Preparation of Catalyst Supported by CuO-CoO-MnO/SiO2 Nanocomposite Aerogel and its Catalytic Performance in the Synthesis of Diphenyl Carbonate

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Abstract. A novel catalyst supported by nano-porous CuO-CoO-MnO/SiO2 composite aerogel was prepared by impregnation method. It was used in the catalytic synthesis of diphenyl carbonate (DPC). The effects of temperature, pressure and reaction time on the yield of DPC were investigated. The results show that Phenol and DPC can smoothly pass through the nano-pores of the composite aerogel during the catalytic synthesis of DPC. When the temperature, pressure and reaction time of DPC synthesis are 110 ºC, 6.0 MPa and 6 h, respectively, the yield of DPC is 27.14 mass%, which is much higher than that of catalysts supported by other porous carriers.

1. Introduction

Aerogel is a porous, non-crystalline solid material with large specific surface area, high porosity, low density and better chemical property. Therefore, it has been used as catalyst carrier, gas absorbent and filter, heat insulator, sound deadening, drug adsorption and release, etc [1-5]. Nano-porous composite aerogel with transition metal oxides can be used as catalyst or catalyst carrier in catalysis [6-8]. In the past decade, some catalyst carriers, such as porous ceramics, 3A molecular sieve, HZSM molecular sieve, activated carbon, SiO2 aerogel, SiO2 aerogel, CuO/SiO2 composite aerogel, CuO/SiO2 composite aerogel, CuO-CoO-MnO/SiO2 composite aerogel and the like have been used in the synthesis of diphenyl carbonate (DPC). DPC can be used as the precursor in the synthesis of polycarbonate (PC) by polymerization, PC is an engineering thermoplastic material and it has been widely used in mechanical parts and elements, electrical insulators of various electrical and electronic products and so on [9-12]. However, DPC yields are usually less than 10.0%. This is because of lack of active transition metal-oxides used as co-catalysts or because of small specific surface area and low porosity in above-mentioned catalyst carriers. The properties of catalysts supported by composite aerogels can be further optimized through the combination of structural constituents and redox constituents [13-15]. CuO-CoO-MnO/SiO2 composite aerogel is a nano-porous material with multiple active transition metal oxides, a specific surface area of 664.4-695.8 m²/g and a pore size distribution of 2-16 nm [15-16]. Catalyst supported by the composite aerogel has been used in the environment-friendly synthesis of DPC, the yield of DPC is much higher than that of catalysts supported by traditional catalyst carriers [18-20].

In this study, a novel catalyst used for the catalytic synthesis of DPC was prepared by impregnation method. The catalytic mechanism of the supported catalyst in the synthesis of DPC was explored. The
effects of temperature, pressure and reaction time on the yield of DPC was investigated. The catalytic performances of the catalysts in the synthesis of DPC were investigated.

2. Experimental

2.1. Preparation of Supported Catalyst
Catalyst supported by nano-porous CuO-CoO-MnO/SiO₂ composite aerogels was prepared by impregnation method. The composite aerogel was firstly ground into fine particles in a mortar and then the fine particles were sieved in standard sieves. The sieved fine particles of the composite aerogel were put into a vacuum drier and then dried at 110 °C for 2 h so as to remove the residual moisture in the pores of the catalyst carrier. PdCl₂ is used as the main catalyst and Co(OAc)₂ is used as the co-catalyst in the heterogeneous catalytic system. They were dissolved in 5 mL aqueous ammonia, the concentrations of PdCl₂ and Co(OAc)₂ in the solution were 0.034 mol/L and 0.24 mol/L, respectively, and then the impregnation solution was obtained. The fine particles of the nano-porous composite aerogel with a mass of 1 g were firstly dispersed in the prepared impregnation solution, then stirred at room temperature for 2.0 h, aged the mixture for 12 h, dried in a vacuum dryer at 60 °C for 3 h, and then calcined in a muffle furnace at 550 °C for 7 h so as to activate the supported catalyst, finally the supported catalyst was obtained.

2.2. Application in the Synthesis of DPC
The synthesis of DPC was carried out in an autoclave reactor, and the autoclave was equipped with a magnetic stirrer, the reactor was pre-filled with 50 mL CH₂Cl₂ (dichloromethane) used as a solvent, 1 g supported catalyst, 0.440 4 g C₆H₄(OH)₂ (hydroquinone or H₂BQ) used as an organic co-catalyst, 7.528 8 g phenol used as a reactant, 3 g 3A molecular sieve with size of 10-230 μm used as a drying agent, 0.967 4 g (C₄H₉)₄BrN (tetrabutylammonium bromide or TBAB) used as a stabilizer and a surfactant. After sealing the autoclave, CO was injected into the reactor so as to replace the air and prevent the oxidation of phenol. When the pressure and the temperature were 0.5 MPa and 40 °C, respectively, O₂ and more CO were injected into the autoclave reactor until the total pressure was 6.0 MPa. When the temperature was 80 °C, the reaction of oxidative carbonylation started in the autoclave reactor. After 6 h, the temperature was 110 °C, the heating apparatus was shut off, and the autoclave was cooled down to room temperature. Gases in the autoclave reactor were exhausted slowly, and then the pressure was decreased gradually. The mixture of the solvent, liquid products and residual phenol was taken out of the autoclave reactor for analysis.

