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An Active and Heterogeneous Catalyst for Synthesis of Diphenyl Carbonate

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$Zn_4O[(O_2C)\text{-}C_6H_4\text{-}(CO_2)]_3$ was prepared by solvothermal method and characterized with XRD and FT-IR. $Zn_4O[(O_2C)\text{-}C_6H_4\text{-}(CO_2)]_3$ was used as the catalyst for the synthesis of diphenyl carbonate *via* the transesterification dimethyl carbonate and phenol and its catalytic activity was compared with $Ti(OBu)_4$, Mg-Al Mg-Al LDH and Zn-Al Mg-Al LDH. The results show that $Zn_4O[(O_2C)\text{-}C_6H_4\text{-}(CO_2)]_3$ is an active and heterogeneous catalyst for the synthesis of diphenyl carbonate *via* the transesterification.

Keywords: Diphenyl carbonate, Transesterification, Dimethyl carbonate, Catalyst.

INTRODUCTION

Diphenyl carbonate (DPC) is a potential substitute material for toxic phosgene in the synthesis of polycarbonate diol[1,2]. The transesterification between dimethyl carbonate (DMC) and phenol is regarded as a more promising route for the synthesis of diphenyl carbonate because dimethyl carbonate is a green chemical and has been commercially produced the oxidative carbonylation of methanol.

Several catalysts, such as $Ti(OBu)_4$, Cp_2TiCl_2, MoO_3/SiO_2, TiO_2/SiO_2, Mg-Al-CO_3 LDH and Zn-Al-CO_3 LDH[3-6], have been developed for the transesterification between dimethyl carbonate and phenol to diphenyl carbonate. $Ti(OBu)_4$ and Cp_2TiCl_2 are homogeneous catalysts and show high catalytic activities, but they are unstable and sensitive to the moisture in the air. MoO_3/SiO_2, TiO_2/SiO_2, Mg-Al-CO_3 LDH and Zn-Al-CO_3 LDH are heterogeneous catalysts and easy to be removed from the product, but their catalytic activities are lower than those of homogeneous catalysts. So the development of more efficient catalysts is desirable.

$Zn_4O[(O_2C)\text{-}C_6H_4\text{-}(CO_2)]_3$ can form a porous cubic structure by connecting a Zn_4O inorgnaic moiety to benzne-1,4-dicarboxylate[7]. $Zn_4O[(O_2C)\text{-}C_6H_4\text{-}(CO_2)]_3$ has drawn more and more attention due to its high surface area, microporosity, well-defined structure and good chemical stability. In this work, $Zn_4O[(O_2C)\text{-}C_6H_4\text{-}(CO_2)]_3$ was prepared by the solvothermal method. Then it was used as a catalyst in the transesterification between dimethyl carbonate and phenol.

EXPERIMENTAL

The zinc nitrate hexahydrate ($Zn(NO_3)\cdot 6H_2O$, 99 %, Shanghai Xinbao Fine Chemical Plant), benzene-1,4-dicarboxylic acid (H_2BDC, 99%, Shanghai Runjie Chemical Reagent Co., Ltd.) and *N*,*N*-dimethylformamide (DMF, 99 %, Shanghai Runjie Chemical Reagent Co., Ltd.) were used to prepared MOFs.

The dimethyl carbonate (DMC, AR, Chongqing Changfeng Chemical Plant) and phenol (AR, Shanghai Runjie Chemical Reagent Co., Ltd.) were used to prepare diphenyl carbonate. All the reagents were used without any further purification.

Preparation of catalyst: 1.36 g H_2BDC and 4.84 g $Zn(NO_3)\cdot 6H_2O$ were dissolved in 160 mL *N*,*N*-dimethylformamide. Then the solution was sealed in a 250 mL round flask and kept at 100 ºC for 24 h. The precipitate was collected by filtration and washed by *N*,*N*-dimethylformamide. The solid $Zn_4O[(O_2C)\text{-}C_6H_4\text{-}(CO_2)]_3$ was dried at 90 ºC in vacuum and then stored in a vacuum desiccator[7,8]. The colorless crystalline materials were characterized with Rigaku D/max 2500 PC X-ray diffraction (XRD) and Nicolet PROTÉGÉ 460 Fourier transform infrared (FTIR) spectroscopy.

