 2e).

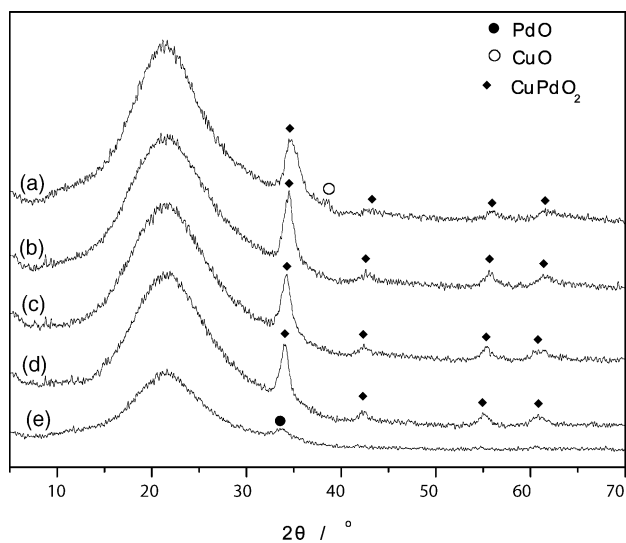


Fig. 2. XRD patterns of the catalysts with different contents of Cu(II). Molar ratio of Cu/Pd: (a) 10; (b) 5; (c) 2; (d) 1; (e) 0.

The strong peaks corresponding to complex oxide CuPdO₂ appeared in Fig. 2d when the molar ratio of Cu/Pd in the catalyst was unity. Since CuPdO₂ was synthesized from the solid-state reaction between CuO and PdO at high temperature, its particles are large in size and then showed strong and sharp diffraction peaks. The peaks corresponding to CuPdO₂ have no obvious change with the increase in the Cu(II) content. This indicates that the formation of CuPdO₂ needs no excess of Cu compounds. It also implied that the excessive Cu compound would decompose to CuO at high temperature during the preparation of the catalyst. But only in the pattern of the catalyst with the Cu/Pd molar ratio of 10, there appeared a weak diffraction peak corresponding to CuO (as shown in Fig. 2a). This may be accounted for by assuming that the particles size of CuO was very small and had a monolayer dispersion, the diffraction peaks being too broad to be regarded as peaks.

Combining with the results of Figs. 1 and 2, we presume that CuPdO₂ as new species on the catalyst which greatly increased the yield of DPC. The excessive Cu(II) promoter will generate CuO which is no use for the synthesis of DPC. On the contrary, CuO promotes the side reaction of phenol oxidation and hinders the active Pd atoms from contacting reactants to produce negative effects on the synthesis of DPC.

The XPS analysis results of the ultrafine embedded catalysts Pd–Cu–O/SiO₂ with different Cu(II) contents are shown in Fig. 3. The binding energy of Pd 3d of the Pd–Cu–O/SiO₂ catalysts was all higher than that of PdO/SiO₂ catalyst (336.7 eV, as shown in Fig. 3a) irrespective of the Cu(II) content. The reason lies in that parts of the Cu atoms enter into the crystal lattice of PdO to form the complex oxide CuPdO₂. According to the electronegativity value scaled by Allred and Rochow [15], element Cu (1.75) has stronger electronegativity than Pd (1.35). This decreases

