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COMMUNICATION

Transesterification of Phenol and Dimethyl Carbonate Catalyzed by Titanium Oxide Acetylacetonate Catalyst

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Abstract: Titanium oxide acetylacetonate ($TiO(acac)_2$) was found to be a novel and efficient heterogeneous catalyst for the transesterification of phenol and dimethyl carbonate (DMC) to diphenyl carbonate (DPC). The conversion of phenol was 45.8% on the $TiO(acac)_2$ pretreated at 180 °C, and the turnover number reached 96, which was better than the more common organic titanium catalyst. The effect of the amount of catalyst on the catalytic performance was investigated. The transesterification selectivity decreased with catalyst loadings over 0.2 g per 100 ml reactants. At the optimized amount of catalyst the conversion of phenol was 42.4%, and no anisole was detected. In particular, the $TiO(acac)_2$ catalyst proved reusable, and catalytic activity of the recovered $TiO(acac)_2$ was almost the same as that of the fresh catalyst. The conversion of phenol 40.0% was attained from $TiO(acac)_2$ recovered for the fifth time.

Key words: titanium oxide acetylacetonate; diphenyl carbonate; transesterification; phenol; heterogeneous catalyst

Diphenyl carbonate (DPC) is an important chemical intermediate and is used extensively for the preparation of many organic compounds and polymer materials, especially for the preparation of polycarbonates without the use of phosgene bisphenol A in a melt transesterification. Transesterification of phenol and dimethyl carbonate (DMC) is considered to be the most promising method for the industrial production of DPC because DMC is a relatively "green" raw material. The synthesis of DPC via transesterification is usually carried out in the liquid phase using homogeneous catalysts such as organic tin or titanium compounds [1,2]. However, the titanium and tin compounds are too poisonous to be considered environmentally benign catalysts. Moreover, homogeneous catalysts are generally difficult to separate from the final product. Solid catalysts are generally the focus of current research. Until now, several heterogeneous catalysts had been investigated for the transesterification, such as complex metal oxides [3–6], heteropoly compounds [7,8], and molecular sieves [9,10]. Ti-HMS shows excellent transesterification selectivity, avoiding the production of anisole and giving a 31.4% conversion of phenol, but Ti-HMS cannot be reused. The stability of the V-Cu complex oxide is better than other heterogeneous catalysts, and the conversion of phenol was 37.0%. However, 3.2% of the byproduct anisole was also produced.

In this work, $TiO(acac)_2$ is the first heterogeneous catalyst for the transesterification of DMC and phenol in the synthesis of DPC to the best of our knowledge. It was found that $TiO(acac)_2$ is a highly efficient and stable heterogeneous catalyst with greater than 99.9% transesterification selectivity.

The transesterification of phenol (AR, Guangdong Guanghua Sci-Tech Co., Ltd., China) and DMC (≥ 99.9%, Huasheng Co. Ltd., Shandong University of Petroleum, China) was carried out in a 100 ml three-neck round-bottomed flask under a nitrogen atmosphere. The mixture of phenol and $TiO(acac)_2$ (≥ 99.9%, Shanghai Dibo Chemical Co. Ltd., China) was stirred and heated to 175 °C. DMC was added dropwise, and the reaction left for 9 h. $TiO(acac)_2$ was used as a heterogeneous catalyst, which is insoluble in the reaction system. The products and the azeotrope of DMC with methanol were analyzed by GC (Shimadzu, GC-12B).

Thermal analysis (Fig. 1) of the catalyst indicates that the decomposition temperature of $TiO(acac)_2$ is 238 °C. When

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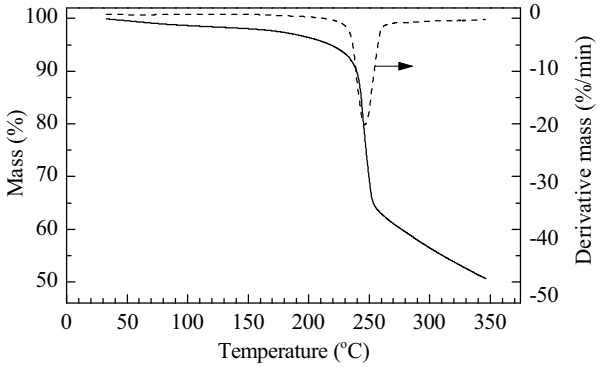

Fig. 1. TG-DTG curves of the $TiO(acac)_2$ sample.

