



Transesterification of dimethyl oxalate with phenol over $\text{MoO}_3/\text{SiO}_2$ catalysts

Jinlong Gong, Xinbin Ma*, Shengping Wang,
Moyi Liu, Xia Yang, Genhui Xu

State Key Laboratory of C1 Chemistry and Technology, School of Chemical Engineering and Technology,
Tianjin University, Tianjin 300072, China

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Abstract

The transesterification of dimethyl oxalate (DMO) with phenol to methyl phenyl oxalate (MPO) and diphenyl oxalate (DPO) was carried out in liquid phase using a variety of solid catalysts. The evaluation results showed that $\text{MoO}_3/\text{SiO}_2$ had a better activity and excellent selectivity to target products compared with many conventional ester exchange catalysts. The effects of supports, loading amount of Mo, catalyst amount and reaction time were investigated. Under catalytic reaction conditions, the total selectivities to methyl phenyl oxalate and diphenyl oxalate were up to 98%. And 49.3% yield of methyl phenyl oxalate and 17.3% yield of diphenyl oxalate were obtained at 453 K in the presence of $\text{MoO}_3/\text{SiO}_2$. A plausible mechanism for the transesterification of dimethyl oxalate with phenol to methyl phenyl oxalate over $\text{MoO}_3/\text{SiO}_2$ was proposed.

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Keywords: Diphenyl carbonate; Dimethyl oxalate; Diphenyl oxalate; Methyl phenyl oxalate; Transesterification; $\text{MoO}_3/\text{SiO}_2$

1. Introduction

Polycarbonates (PCs) are important engineering thermoplastics with excellent mechanical and optical properties as well as electrical and heat resistance properties [1]. They have been used in many fields as the substitutes of glass and metals. PCs have been commercially prepared by the interfacial polycondensation of bisphenol-A with phosgene. The disadvantages of the conventional phosgene process include: (1) the use of a large amount of methylene chloride as the solvent, which is about 10 times the weight of the products; (2) the highly toxic and corrosive phosgene as the reagent; (3) the complex process to remove ionic materials.

In recent years, there has been an increasing demand for safe and environmentally friendly processes for PCs synthesis. Phosgene-free processes for polycarbonate synthesis have been proposed to replace the conventional phosgene process [2]. One such process is composed of the synthesis

of diphenyl carbonate (DPC) followed by the transesterification between DPC and bisphenol-A [3]. In this method, no toxic solvents are used and the by-product phenol may be recycled.

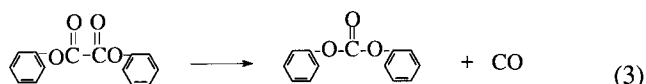
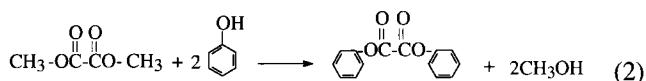
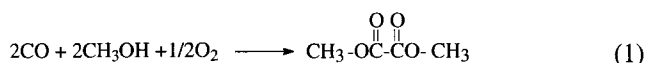
However, DPC is prepared commercially by the reaction of phenol and phosgene in the presence of bases such as sodium hydroxide [4]. Evidently, this traditional process for DPC has the same shortcomings as mentioned above because of the use of phosgene. Therefore, in order to produce PCs without social effects of pollution, the key technology is the synthesis of DPC via a green process.

Several alternative methods for DPC synthesis have been developed or proposed [5–12]. Among them, the transesterification of dimethyl oxalate (DMO) and phenol via a three-step reaction has been deemed as the most promising and possible routes for DPC synthesis from the raw materials such as carbon monoxide, phenol and oxygen [13,14]. In the first step, dimethyl oxalate is produced by carbonylation of methanol [15], as shown in reaction (1), and in the second step, diphenyl oxalate (DPO) is obtained from transesterification of dimethyl oxalate with phenol, as shown in reaction (2), and in the third, the decarbonylation of DPO [16], as shown in reaction (3),

* Corresponding author. Tel.: +86-22-27406498;
fax: +86-22-27890905.

