

Preparation of Diphenyl Oxalate from Transesterification of Dimethyl Oxalate with Phenol over TS-1 Catalyst

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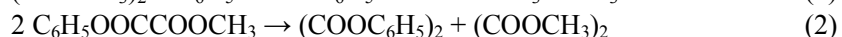
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Abstract: Diphenyl oxalate was synthesized from transesterification of dimethyl oxalate with phenol over TS-1 (2.5 wt% Ti) catalyst. TS-1 catalyst, as a heterogeneous catalyst, showed excellent selectivity of diphenyl oxalate and methylphenyl oxalate compared with other homogeneous catalysts. Lewis acid sites on TS-1 catalyst were the active sites for transesterification of dimethyl oxalate with phenol. The high selectivity was closely related to the weak acid sites over TS-1.

Keywords: Diphenyl oxalate, transesterification, dimethyl oxalate, weak acid sites, TS-1.

Polycarbonates (PCs) are excellent engineering thermoplastics and substitutes for metals and glass because of their good impact strength and transparency¹. In recent years, there has been an increasing demand for safer and environmentally friendly processes for PCs synthesis. Non-phosgene processes have been proposed to replace the traditional phosgene process². One such process included the synthesis of diphenyl carbonate (DPC) followed by the transesterification between DPC and bisphenol A. Several alternative non-phosgene methods for DPC synthesis have been proposed. Among them, transesterification of dimethyl oxalate (DMO) with phenol is conducted following the step of transesterification of DMO with phenol to prepare diphenyl oxalate (DPO) and decarbonylation of DPO to DPC. This method is an effective route because azeotrope does not form in the reaction system and co-products methanol and CO can be separated easily.

The synthesis of DPO from transesterification of phenol with DMO followed 2-step reaction module consisting of transesterification of DMO with phenol into MPO and disproportionation of MPO into DPO and DMO, proceeding as shown in reaction (1) and (2)³.



Usually, transesterification of DMO with phenol was carried out in the liquid phase using homogeneous catalysts such as Lewis acids and soluble organic Pb, Sn, or Ti compounds^{4,5}. However, there were some disadvantages such as the difficulties of

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catalyst separation and recovery in these reaction systems. There were few reports on the development of active heterogeneous catalysts for the reaction. Hence we report that the titanium silicate molecular sieve TS-1 is a good solid catalyst for this transesterification. TS-1 is a Ti-containing zeolite with the MFI structure that was first synthesized in 1983 by Enichem researchers⁶. The presence of Ti atoms occupying framework positions in the zeolite lattice is responsible for the remarkable catalytic properties of this material. TS-1 has been reported to catalyze a variety of oxidation reactions carried out in liquid phase at low temperature with H₂O₂ as oxidant: aromatic hydroxylation, olefin epoxidation, ketone ammoximation, alcohol oxidation, alkane oxyfunctionalization, *etc*⁷⁻¹⁰. Reported herein is a novel application of TS-1 as an acid catalyst.

Experimental

TS-1 (2.5wt%Ti) obtained from SINOPEC Research Institute of Petroleum Processing was dried in an oven at 120°C for 2 h to remove the absorbed water and calcined at 550°C for 4 h in the air atmosphere.

Ester exchange reaction was performed by mixing 0.1 mol DMO, 0.5 mol phenol and 1.8 g TS-1 catalyst in a 250 mL glass flask equipped with a thermometer, a reflux condenser, a stirrer under refluxing condition at atmosphere pressure and 180°C. Especially, the condensing water of 80°C was used to remove methanol from the reaction system. By this means, the reaction equilibrium was broken and the reaction was accelerated to develop towards the desired direction. Qualitative and quantitative analysis of reaction products were carried out using a GC-MS spectrometer of HP 5890-HP 5971MSD and a gas chromatograph equipped with a flame ion detector (FID). An OV-101 packed column was used to separate products for GC analysis.

The FTIR spectrum was recorded using Bruker Co. Model Vector 22 FTIR spectrometer. The acidity of TS-1 was measured using pyridine as a molecular probe. The NH₃-TPD spectrum was recorded using Micromeritics Co. Model 2910 chemical adsorption spectrometer.

Results and Discussion

In catalysts screening experiments, it was found that TS-1 is one of the efficient catalysts for transesterification of dimethyl oxalate with phenol. Especially, it exhibited better selectivity of MPO and DPO than such catalysts as shown in **Table 1**. The total selectivity of MPO and DPO based on DMO over TS-1 could reach 99.2 % while other catalysts only had 20~30%. Although Ti(OC₄H₉)₄ and AlCl₃ showed good activities according to the conversion of DMO, but the selectivity of MPO and DPO was poor. When Ti(OC₄H₉)₄ was chosen as the catalyst for transesterification of DMO with phenol, the major by-products were *n*-butyl alcohol, *n*-butyl ether, butylphenyl oxalate and ethyl benzene, and the selectivity of by-products could reach 76.6%. It was observed that the major by-product was anisole when AlCl₃ and MgCl₂ were used as catalyst, and the selectivity of anisole was more than 60%. Overall, TS-1 showed more significant

selectivity to MPO and DPO than other catalysts. However, the conversion of DMO was not too high over TS-1. This may be related to the small pore size of TS-1, which made the formed MPO and DPO diffuse outside the pore difficultly. So, the transesterification of DMO with phenol just occurred on the outer surface of TS-1.