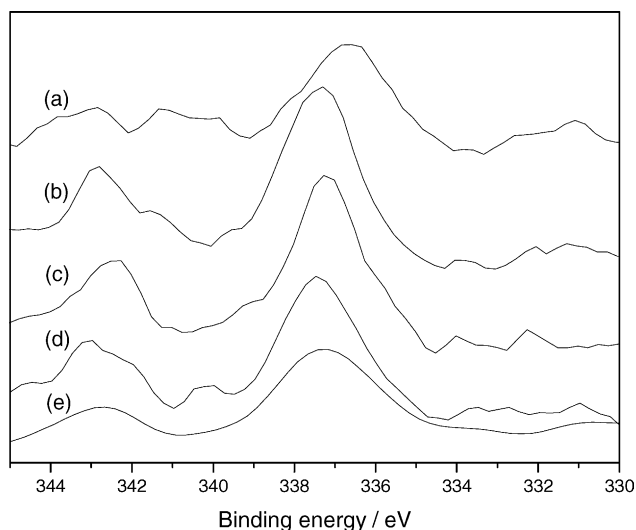


Fig. 3. XPS spectra of the ultrafine embedded catalysts Pd–Cu–O/SiO₂ with different Cu(II) contents. Molar ratio of Cu/Pd: (a) 0; (b) 1; (c) 2; (d) 5; (e) 10.

the density of electrons around the Pd atomic nucleus in the CuPdO_2 and increases the electrostatic attraction between Pd nucleus and electrons in the 3d orbit. Moreover, the binding energy of Pd 3d of the catalysts was hardly affected by the Cu(II) content, which showed that only the Cu(II) atoms in the crystal lattice of Pd–Cu–O/SiO₂ could affect the Pd atoms. The excessive Cu(II) existing as CuO has little effect on the Pd atoms, being no use for the reoxidation of Pd(0) to Pd(II). Now, it is clear that the reason for the increase in the catalytic activities is the formation of complex oxide CuPdO_2 , where the Pd atoms can transfer electrons easily to Cu atoms to recover their catalytic activities.

2.2. Effect of homogeneous Cu^{2+} promoter on the synthesis of DPC

Besides the heterogeneous Cu(II) promoter aforementioned, the homogeneous Cu^{2+} promoter was required to be charged into the reaction system when the synthesis of DPC was carried out over the ultrafine embedded catalyst Pd–Cu–O/SiO₂. The difference between the two kinds of Cu promoter was investigated and the results are shown in Fig. 4. It can be concluded from the results that both of the two promoters are able to increase the yield of DPC and the homogeneous Cu^{2+} is more effective than the heterogeneous Cu(II), when the Cu^{2+} /Pd molar ratio of 4 was employed. All the Cu^{2+} charged into the system could take part in the reoxidation of Pd(0) to Pd(II). The Pd atom has a high probability to contact the Cu^{2+} , or to contact several Cu^{2+} ions simultaneously. So, the change from Pd(0) to Pd(II) is easy to occur. However, when the heterogeneous Cu(II) is used as a promoter, only the Cu(II) that enters into the crystal lattice of PdO to form CuPdO_2 can receive electrons from Pd(0). Thus the number of the effective Cu(II) atoms is equal to the

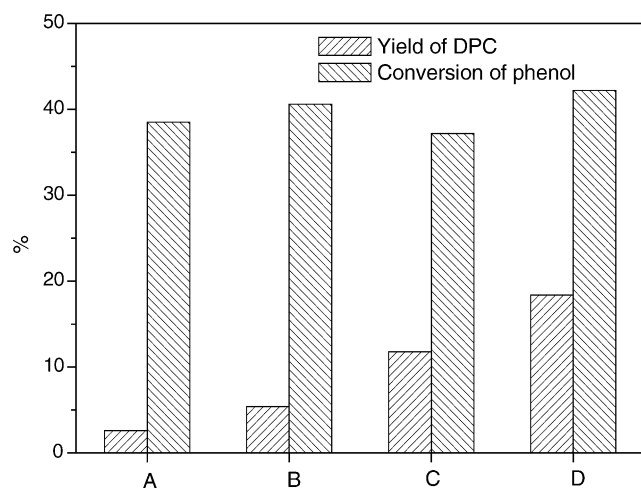


Fig. 4. Effect of promoter Cu^{2+} on the catalytic behavior of the ultrafine embedded catalyst: (A) PdO/SiO₂ as catalyst without Cu^{2+} promoter; (B) Pd–Cu–O/SiO₂ as catalyst without Cu^{2+} promoter, Cu(II)/Pd molar ratio of unity; (C) PdO/SiO₂ as catalyst with Cu^{2+} promoter, Cu^{2+} /Pd molar ratio of 4; (D) Pd–Cu–O/SiO₂ as catalyst with Cu^{2+} promoter, Cu(II)/Pd molar ratio of unity and Cu^{2+} /Pd molar ratio of 4.