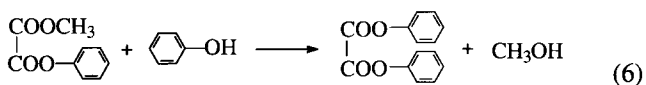
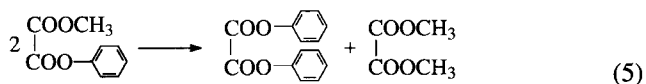
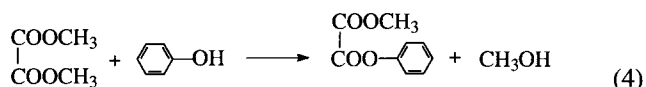
E-mail address: xbma@tju.edu.cn (X. Ma).

is carried out to produce DPC and by-product carbon monoxide.



Usually, the transesterification of DMO with phenol in reaction (2) is carried out in the liquid phase using traditional transesterification catalysts such as Lewis acids and soluble organic Pb, Sn, or Ti compounds [16]. However, in these homogeneous transesterification systems, the separation of the catalysts from the products will be complicated when these catalyst systems are applied to the industrial process. Therefore, the development of active solid catalysts is highly desirable in view of regeneration and separation. However, to our knowledge, there are few reports on the development of active heterogeneous catalysts for the reaction up to present time.

In this work, we attempt to quest active solid catalysts for the transesterification of DMO with phenol and several kinds of ester exchange catalysts have been used for the transesterification. Here, we propose that $\text{MoO}_3/\text{SiO}_2$ is an excellent solid catalyst for the transesterification of DMO with phenol. Moreover, DPO cannot be obtained directly from dimethyl oxalate and phenol through one step as illustrated in reaction (2). In fact, it experiences two steps to produce DPO due to low equilibrium constants for the forward reaction: the first step is the formation of methyl phenyl oxalate (MPO) and then the production of DPO via a further transesterification or disproportionation of MPO, as shown in the following:



Apparently, reaction (2) is the sum of reaction (4) with reaction (5) or (6). So, we mainly give discussion on the transesterification of DMO with phenol represented by reaction (2) in the present paper.

2. Experimental

2.1. Catalysts preparation

$\text{MoO}_3/\text{SiO}_2$ catalyst was prepared by conventional impregnation of SiO_2 (231 m^2/g , average pore size 80 Å) with an aqueous solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$. The water was evaporated to dryness at 353 K using a rotary evaporator, followed by drying the solid catalyst in an oven at 393 K overnight and calcining it in a muffle furnace at 823 K overnight. The surface areas of SiO_2 , 1 and 8 wt.% $\text{MoO}_3/\text{SiO}_2$ were 231, 155, 129 m^2/g , respectively.

The formation of MoO_3 was confirmed by XRD and XPS. It was observed that the Mo(VI) species was highly dispersed on silica. At low Mo loading, the molybdenum phase was not observed, whereas weak peaks of orthorhombic molybdenum oxide were detected at higher loadings. XPS analysis provided bond energy values equal to 232.4 ± 0.2 eV referring to Mo 3d_{5/2}, which is characteristic of Mo^{6+} and corresponds to the binding energy of MoO_3 . The XPS analysis also indicated that Mo(VI) species in the form of a monolayer was dominant at 1% Mo loading and MoO_3 of the orthorhombic crystal structure appeared at higher loading.

$\text{V}_2\text{O}_5/\text{SiO}_2$ and $\text{ZrO}_2/\text{SiO}_2$ catalysts were prepared by impregnating SiO_2 with an aqueous solution of ammonium metavanadate and zirconium oxychloride, respectively, followed by drying at 393 K overnight and calcining at 823 K in air overnight.

$\text{TiO}_2/\text{SiO}_2$ and $\text{SnO}_2/\text{SiO}_2$ catalysts were prepared by impregnating SiO_2 with a toluene solution of tetrabutyl titanate and dibutyltin dilaurate, respectively, followed by drying to remove the solvent at 393 K and calcining at 823 K in a muffle furnace overnight.

