

Oxidative carbonylation of phenol over the mesoporous palladium-copper-oxide/silica catalyst prepared by sol–gel coupling with W/O microemulsion

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Abstract

A novel mesoporous catalyst Pd-Cu-O/SiO₂ were prepared by sol–gel method coupling with W/O microemulsion for oxidative carbonylation of phenol to diphenyl carbonate (DPC). It has larger specific surface area, pore volume and rather narrow pore size distribution in the range of mesopore. The catalyst shows a comparatively good activity for the synthesis of DPC and the yield reaches to 20.3%, the turnover frequency (TOF) is 15.1 mol-DPC/mol-Pd h, at certain conditions. The less dispersed active centers and the diffusion resistance caused by the numerous pores influence the reaction negatively.

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1. Introduction

Polycarbonates (PCs) are excellent engineering thermoplastics and substitutes for metals and glass because of their good impact strength, heat resistance and transparency [1]. In recent years, there has been an increasing demand for safer and environmentally favorable processes for PC synthesis. The transesterification process using 2,2-bis(4-hydroxyphenyl)-propane (bisphenol A) and diphenyl carbonate (DPC) has been expected instead of the interfacial polycondensation of diphenols with phosgene because of the following advantages: no toxic phosgene, no solvent, and no salt formation. Therefore, there has been of great interest on the synthesis of DPC. Several methods have been developed for the manufacturing of DPC. Among them, oxidative carbonylation of phenol with CO and O₂ is one of the most attractive methods, in that it is a one-step process with H₂O being the sole by-product in theory, and the use of highly toxic phosgene can be avoided. Homogeneous palladium

compounds with co-catalysts have been reported to be the highly efficient catalytic system for this process [2–4]. To facilitate the separation of catalysts from products and increase the thermal stability and amenability of the catalyst to bear the continuous processing, heterogenization of homogeneous catalysts was also explored. Iwane et al. [5] used porous carriers, such as carbon, alumina, silica and the like, supported palladium catalysts to promote the synthesis of DPC and the yield of DPC was up to 12.6%. Takagi et al. [6] reported that 9.55% DPC yield was obtained when using 5 wt% Pd/C as catalyst and PbO as co-catalyst. They also indicated that Pd species seemed to work as a homogeneous catalyst although heterogeneous Pd/C was used as a palladium source. Song et al. [7] reported that in the supported palladium catalyst, the surface characteristics of the supports and Pd dispersion appeared to be critical to the yield of DPC and that the carbon-supported Pd catalyst showed a better DPC yield than other supports because of the good hydrophobicity. Ishii et al. [1] reported the oxidative carbonylation of phenol catalyzed by the palladium–pyridyl complexes tethered on polymer support in the absence of ammonium halide. We have prepared an

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ultrafine embedded catalyst using a water-in-oil (W/O) microemulsion as nano reactor for oxidative carbonylation of phenol [8,9]. In this catalyst, active species is embedded in the silica particles to form the core/shell structure. The silica shell acts as the supports and protective layer simultaneously, which can decrease the loss amount of the active species effectively and prolong the catalyst's service time. Here, we report our study on the preparation of a novel mesoporous catalyst by sol-gel method coupling with W/O microemulsion and its catalytic activity for the synthesis of DPC by oxidative carbonylation.

2. Experimental

2.1. Preparation of the novel mesoporous catalysts

In this paper, the W/O microemulsion is composed of cyclohexane, nonylphenyl polyoxyethylene (10) ether (NP-10), hexanol and water phase. The water phase is prepared beforehand by mixing tetraethyl orthosilicate (TEOS), ethanol, PdCl₂ and Cu(OAc)₂ solution in hydrochloric acid (2 mol l⁻¹) at the volume ratio of 5/3/5. Both of the concentration of PdCl₂ and Cu(OAc)₂ in hydrochloric acid are 0.025 mol l⁻¹. This microemulsion is a transparent system with light yellow color. At a constant temperature of 30 °C, a little amount of NH₃·H₂O is charged into the microemulsion system with the stirring until the gel come into being. Then, the gel is filtrated and thoroughly washed with ethanol. Subsequently, it is dried at 60 °C overnight and calcined at 700 °C for 5 h. The catalyst is denoted as Pd-Cu-O/SiO₂ and the preparation method is called as coupling method.