3. Results and Discussion

3.1. Geometric Parameters Calculation and Molecular Configuration Simulation
The geometric parameters of phenol and DPC were calculated, and the molecular configurations of phenol and DPC were simulated by using Material Studio 7.0 software so as to prepare suitable catalyst carrier and optimize the structure of catalyst in the synthesis of DPC. Table 1 shows the geometric parameters of a single molecule of phenol. Table 2 shows the geometric parameters of a single molecule of DPC. Figure 1 shows the steric configurations of a single molecule of phenol and a single molecule of DPC.

| Band angle | Band length | Molecule size |
|------------|-------------|---------------|
| Key atom   | θ (°)       | Key atom      | γ (nm) | Direction | Size (nm) |
| C(2)-C(1)-O | 122.310     | C(1)-C(2)     | 0.138 7 | X         | 0.618 8   |
| C(3)-C(1)-O | 117.611     | C(1)-O        | 0.135 7 | Y         | 0.464 2   |
| C(1)-O-H   | 108.261     | H-O           | 0.098 2 |           |           |
Table 2. Geometric parameters of a single molecule of DPC

| Key atom       | Band angle | Key atom     | Band length | Direction | Molecule size |
|----------------|------------|--------------|-------------|-----------|---------------|
| C(4)-C(1)-O(8) | 123.826    | C(4)-C(1)    | 0.1384      | X         | 1.0549        |
| C(5)-C(1)-O(8) | 134.495    | C(1)-C(5)    | 0.1384      | Y         | 0.7090        |
| C(1)-O(8)-C(2) | 121.328    | C(1)-O(8)    | 0.1381      | Z         | 0.4526        |
| O(8)-C(2)-O(9) | 127.285    | O(8)-C(2)    | 0.1344      |           |               |
| O(9)-C(2)-O(10)| 121.682    | C(2)-O(9)    | 0.1196      |           |               |
| O(10)-C(3)-C(7)| 116.428    | C(3)-O(10)   | 0.1374      |           |               |
| O(10)-C(3)-C(6)| 122.240    | C(3)-C(7)    | 0.1384      |           |               |
| C(4)-C(1)-C(5)| 121.665    | C(3)-C(6)    | 0.1387      |           |               |
| C(6)-C(3)-C(7)| 121.071    |              |             |           |               |

**Figure 1.** Steric configurations of a single molecule of phenol and a single molecule of DPC

The geometric dimensions of phenol are $X = 0.6188$ nm and $Y = 0.4642$ nm, and the geometric dimensions of DPC are $X = 1.0549$ nm, $Y = 0.7090$ nm and $Z = 0.4526$ nm (Table 1 and Table 2), whereas the average pore size of the nano-porous composite aerogel is 7.68 nm [16, 20]. Therefore, phenol and DPC can smoothly pass through the nanopores of the composite aerogel and then DPC can gradually disperse in the mixture of solvent and residual phenol during the heterogeneous catalytic synthesis of DPC because the average pore size of the composite aerogel is obviously bigger than that of phenol and DPC.

CuO-CoO-MnO/SiO$_2$ composite aerogel is a nano-porous material with a specific surface area of 664.4–695.8 m$^2$·g$^{-1}$, and the mole fraction of active transition metals in the nano-porous composite aerogel is 0.71 mol%–13.77 mol% [16]. The structure and composition can not only promote the loading of PdCl$_2$ and Co(OAc)$_2$, but also make full use of the catalysis of active transition metal oxides as co-catalysts.

3.2. Effect of Technological Parameters on the Yield of DPC

3.2.1. Effect of temperature on the yield of DPC. Effect of temperature in the autoclave reactor on the yield of DPC was investigated in the temperature range of 80-130 °C. Figure 2 shows the effect of temperature in the reactor on the yield of DPC. According to chemical reaction kinetics, the reaction rate increases with the increase of temperature in the autoclave reactor, and then the yields of DPC increase with the increase of temperature in the temperature range of 80-110 °C. On the other hand, the
yields of DPC decrease in the temperature range of 110-130 °C, because the reaction of oxidative carbonylation for DPC synthesis is an exothermic reaction [20], higher temperature in the autoclave reactor is not favorable to the synthesis of DPC. Therefore, the optimum temperature of the catalytic synthesis of DPC is 110 °C.