2.2. Transesterification of DMO with phenol

The transesterification of DMO with phenol was carried out in a three-neck flask (250 ml) equipped with a distillation apparatus and a thermocouple to monitor and control the reaction temperature. Especially, the top of distillation column was kept at 353 K by following through recycled water in order to remove methanol from the reaction system. By this means, the reaction equilibrium limitation in reaction (2) was broken and the reaction was accelerated to develop towards the desired direction. The reaction mixture contained 0.1 mol DMO, 0.5 mol phenol and catalyst. After the raw materials and catalyst were placed into the batch reactor, nitrogen gas was flowed at 30 sccm to purge the air from the reaction system. After 10 min, nitrogen was stopped and the flask was heated at a rate of 8 K/min. The reaction was conducted at 453 K at an atmospheric pressure. In order to eliminate concentration grads, a magnetic beater was used. Qualitative and quantitative analysis [17,18] of reaction products and distillates were carried out on a HP 5890-HP5971MSD and a HP 5890 gas chromatograph equipped with a flame

ionization detector (FID). An OV-101 packed column was used to separate products for GC analysis. The selectivity to MPO and DPO was defined as the moles of MPO and DPO produced per 100 mol of consumed DMO, and the yields of MPO and DPO were obtained from multiplication of DMO conversion by the selectivity to MPO and DPO.

3. Results and discussion

3.1. Catalytic activities of DMO with phenol

A variety of catalysts were prepared and their catalytic activities were investigated for the transesterification of dimethyl oxalate with phenol.

The activities of traditional acid and base catalysts for the transesterification of dimethyl oxalate with phenol are listed in Table 1. Generally, these acids and bases were not effective on the formation of target products (MPO and DPO) and give anisole as the main product. Especially, K_2CO_3 and $AlCl_3$ were very favorable for the generation of anisole.

Different oxide catalysts were investigated because of their easiness of catalyst–product separation and regeneration due to their heterogeneous nature. Table 2 presents the results of reaction between dimethyl oxalate with phenol. MoO_3 gives 54.1% DMO conversion and 7.0% DPO yield. And benzyl alcohol and methyl phenol was observed in this transesterification reaction besides anisole. But formation of these by-products was suppressed by using SiO_2 support.

Several other oxide catalysts were screened for the transesterification of dimethyl oxalate to diphenyl oxalate. TiO_2 was a good catalyst, which gave a high DPO yield of 6.3% but the DMO conversion was not very high (32.1%). Al_2O_3 was also an active catalyst, giving 67.6% DMO conversion. Unfortunately, the selectivities to MPO and DPO were only 31.5 and 7.4%, respectively. A catalyst such as ZrO_2 having both acidic and basic properties gave only 27.5% conversion with a low DPO selectivity of 7.5%. A relatively more active catalyst of MgO , compared with MoO_3 , gave 25% conversion and 4.2% DPO yield. Although 100% selectivity

Table 1

The catalytic activities of solid acids and bases for the transesterification of dimethyl oxalate with phenol^a

Catalyst	Conversion ^b (%)	Selectivity (%)			Yield (%)	
		AN	MPO	DPO	MPO	DPO
$ZnCl_2$	37.8	11.3	46.9	10.0	17.7	0.4
$AlCl_3$	79.8	60.4	30.8	2.1	24.6	1.7
K_2CO_3	77.4	70.8	14.9	0.3	11.5	0.2
$MgCl_2 \cdot 6H_2O$	30.5	39.6	19.7	0.0	10.9	0.0
$Zn(OAc)_2 \cdot 2H_2O$	28.1	35.8	53.9	2.6	16.4	0.1

Methyl phenyl oxalate (MPO), diphenyl oxalate (DPO), anisole (AN).

^a Reaction conditions: catalyst 0.01 mol, phenol 0.5 mol, $PhOH/DMO = 5.0$, reaction time 2 h, reaction temperature 453 K.

^b Based on charged DMO.

Table 2

The catalytic activities of different oxide catalysts for the transesterification of dimethyl oxalate with phenol^a

Catalyst	Conversion ^b (%)	Selectivity (%)			Yield (%)	
		AN	MPO	DPO	MPO	DPO
SiO_2	1.7	0.0	100	0.0	1.7	0.0
Al_2O_3	67.6	55.5	31.5	7.4	21.3	5.0
MgO	25.0	20.9	62.3	16.7	15.6	4.2
MoO_3	54.1	2.1	42.7	13.0	23.1	7.0
V_2O_5	35.0	1.1	73.1	2.6	25.6	0.9
ZrO_2	27.5	0.6	57.8	7.5	15.9	2.1
SnO_2	2.8	7.2	57.1	35.7	1.6	1.0
TiO_2	32.1	0.6	79.9	19.5	25.7	6.3
CaO	5.2	17.6	72.4	0.0	3.8	0.0
PbO	3.0	10.1	89.9	0.0	2.7	0.0
ZnO	4.2	5.6	94.4	0.0	3.9	0.0
La_2O_3	1.8	16.9	83.1	0.0	1.5	0.0
Bi_2O_3	4.5	12.8	87.2	0.0	3.9	0.0
Fe_2O_3	1.2	6.0	94.0	0.0	1.1	0.0

Methyl phenyl oxalate (MPO), diphenyl oxalate (DPO), anisole (AN).