Table 1 The Activities of the Different Catalysts

Catalyst	DMO conversion /%	MPO selectivity /%	DPO selectivity /%
TS-1 ^a	26.5	89.2	10.0
Ti(OC ₄ H ₉) ₄	92.5	20.6	2.8
MgCl ₂	30.5	19.7	0.0
AlCl ₃	79.8	30.8	2.1

Reaction condition: 0.1 mol DMO, 0.5 mol phenol, 0.01 mol catalyst, 180°C, 2 h.

a: 1.8 g TS-1 calcined at 550°C.

When the transesterification was conducted over TS-1 catalyst, it was also observed that the little by-product was mainly anisole, which could be produced *via* a methylation of phenol with DMO through a nucleophilic attack of methyl group in DMO with the phenoxy compound, followed by a decarboxylation. This reaction mechanism could be confirmed by the detection of methyl formate in the distillates and carbon dioxide in non-condensed gas from the top of the column. The methylation of phenol could be illustrated as reaction (3).

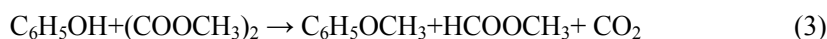


Figure 1 IR spectra of pyridine adsorbed on TS-1

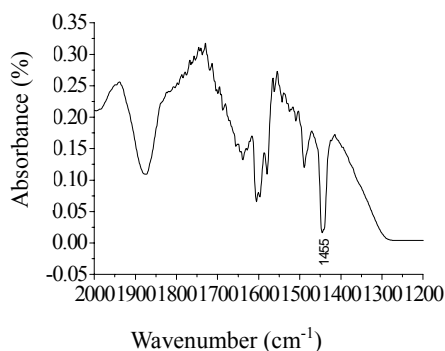
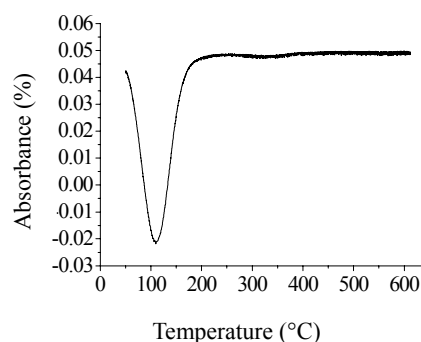


Figure 2 NH₃-TPD profile of TS-1



The FTIR spectrum adsorbed pyridine of TS-1 was shown in **Figure 1**. IR band at 1455 cm⁻¹ is attributed to pyridine adsorbed on Lewis acid sites, IR band at 1545 cm⁻¹ to that adsorbed on Brønsted acid sites. According to **Figure 1**, there were significant peaks at 1455 cm⁻¹, but no peak was found at 1545 cm⁻¹. These indicated that many Lewis acid sites were present on TS-1 catalyst, while Brønsted acid sites were absent. Therefore, Lewis acid sites on TS-1 catalyst were active sites for transesterification of dimethyl oxalate with phenol.

NH₃-TPD characterization was conducted to survey the acid strength of TS-1. The peaks in the high temperature region can be attributed to the desorption of NH₃ from the strong acid sites, and the peaks in the low temperature region is attributed to the desorption of NH₃ from the weak acid sites. It can be found there only existed weak acid sites on TS-1 as shown in **Figure 2**. In catalysts screening experiments, the selectivity of anisole was only 0.8% when TS-1 was used as catalyst. However, the selectivity of anisole was more than 60% over AlCl₃ and MgCl₂, which were strong acids. Therefore, acid strength was related to the selectivity of products, and the strong acid sites were responsible to the formation of anisole. So, the result of TPD gave the reason for high selectivity of MPO and DPO over TS-1.

Acknowledgments

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References

1. D. Freitag, U. Grigo, P. R. Müller, *et al.*, *Encyclopaedia of Polymer Science and Engineering*, New York, **1988**, Vol. *11*, p. 648.
2. Y. Ono, *Pure Appl. Chem.*, **1996**, *68*, 367.
3. S. P. Wang, X. B. Ma, H. L. Guo, *et al.*, *Chemistry*, **2002**, *65*, 476.
4. N. Keigo, T. Shuji, H. Katsumasa, S. Ryoji, U.S. Patent 5834651, **1998**.
5. N. Keigo, T. Shuji, H. Katsumasa, *et al.*, U.S. Patent 5922827, **1999**.
6. M. Taramasso, G. Perego, B. Notari. U.S. Patent 4410501, **1983**.
7. M. G. Clerici, G. Bellussi, U. Romano, *J. Catal.*, **1991**, *129*, 159.
8. D. R. C. Huybrechts, L. De Bruycker, P. A. Jacobs, *Nature*, **1990**, *345*, 240.
9. A. J. H. P. Vanderpol, J. H. C. van Hooff, *Appl. Catal. A*, **1993**, *106*, 97.
10. A. Thangavaj, R. Kumar, P. Ratnasamy, *J. Catal.*, **1991**, *131*, 394.

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