Preparation of diphenyl carbonate: 0.2 mol phenol and $Zn_4O[(O_2C)\text{-}C_6H_4\text{-}(CO_2)]_3$ were placed in a 100 mL flask equipped with a thermometer, a mechanical stirrer and a reflux condenser. When the reactor temperature was increased to 160 °C at the nitrogen atmosphere, 0.4 mol dimethyl carbonate was added gradually to the reactor. This process continued until there was no methanol distilled off.

Measurements: The X-ray diffraction (XRD) was undertaken on a Rigaku D/max 2500 PC powder X-ray diffractometer using CuK_α radiation. Infrared spectroscopy (FTIR) was recorded in a Nicolet 560 FTIR spectrometer. The specific surface area measurement and pore analysis was carried out on a Micromeritics ASAP 2020 V3.00 H (USA) surface area analyzer by N_2 adsorption at 77 K. A Shimadzu GC-2010 gas chromatograph equipped with a flame-ionization detector was used to qualitatively and quantitatively analyze the distillate.

RESULTS AND DISCUSSION

Characterization of catalyst: Fig. 1 shows the FTIR spectrum of $Zn_4O[(O_2C)\text{-}C_6H_4\text{-}(CO_2)]_3$ prepared by the solvothermal method. The peaks at 1593 and 1504 cm^{-1} correspond to the asymmetric stretching vibration of -COO. The peaks at 1402 and 1321 cm^{-1} are attributed to the symmetric stretching vibration of -COO. The peaks at 1153, 1151 and 1016 cm^{-1} crepresent the in-plane bending vibration of C-H. The peaks at 827, 762 and 598 cm^{-1} correspond to the out-of-plane bending vibration of C-H. Fig. 2 shows the XRD pattern of $Zn_4O[(O_2C)\text{-}C_6H_4\text{-}(CO_2)]_3$. As shown in Fig. 1, the sharp reflection peaks are observed at 8.8 , 14.08, 15.62, 17.64, 28.58, 30.40, 31.02 and 36.68°, which are well matched with the reported peaks[8].

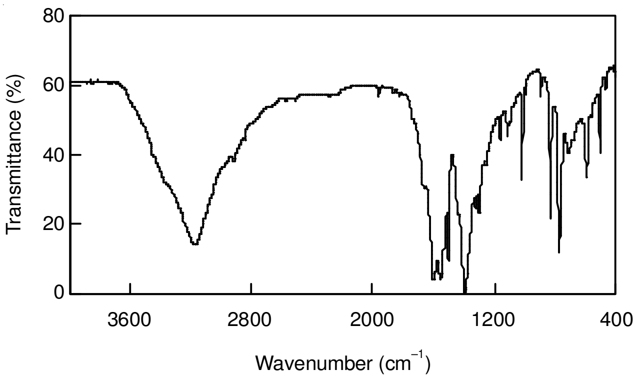

Fig. 1. FTIR spectrum of $Zn_4O[(O_2C)\text{-}C_6H_4\text{-}(CO_2)]_3$

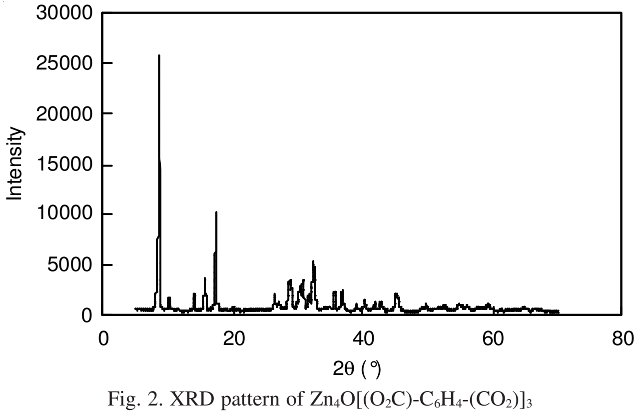

Fig. 2. XRD pattern of $Zn_4O[(O_2C)\text{-}C_6H_4\text{-}(CO_2)]_3$

Catalytic activity of $Zn_4O[(O_2C)\text{-}C_6H_4\text{-}(CO_2)]_3$: $Ti(OBu)_4$, Mg-Al-CO_3 LDH and Zn-Al-CO_3 LDH are efficient catalysts for the transesterification between dimethyl carbonate and phenol to diphenyl carbonate[3-6]. For comparisons, $Ti(OBu)_4$, Mg-Al-CO_3 LDH, Zn-Al-CO_3 LDH and $Zn_4O[(O_2C)\text{-}C_6H_4\text{-}(CO_2)]_3$ were investigated in reactor. As shown in Table-1, $Zn_4O[(O_2C)\text{-}C_6H_4\text{-}(CO_2)]_3$ exhibits highest catalytic activity.