2.2. Catalyst characterization

The X-ray diffraction (XRD) studies were carried out by a Rigaku D/Max-2500 X-ray diffractometer. Nitrogen adsorption-desorption was conducted on a gas sorption analyzer (Micromeritics ASAP 2020) at liquid nitrogen temperature. The specific surface area was determined by the BET method. The catalyst samples were observed by the transmission electron microscopy (TEM, Philips TECNOL 20).

2.3. 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: $T = 80\text{ °C}$, $P = 3.9\text{ MPa}$ (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

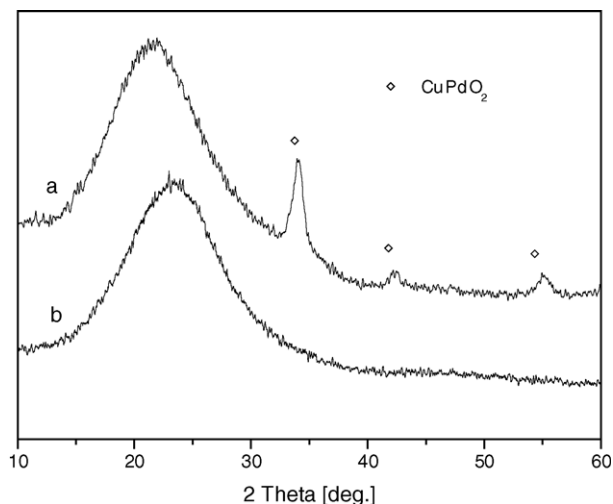


Fig. 1. XRD patterns of Pd-Cu-O/SiO₂: (a) calcined at 700 °C and (b) as-dried.

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).

3. Results and discussions

3.1. Characterizations of the catalyst

Fig. 1 shows the XRD patterns of this mesoporous catalysts as-dried and after calcination at 700 °C. There are no obvious peaks in the pattern of the as-dried catalyst and it shows that the metal compounds dispersed well on the silica. The pattern of the catalyst after calcination shows the diffraction peaks corresponding to complex oxide CuPdO₂, which is the result of solid-state reaction between CuO and PdO at high temperature and greatly increased the activity of the catalyst [9].

The surface characteristics of the catalyst prepared by different methods (calcined at 700 °C) were determined and the results are shown in Table 1. The BET specific surface area and the pore volume of the catalyst prepared by coupling method were the largest among the catalysts. Fig. 2 shows the pore size distribution and N₂ adsorption-desorption isotherm of the catalyst prepared by coupling method. Compared with Figs. 3 and 4, this mesoporous catalyst shows the rather narrow pore size distribution in the range of mesopores. In addition, the adsorption-desorption isotherm shows that it has different type of pores from the catalyst prepared by the other two methods.

Table 1
Surface characteristics of catalysts prepared through different methods

Preparation method	W/O microemulsion [8]	Sol-gel	Coupling method
S_{BET} (m^2/g)	58.40	346.04	558.52
Average pore size (nm)	21.12	15.40	10.77
Cumulative volume of pores (cm^3/g)	0.31	1.13	1.80

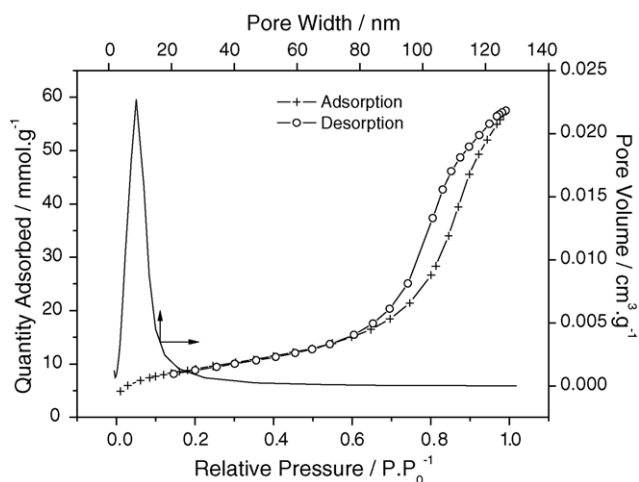


Fig. 2. Pore size distribution and N_2 adsorption–desorption isotherm of the catalyst prepared through the coupling method.