$TiO(acac)_2$ was pretreated at 180 °C, the catalytic activity and the transesterification selectivity increased significantly. The conversion of phenol increased from 19.8% to 39.4%, and the transesterification selectivity increased from 98.5% to 99.8% with the use of 0.4 g of $TiO(acac)_2$.

Figure 2 shows the effect of the amount of catalyst on the transesterification. The conversion of phenol increased with increasing catalyst amount up to 0.4 g, giving the highest phenol conversion of 45.8% and transesterification selectivity of 99.4%. Meanwhile, the turnover number (TON, *n*(phenol)/*n*(Ti)) reached 96, which is superior to that of the organic titanium homogeneous catalyst [2] (TON = 92). However, the transesterification selectivity decreased as the amount of catalyst increased. No anisole was produced using less than 0.2 g of the catalyst. The weak acidity of $TiO(acac)_2$ is advantageous to the transesterification of phenol with DMC to DPC, but in excess, the acidity produces anisole by methylation of phenol or by the decomposition of MPC was detected [8,11–14]. Therefore, 0.2 g was the optimized amount of catalyst giving 42.4% conversion of phenol and 100% transesterification selectivity.

Stability is an important factor for heterogeneous catalysts. $TiO(acac)_2$ was recovered by filtration, washed with DMC, dried at 100 °C, and again heat treated at 180 °C.

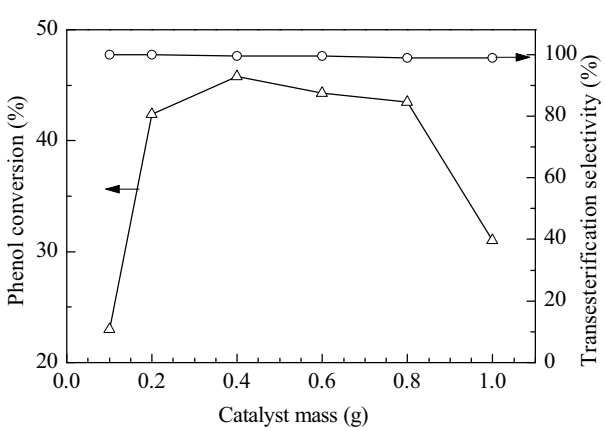

Fig. 2. Effect of the amount of catalyst on the transesterification reaction. Reaction conditions: *n*(phenol) = *n*(DMC) = 160, 150–180 °C, 9 h.

Table 1 Reuse of $TiO(acac)_2$ in the transesterification of DMC and phenol

Run	Phenol conversion (%)	Yield (%)	
		MPC	DPC
1	42.4	23.7	18.7
2	41.5	21.9	19.6
3	39.8	21.2	18.6
4	42.6	23.9	18.7
5	40.3	20.7	19.6

Reaction conditions: *n*(phenol) = *n*(DMC) = 160, *m*(catalyst) = 0.2 g, 150~180°C, *t* = 9 h.

Table 1 shows that the catalytic activity of the recovered $TiO(acac)_2$ was similar to the fresh catalyst. The conversion of phenol remained above 40.0%, and no anisole was detected.

For the transesterification of DMC and phenol, $TiO(acac)_2$ has been found to be a novel and efficient heterogeneous catalyst, with both high phenol conversion and good transesterification selectivity. In particular, the selectivity and stability of $TiO(acac)_2$ are superior to other heterogeneous catalysts. Under the optimized reaction conditions, using 0.2 g $TiO(acac)_2$, the conversion of phenol was 42.4% and the transesterification selectivity was 100%. The TON reached 89, which is similar to the best homogeneous catalyst. Therefore, $TiO(acac)_2$ is a highly efficient heterogeneous catalyst for the transesterification of phenol and DMC to DPC.

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