The high catalytic activity of $Zn_4O[(O_2C)\text{-}C_6H_4\text{-}(CO_2)]_3$ can be related to its framework structure. First, here are Lewis acid sites and basic sites on the framework of $Zn_4O[(O_2C)\text{-}C_6H_4\text{-}(CO_2)]_3$[9,10]. The carbonyl carbon atoms in dimethyl carbonate molecules become highly electrophilic because the carbonyl oxygen atoms may coordinate with Lewis acid sites. So it is easy for nucleophilic regents to attack the carbonyl carbon atoms in dimethyl carbonate molecules. And the nucleophilicity of hydroxybutyl groups in phenol molecules is improved because of the coordination of hydroxyl hydrogen atoms with basic sites on the framework of $Zn_4O[(O_2C)\text{-}C_6H_4\text{-}(CO_2)]_3$. Second, $Zn_4O[(O_2C)\text{-}C_6H_4\text{-}(CO_2)]_3$ has higher surface area, porosity and well-defined structure. Thus the carbonyl carbon atoms in dimethyl carbonate molecules and hydroxyl hydrogen atoms in phenol molecules are easier to coordinate with Lewis acid sites and basic sites on the framework of $Zn_4O[(O_2C)\text{-}C_6H_4\text{-}(CO_2)]_3$, respectively. Third, the good chemical and thermal stability of $Zn_4O[(O_2C)\text{-}C_6H_4\text{-}(CO_2)]_3$ framework also contribute its higher catalytic activity.

TABLE-1
EFFECT OF DIFFERENT CATALYSTS
ON THE TRANSESTERIFICATION

Catalyst	Yield (%)	Selectivity (%) MPC	Selectivity (%) DPC	Selectivity (%) MPC+DPC
$Ti(OBu)_4$	62.7	41.3	18.7	95.7
Mg-Al-CO_3 LDH	48.9	33.6	10.1	89.4
Zn-Al-CO_3 LDH	51.6	36.6	12.1	94.3
$Zn_4O[(O_2C)\text{-}C_6H_4\text{-}(CO_2)]_3$	71.2	41.7	27.2	96.7

Reaction conditions: n(phenol): n(DMC) = 2, w(catalyst) = 1 %, time = 10 h, temperature = 160-180 ºC, DMC: dimethyl carbonate, MPC: methyl phenyl carbonate, DPC: diphenyl carbonate

Effect of the amount of the catalyst on the synthesis of diphenyl carbonate: Table-2 shows the effect of catalyst $Zn_4O[(O_2C)\text{-}C_6H_4\text{-}(CO_2)]_3$ on the synthesis of diphenyl carbonate. It can be seen that, the amount of $Zn_4O[(O_2C)\text{-}C_6H_4\text{-}(CO_2)]_3$ has a notable effect on the transesterification. As shown in Table-2, when the amount of $Zn_4O[(O_2C)\text{-}C_6H_4\text{-}(CO_2)]_3$ increases from 0.2 to 1 wt. %, the conversion of dimethyl carbonate is increased to 71.2 % from 42.7 %. At the same time, the yield of methyl phenyl carbonate is increased by 17.4 to 41.7 % and the yield of diphenyl carbonate is increased by 11.3 to 27.2 %. However, above 1 %, the conversion of dimethyl carbonate, yields of methyl phenyl carbonate and diphenyl carbonate remain almost unchanged.

Effect of reaction time on the synthesis of diphenyl carbonate: Table-3 shows the effect of reaction time on the transesterification between dimethyl carbonate and phenol to diphenyl carbonate. As shown in Table-3, when the reaction time is increased from 2 to 10 h, the conversion of dimethyl carbonate increases to 71.2 % from 16.2 %. At the same time, the yield of methyl phenyl carbonate is increased by 30.1 % to 41.7 and the yield of diphenyl carbonate is increased by 23.5 to 27.2 %. However, above 10 h, the conversion of dimethyl carbonate, yields of methyl phenyl carbonate and diphenyl carbonate remain almost unchanged.

