The nature of surface acidity and reactivity of MoO_3/SiO_2 and MoO_3/TiO_2–SiO_2 for transesterification of dimethyl oxalate with phenol: A comparative investigation

Yue Liu [a], Xinbin Ma [a,*], Shengping Wang [a], Jinlong Gong [b,**]

[a] Key Laboratory for Green Chemical Technology, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China
[b] Department of Chemical Engineering, University of Texas at Austin, Austin, TX 78712-0231, USA

Abstract

This paper presents results of a comparative investigation of the transesterification of dimethyl oxalate (DMO) with phenol to produce methyl phenyl oxalate (MPO) and diphenyl oxalate (DPO) over MoO_3/SiO_2 and MoO_3/TiO_2–SiO_2 catalysts. The evaluation results show that MoO_3/TiO_2–SiO_2 is much more active and selective than MoO_3/SiO_2. The surface structure and acidity of MoO_3/SiO_2 and MoO_3/TiO_2–SiO_2 were investigated by a series of characterization approaches. XRD and FT-IR demonstrated that the incorporation of amorphous TiO_2 could not only enhance the interaction between MoO_3 and SiO_2, but also improve the dispersion state of MoO_3 on the surface of SiO_2. NH_3-TPD and FT-IR of adsorbed pyridine measurements indicated that amorphous TiO_2 incorporation into and further interaction with MoO_3 and SiO_2 formed more weak acid sites on the surface of the catalysts. However, Brönsted acid sites were also detected on the surface of the MoO_3/TiO_2–SiO_2 catalysts, which further motivated us to study the nature of Brönsted acid sites in detail. Several conventional Brönsted acids were also tested in the transesterification. The results unexpectedly showed that conventional Brönsted acids have better reactivities than those of conventional Lewis acids from selective point of view. In addition, the combination of reactivity tests, NH_3-TPD spectra, and FT-IR measurements of adsorbed pyridine strongly suggest that the strong Lewis acid is more responsible for the production of the by-product anisole than the strong Brönsted acid. The results indicated that the improvement of catalytic efficiency of MoO_3/TiO_2–SiO_2, compared to MoO_3/SiO_2, could be ascribed to the increased dispersion capacity of MoO_3 and the dominant weak acid sites (including the synergistic effect of the weak Lewis acid sites with the weak Brönsted acid sites). A tentative mechanism for the transesterification reaction over Brönsted acid was proposed.

1. Introduction

Polycarbonates (PCs) are important engineering thermoplastics with excellent mechanical and optical properties as well as electrical and heat resistance properties. They have been used in many fields as substitutes for glasses and metals. PCs have been commercially prepared by the interfacial polycondensation of bisphenol-A with phosgene. The disadvantages of this conventional phosgene process include the use of large amounts of methylene chloride as the solvent, about ten times the products' weight, and highly toxic phosgene as a reagent [1].

Over the past years, there has been increasing demand for safe and environmentally friendly processes for PC synthesis. One such process is the synthesis of diphenyl carbonate (DPC) followed by transesterification between DPC and bisphenol-A [2,3]. In this scheme, no toxic solvents are used and the by-product, phenol, can be recycled.

However, DPC is prepared commercially by the reaction of phenol and phosgene in the presence of bases such as sodium hydroxide [4]. Obviously, this traditional process for DPC synthesis has the same environmental concerns as mentioned
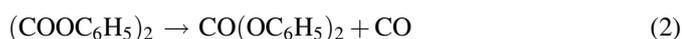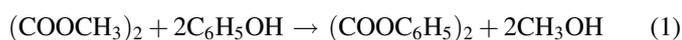
above due to the use of phosgene. Thus, utilizing green DPC synthesis has great potential to help avoid the social and environmental effects of pollution.

So far, several non-phosgene alternatives for DPC synthesis have been developed or proposed [5–14], e.g., the oxidative carbonylation of phenol and transesterification reactions. Most literature covering the catalytic oxidative carbonylation of phenol process makes clear that it suffers from low phenol conversions, poor diphenyl carbonate selectivity, and difficult regeneration of the palladium catalyst [7–12]. Alternatively, dimethyl carbonate (DMC) can be used as a substitute for phosgene in the synthesis of DPC through transesterification with phenol. Unfortunately, the involved reaction rate is low and the formation of azeotropes between DMC and methanol causes separation problems [4–6]. The transesterification of dimethyl oxalate (DMO) with phenol to prepare diphenyl oxalate (DPO), followed by the decarbonylation of DPO to produce DPC, as shown in reactions (1) and (2), is an another available route [13,14].

$$(COOCH_3)_2 + 2C_6H_5OH \rightarrow (COOC_6H_5)_2 + 2CH_3OH \quad (1)$$

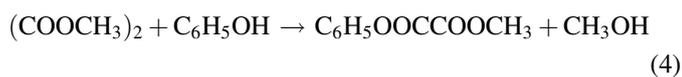$$(COOC_6H_5)_2 \rightarrow CO(OC_6H_5)_2 + CO \quad (2)$$