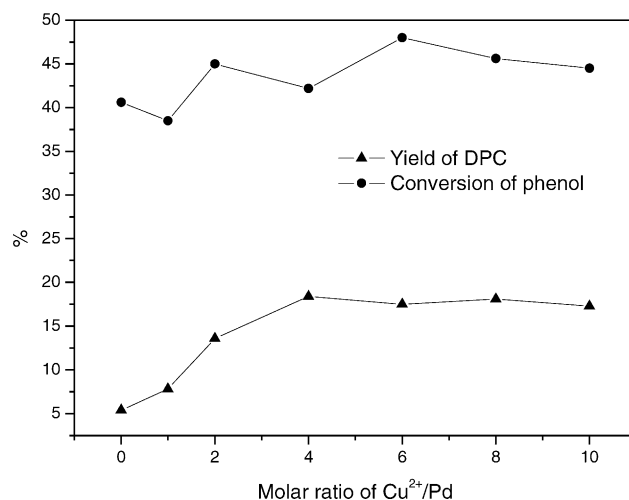


Fig. 5. Effect of Cu^{2+} amounts on the synthesis of DPC reaction conditions: phenol, 28 mmol; [Pd], 0.047 mmol; TBAB, 2.7 mmol; H₂BQ, 2.7 mmol; MS 4A, 4.0 g; CH₂Cl₂, 20 ml; CO, 3.6 MPa; O₂, 0.3 MPa; reaction temperature, 80 °C; reaction time, 4 h.

number of Pd atoms. Therefore, the efficiency of Cu(II) must be not as good as the homogeneous Cu^{2+} .

Effect of the Cu^{2+} amount on the oxidative carbonylation of phenol to DPC was studied and the results are shown in Fig. 5. The yield of DPC increased with increasing Cu^{2+} /Pd molar ratio, reached a maximum at the molar ratio Cu^{2+} /Pd of 4 and then leveled off. The maximum TOF of DPC reached 13.7 mol DPC/(mol Pd h), the yield of DPC based on phenol being 18.4%.

2.3. Side products of oxidative carbonylation of phenol

Under the present conditions, there were some side products formed along with DPC. Unlike the results reported by Goyal et al. [2], a small amount of *o*-phenylene carbonate was detected and the major side product was *p*-benzoquinone. In addition, phenyl acetate, *o*-, *m*-, and *p*-bromophenols and tributylamine were also detected by GC–MS. However, phenyl salicylate, which was mentioned as one of the main side products in many literatures, was not found. CO₂ was found as the gaseous side product by GC analysis of the residual gaseous mixture. It should be pointed out that there were still some ‘unknown’ compounds identified by GC–MS in the reaction solution.

3. Conclusion

In the oxidative carbonylation of phenol to diphenyl carbonate over the ultrafine embedded catalyst Pd–Cu–O/SiO₂, Cu promoters have an important effect on the activity of the catalyst:

- (1) Because of the existence of the heterogeneous Cu(II) promoter, the active species change from PdO to complex oxide CuPdO_2 . This enables Pd atoms to easily

transfer electrons to Cu atoms to recover their activities. However, excessive Cu(II) also promotes the side reactions in phenol oxidation and decreases the selectivity for DPC.

- (2) The homogeneous Cu²⁺ promoter has higher efficiency than the heterogeneous Cu(II) in promoting the change from Pd(0) to Pd(II), since all the Cu²⁺ charged into the system can be in action. However, only the heterogeneous Cu(II) that enters into the crystal lattice of PdO to form the CuPdO₂ can receive electrons from Pd(0).

Acknowledgements

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