TABLE-2
EFFECT OF THE AMOUNT OF $ZN_4O[(O_2C)\text{-}C_6H_4\text{-}(CO_2)]_3$ ON THE TRANSESTERIFICATION

Amount of the catalyst (%)	Conversion of DMC (%)	Yield (%)		Selectivity (%)
		MPC	DPC	MPC+DPC
0.2	42.7	24.3	15.9	93.7
0.4	51.6	29.8	18.22	94.6
0.6	60.2	34.4	22.9	95.2
0.8	66.7	38.5	25.7	96.3
1.0	71.2	41.7	27.2	96.7
1.2	71.6	41.5	27.7	96.9
1.4	71.5	41.6	27.5	96.7

Reaction conditions: n(phenol): n(DMC) = 2, w($Zn_4O[(O_2C)\text{-}C_6H_4\text{-}(CO_2)]_3$) = 1 %, time = 10 h, temperature = 160-180 ºC, DMC: dimethyl carbonate, MPC: methyl phenyl carbonate, DPC: diphenyl carbonate

TABLE-3
EFFECT OF REACTION TIME ON TRANSESTERIFICATION

Reaction time (h)	Conversion of DMC (%)	Yield (%)		Selectivity (%)
		MPC	DPC	MPC+DPC
2	16.2	11.6	3.7	95.7
4	27.8	19.8	6.9	96.1
6	47.2	32.8	12.7	96.4
8	67.1	38.7	25.9	96.3
10	71.2	41.7	27.2	96.7
12	71.8	41.0	28.4	96.8
14	71.6	41.4	27.7	96.5

Reaction conditions: n(phenol): n(DMC) = 2, w($Zn_4O[(O_2C)\text{-}C_6H_4\text{-}(CO_2)]_3$) = 1 %, time = 10 h, temperature = 160-180 ºC, DMC: dimethyl carbonate, MPC: methyl phenyl carbonate, DPC: diphenyl carbonate

Conclusion

In summary, the advantages of this catalytic system are that the preparation method of the catalyst is simple, fast and economical and the catalyst is heterogeneous and easier to separate from the product. Therefore, $Zn_4O[(O_2C)\text{-}C_6H_4\text{-}(CO_2)]_3$ is an effective catalyst for synthesis of diphenyl carbonate *via* the transesterification.

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REFERENCES

1. L.P. Wang, B. Xiao and G.Y. Wang, *Polym. Mater. Sci. Eng*., **10**, 8 (2011).
2. L.P. Wang, B. Xiao, J.G. Li, Sh.Y. Liu, X.G. Yang and G.Y. Wang, *J. Chem. Eng. Chinese Univ*., **1**, 99 (2012).
3. H.Y. Niu, J. Yao, Y. Wang and G.Y. Wang, *Catal. Commun*., **8**, 355 (2007).
4. H.Y. Niu, J. Yao, Y. Wang and G.Y. Wang, *J. Mol. Catal. Chem*., **235**, 240 (2005).
5. Q.Q. Yu, Sh. Wang, R. X. Bai, F. M. Mei and G. X. Li, *Chem. J. Chin. Univ*., **8**, 1502 (2005).
6. Sh. Wang, Q.Q. Yu, J. M. Huang, R. X. Bai and G. X. Li, *Acta Chim. Sin*., **17**, 1575 (2005).
7. S. Turner, O.I. Lebedev, F. Schroder, D.E. Esken, R.A. Fischer and G. Van Tendeloo, *Chem. Mater*., **20**, 5622 (2008).
8. Y.X. Zhou, S.G. Liang, J.L. Song, T.B. Wu, S.Q. Hu, H.Z. Liu, T. Jiang and B.-X. Han, *Acta Phys. Chim. Sin*., **26**, 939 (2010).
9. B. Civalleri, F. Napoli, Y. Noel, C. Roetti and R. Dovesi, *Cryst. Eng. Comm*., **5**, 364 (2006).
10. S. Horike, M. Dinca, K. Tamaki and J.R. Long, *J. Am. Chem. Soc*., **130**, 5854 (2008).