Technically, this method is more effective because no azeotropes are formed in the reaction system and the co-products, methanol and CO, can be separated easily. These, in turn, can be reused in DMO production via oxidative carbonylation of methanol as shown in reaction (3) [15].

$$2CO + 2CH_3OH + 1/2O_2 \rightarrow (COOCH_3)_2 + H_2O \quad (3)$$
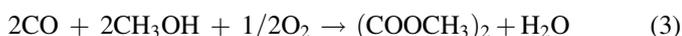
As a matter of fact, a pilot plant test in DMO production has been completed by Ube Industries and the technology for large-scale commercial production has been established. One of the proposed applications of this process is to supply DMO for the preparation of DPC [16].

With respect to DPC synthesis from the transesterification of DMO with phenol, the decarbonylation of DPO to produce DPC could be carried out easily over PPh$_4$Cl catalyst, and the yield of DPO could be up to 99.5% [17,18]. The synthesis of DPO from the transesterification of phenol with DMO follows a two-step reaction consisting of the transesterification of DMO with phenol into methyl phenyl oxalate (MPO) (Reaction 4), followed by the production of DPO via the disproportionation of MPO (Reaction 5), as shown in the following reactions.

$$(COOCH_3)_2 + C_6H_5OH \rightarrow C_6H_5OOCCOOCH_3 + CH_3OH \quad (4)$$

$$2C_6H_5OOCCOOCH_3 \rightarrow (COOC_6H_5)_2 + (COOCH_3)_2 \quad (5)$$

The thermodynamic equilibrium constants of reactions (4) and (5) at 453 K are only 0.23 and 2.09×10^{-7}, respectively, based on thermodynamic calculations including group contributions on liquid components. This result implies that transesterification between DMO and phenol, especially the disproportionation of MPO, is not thermodynamically favored. The equilibrium conversion of DMO is only 32.4% based on Eq. (4) [19].

The transesterification of DMO with phenol has been generally performed in the liquid phase with homogeneous acid catalysts like Lewis acids or soluble organic Pb, Sn, or Ti compounds [13,14]. To our best knowledge, few studies have been reported regarding the development of Brönsted acids catalysts for the reaction. Therefore, some Brönsted acids were tested in the present study to extend the scope of homogeneous acid catalysts in the transesterification reaction. The results unexpectedly showed that the conventional Brönsted acids had better catalytic reactivities than the homogeneous acid catalysts mentioned above regarding product selectivities. However, from an industrial point of view, the difficulty of separating catalysts from products in a homogeneous system and the potential environmental impact must be considered. Based on these concerns, the development of heterogeneous catalysts with excellent catalytic performance is highly desirable, and some efforts have been made in this direction [19–24]. Gong et al. presented results of an investigation into the reactivities of supported MoO$_3$ catalysts in the transesterification of DMO with phenol [20]. Due to low DPO selectivity and yield obtained, the development of novel improved transesterification catalysts with desirable general activity and excellent DPO selectivity is necessary. This motivated some of the studies we present here.

Recently, TiO$_2$ supported MoO$_3$ catalysts have attracted increased attention in many industrially relevant reactions such as hydrodesulfurization, because of their high catalytic activity and the strong interaction of active species with the support [25,26]. However, TiO$_2$ supports have relatively small specific surface areas compared to those of silica, alumina, etc., and are difficult to make into pellets. Moreover, the active anatase structure possesses only low thermal stability, which makes TiO$_2$ support alone unsuitable for industrial applications [27]. In order to make good use of these advantages while overcoming the barriers, we prepared composite TiO$_2$–SiO$_2$ supports, where MoO$_3$ was deposited by slurry impregnation, which is an environmentally friendly process and a simple, clean, effective alternative to the conventional preparation using a solution of (NH$_4$)$_6$Mo$_7$O$_{24}$ [28]. The synthesis of DPC from the transesterification of DMO with phenol over MoO$_3$/SiO$_2$ and the novel MoO$_3$/TiO$_2$–SiO$_2$ catalysts was well investigated and compared. Specifically, to gain a better understanding of the relationships between the dispersion of surface species, distribution of the surface acid sites (Brönsted and Lewis acidities), and the catalytic activity, MoO$_3$/SiO$_2$ and MoO$_3$/TiO$_2$–SiO$_2$ catalysts were characterized by XRD, FT-IR, NH$_3$-TPD, and FT-IR of adsorbed pyridine measurements. We also present results of reactivity measurements of conventional Brönsted acids to examine their effects on our MoO$_3$/TiO$_2$–SiO$_2$ catalysts. A tentative mechanism for the transesterification reaction over a Brönsted acid has been proposed.

2. Experimental

2.1. Catalyst preparation

Commercial silica (average particle size 4 mm, Jiangyan City Chemical Auxiliary Factory of China) was used as a