Fig. 5 shows the small angle X-ray diffraction pattern ($1\text{--}10^\circ$) of the mesoporous catalyst calcined at 700°C . There are no peaks corresponding to the mesopores in the pattern. It indicated that the mesopores in the catalyst were arranged in disorder. To prove the presumption, the TEM image of the catalyst, which is shown in Fig. 6, was obtained by the Philips TECNOL 20. The sizes of the catalyst particles are in the range of $100\text{--}300\text{ nm}$. There are lots of mesopores, which size are around 10 nm , in the catalyst particles with ununiformity in shape and arrangement. The results are accord well with the small angle X-ray diffraction pattern.

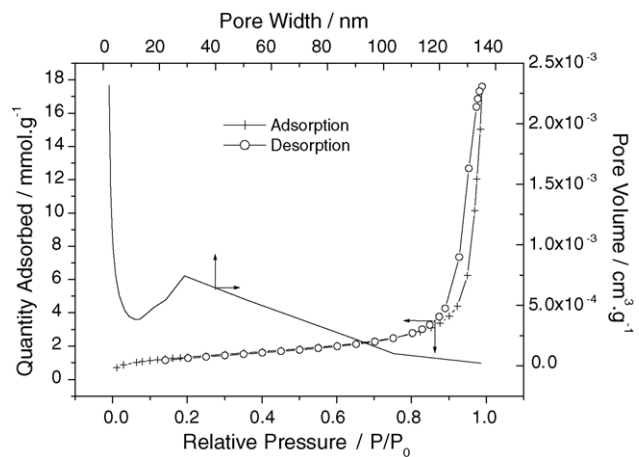


Fig. 3. Pore size distribution and N_2 adsorption–desorption isotherm of the catalyst prepared in W/O microemulsion.

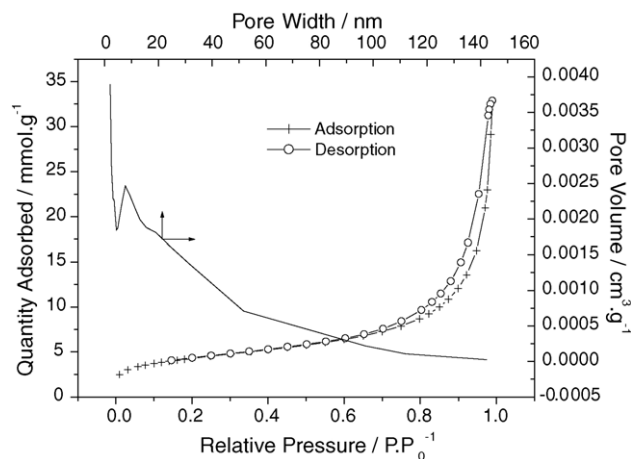


Fig. 4. Pore size distribution and N_2 adsorption–desorption isotherm of the catalyst prepared through sol-gel method.

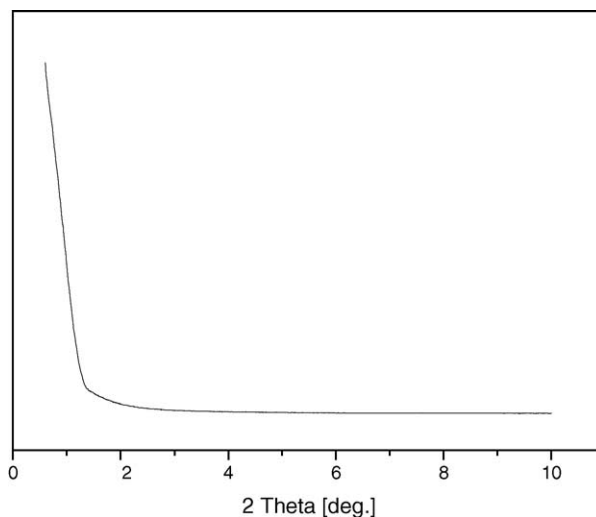


Fig. 5. Small angle X-ray diffraction of the mesoporous catalyst calcined at 700°C .