3.2.2. Effect of Pressure on the Yield of DPC. Effect of pressure in the autoclave reactor on the yield of DPC was investigated at a constant temperature of 110 °C. Figure 3 shows the effect of pressure in the reactor on the yield of DPC. The reaction of oxidative carbonylation for the catalytic synthesis of DPC is shown by equation (5).

\[
2\text{PhOH} + \text{CO} + \frac{1}{2}\text{O}_2 \xrightarrow{T, P} \text{PhO(CO)OPh} + \text{H}_2\text{O}
\]  

(1)

According to the equation, because the number of molecules decreases after the reaction, the increase of pressure in the reactor is favorable to the increase of resultants. In addition, according to Henry’s law or \( x = kP \), the increase of pressure is also favorable to the increase of the solubility of CO or O\(_2\) in solvent or CH\(_2\)Cl\(_2\), and the reaction probability between reactants and catalysts or co-catalysts increase. Accordingly, the reaction rate increases with the increase of pressure, the yields of DPC increase with the increase of pressure in the autoclave reactor, and the yield of DPC increases to maximum at 6.0 MPa (Figure 3).
3.2.3. Effect of Reaction Time on the Yield of DPC

When the pressure in autoclave reactor was 6.0 MPa, the partial pressures of CO and O\textsubscript{2} were 5.0 MPa and 1.0 MPa, respectively, the effect of reaction time on DPC yield was investigated at 110 °C. Figure 4 shows the effect of reaction time in the reactor on DPC yield. The yields of DPC obviously increase with the increase of reaction time in 6 h, but the yields of DPC increase slightly after 6 h and the yields of DPC is almost constant, because oxidative carbonylation almost reaches chemical equilibrium after 10 h. Therefore, the optimum reaction time of DPC synthesis is 6 h (Figure 4).

3.3. Evaluation of Catalytic Performances

Figure 5 shows the gas chromatograms of chemical substances. The abscissa of the graph shows peaks appearance time of CH\textsubscript{2}Cl\textsubscript{2}, phenol and DPC, and the ordinate of the graph indicates the energy release intensity after burning of CH\textsubscript{2}Cl\textsubscript{2}, phenol and DPC. The left peak in the graph at 0.490 min corresponds to CH\textsubscript{2}Cl\textsubscript{2}, and it is used as the solvent in the catalytic system. The middle peak in the graph at 1.725 min indicates the phenol, and it is used as a reactant. The right peak in the graph at 6.255 min represents the target product or DPC (Figure 5).

![Figure 4. Effect of reaction time on yield of DPC.](image1)

![Figure 5. Gas chromatograms of CH\textsubscript{2}Cl\textsubscript{2}, phenol and DPC](image2)

In order to measure the standard curves of phenol and DPC, using CH\textsubscript{2}Cl\textsubscript{2} as the solvent, five kinds of standard solutions with different concentrations were prepared by dilution method, and their compositions were similar to those of the reaction liquids. Fig. 6 shows the standard curve of phenol. Fig. 7 shows the standard curve of phenol and DPC. The linear equations were obtained by least
square regression analysis. The linear regression equation of phenol is shown by equation (6), and the linear regression equation of phenol and DPC is shown by equation (7).

Figure 6. The standard curve of phenol

\[ w = -0.2876 + 3.07 \times 10^6 A \] (2)

Where \( A \) is the peak area of phenol, \( w \) is the percentage of phenol, and 0.99883 is a correlation coefficient.

Figure 7. The standard curve of phenol and DPC.

\[ y = 0.79176 + 1.324x \] (3)

Where \( x \) is the peak area ratio of phenol and DPC, \( y \) is the mass ratio of phenol and DPC, and 0.99816 is a correlation coefficient.

The analysis results show that the yield of DPC catalyzed by the supported catalyst is 27.14 mass%. The comparison of catalytic performances of catalysts supported by different carriers in the synthesis of DPC is shown in Figure 8. The yield of DPC catalyzed by the novel supported catalyst is much higher than that of catalysts supported by other carriers, such as porous ceramics, 3A molecular sieve, activated carbon, HZSM molecular sieve, SiO\(_2\) xerogel, SiO\(_2\) aerogel, CuO/SiO\(_2\) composite xerogel, CuO/SiO\(_2\) composite aerogel and CuO-CoO-MnO/SiO\(_2\) composite xerogel (Figure 8).
4. Conclusions
Phenol and DPC can smoothly pass through the nano-porous CuO-CoO-MnO/SiO₂ composite aerogel during the catalytic synthesis of DPC because the average pore size of the composite aerogel is obviously bigger than that of phenol and DPC.

When the temperature, pressure and reaction time of DPC synthesis are 110 °C, 6.0 MPa and 6 h, respectively, the yield of DPC is 27.14 mass%, which is much higher than that of catalysts supported by other porous catalyst carriers.

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