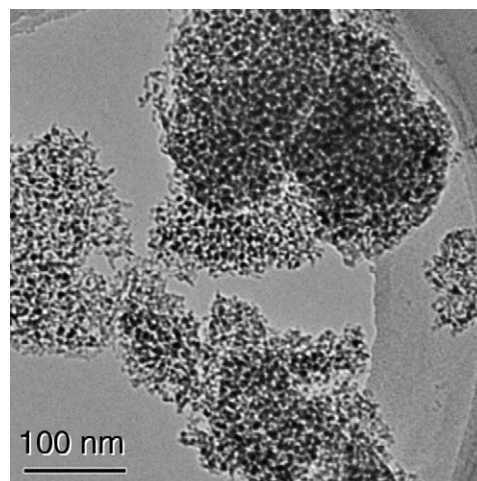


Fig. 6. TEM image of the mesoporous catalyst calcined at 700°C .

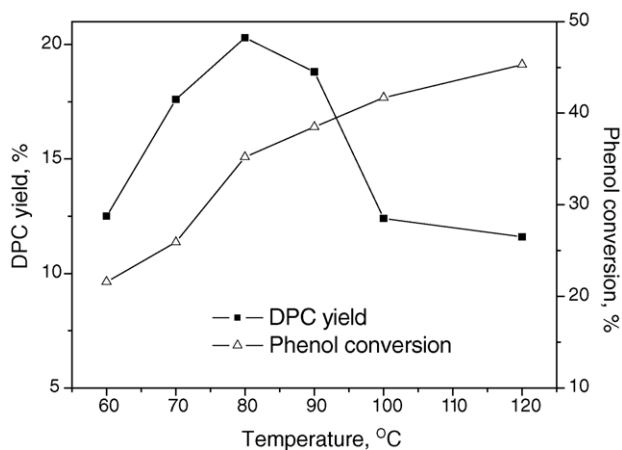


Fig. 7. Effect of temperature on DPC yield and phenol conversion. Conditions: CO 3.6 MPa; O₂ 0.3 MPa, others are same as in Section 2.3.

3.2. Oxidative carbonylation of phenol over the mesoporous catalyst

The synthesis of DPC by oxidative carbonylation of phenol over the novel mesoporous catalyst at different temperatures and different pressures were investigated. The results are shown in Figs. 7 and 8. High temperature can promote the conversion of phenol because the value increases monotonously with the reaction temperature. However, the DPC yield changes in a different manner. With the elevation of the temperature, the DPC yield increases first and gets its maximum, 20.3% (turnover frequency, TOF = 15.1 mol-DPC/mol-Pd h), at 80 °C, and then decreases because phenol is easy to be oxidized by O₂ at high temperature to obtain the undesirable by-product, such as dimeric, trimeric compounds and polymers. As a matter of fact, a large amount of brown polymer is found at the end of the reaction above 80 °C.

Fig. 8 shows the effect of the system pressure on the synthesis of DPC. The phenol conversion increases little

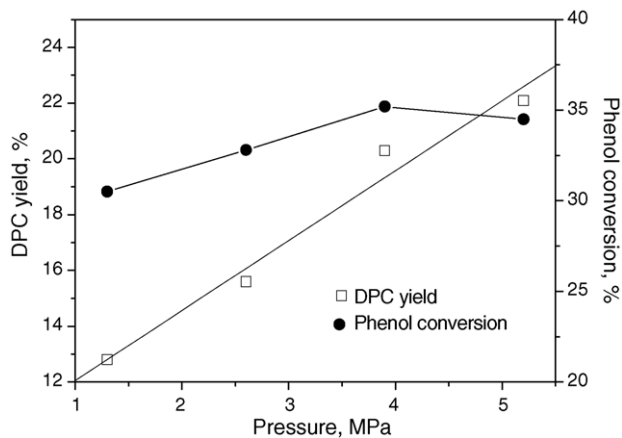


Fig. 8. Effect of pressure on DPC yield and phenol conversion. Conditions: $T = 80\text{ }^{\circ}\text{C}$, $P(\text{CO})/P(\text{O}_2) = 12/1$, others are same as in Section 2.3.

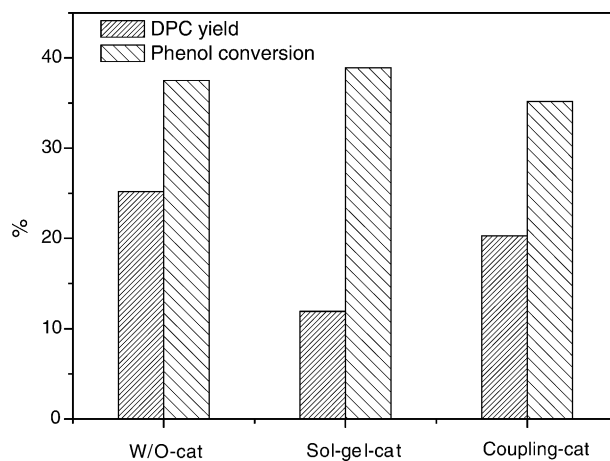


Fig. 9. Comparison of the catalytic activity among the catalysts prepared through different methods. Conditions: $T = 80\text{ }^{\circ}\text{C}$, $P = 3.9\text{ MPa}$, $P(\text{CO})/P(\text{O}_2) = 12/1$, others are same as in Section 2.3.

with the pressure. The DPC yields increase monotonously with the pressure and represent a linear relation between them. This is due to that the number of the gaseous reactants molecule decreases after reaction and the elevation of the pressure are in favor of the formation of the products.

3.3. Comparison of the catalytic activity over the different catalysts

To investigate the advantage of the novel mesoporous catalyst, oxidative carbonylation of phenol over the catalysts prepared through different methods, which are listed in Table 1, were carried out at a selected reaction conditions. All of the catalysts have the same components and the results are shown in Fig. 9. Among the three catalysts, the catalyst prepared in W/O microemulsion (W/O-cat) has the highest activity, the DPC yield reaches 25.2% and the TOF is 18.8 mol-DPC/mol-Pd h. However, it has the smallest specific surface area according to the data in Table 1. That is to say, the large surface area did not bring the high activity, not as we have imagined. The reason may be lies in that the active centers in the mesoporous catalyst are not dispersed well and the inert SiO₂ with large surface area is no use for the synthesis of DPC. Moreover, the numerous pores may increase the diffusion resistance and show negative effect on the reaction. The lowest DPC yield over the catalyst prepared by sol-gel process (sol-gel-cat) can be attributed to the great diffusion resistance brought by the large sizes of the catalyst particles because the active centers are located inside the SiO₂ particles [9].

In conclusion, we have prepared a catalyst with comparatively good activity for oxidative carbonylation of phenol. Moreover, we have also explored a novel method for the preparation of silica-supported catalyst with ultrafine particles, large specific surface area and rather narrower pore size distribution. It can also be used in the preparation of other oxides.

4. Conclusion

In this article, a novel catalyst Pd-Cu-O/SiO₂ with mesoporous structure was prepared by sol-gel method coupling with W/O microemulsion.

- (1) It has larger specific surface area ($S_{\text{BET}} = 558.52 \text{ m}^2/\text{g}$) and rather narrow pore size distribution in the range of mesopore (average pore size = 10.77 nm). But the mesopores in the catalyst are arranged indistinctly and they have great ununiformity in shape and arrangement.
- (2) The novel catalyst shows a good activity for the synthesis of DPC and the DPC yield reaches to 20.3%, the turnover frequency is 15.1 mol-DPC/mol-Pd h, at certain conditions.
- (3) Compared with the catalysts prepared through W/O microemulsion and sol-gel process, the novel catalyst does not show the highest activity. We think the less dispersed active centers may commit the results. Moreover, the numerous pores also increase the diffusion resistance and influenced the reaction negatively.

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