^a Reaction conditions: catalyst 0.01 mol, phenol 0.5 mol, $PhOH/DMO = 5.0$, reaction time 2 h, reaction temperature 453 K.

^b Based on charged DMO.

to MPO was obtained for SiO_2 catalyst, the conversion of DMO was very low (1.7%).

Table 3 shows the catalytic activities of metal oxide supported on the silica. The loading amount of metal compound was 1% in weight. From the chart, we can see MoO_3/SiO_2 exhibited the highest selectivity and activity for the transesterification. The yields of MPO and DPO based on DMO were 40.5 and 13.9%, respectively. And the total selectivities to MPO and DPO exceeded 99%. Synchronously, only a trace amount of anisole was formed as a by-product.

3.2. Effect of supports

The effect of supports on the catalytic activity of MoO_3 is showed in Table 4. When MoO_3 was supported on the different carriers, specific surface area increased largely compared

Table 3

The catalytic activities of metal oxides supported on silica for the transesterification of dimethyl oxalate with phenol^a

Catalyst ^b	Conversion ^c (%)	Selectivity (%)			Yield (%)	
		AN	MPO	DPO	MPO	DPO
MoO_3	54.6	0.4	74.2	25.4	40.5	13.9
ZrO_2	22.8	1.2	62.3	6.4	14.2	1.5
V_2O_5	5.4	3.1	73.2	3.4	4.0	1.7
SnO_2	16.3	1.8	78.6	19.6	12.8	3.2
TiO_2	45.6	0.5	80.9	18.6	36.9	8.5

Methyl phenyl oxalate (MPO), diphenyl oxalate (DPO), anisole (AN).

^a Reaction conditions: catalyst 1.8 g, phenol 0.5 mol, $PhOH/DMO = 5.0$, reaction time 2 h, reaction temperature 453 K.

^b Metal compound was supported on silica in 1% as the corresponding oxide.

^c Based on charged DMO.

Table 4
Effect of supports on the catalytic activities of MoO₃ for the transesterification of dimethyl oxalate with phenol^a

Catalyst ^b	S_{BET}^c (m ² /g)	Conversion ^d (%)	Selectivity (%)			Yield (%)	
			AN	MPO	DPO	MPO	DPO
MoO ₃ /Al ₂ O ₃	263.6	62.7	5.9	53.9	35.4	33.7	3.7
MoO ₃ /ZrO ₂	32.1	53.7	0.7	85.9	8.4	46.1	4.5
MoO ₃ /MgO	47.2	60.2	20.9	64.5	12.6	38.8	7.6
MoO ₃ /SiO ₂	154.7	54.4	0.8	81.7	17.5	44.4	9.5
MoO ₃ /SiO ₂ -Al ₂ O ₃	186.3	73.5	9.0	72.2	16.6	53.1	12.2

Methyl phenyl oxalate (MPO), diphenyl oxalate (DPO), anisole (AN).

^a Reaction conditions: catalyst 1.8 g, phenol 0.5 mol, PhOH/DMO = 5.0, reaction time 2 h, reaction temperature 453 K.

^b Metal compound was supported in 8% as the corresponding oxide.

^c The surface areas of the catalysts were determined on a constant volume adsorption apparatus (CHEMBET-3000) by the N₂ BET method at the liquid nitrogen temperature.

^d Based on charged DMO.

with MoO₃ and was close to supports surface area. Although they all showed high activities for the transesterification of DMO with phenol, the selectivities to MPO and DPO were dependent on different supports. When MoO₃ was supported on Al₂O₃, MgO and SiO₂-Al₂O₃, anisole yield was comparatively high. In the previous study [19,20], we had found that acid strength was related to the selectivity of products and the strong acidic sites were responsible to the formation of by-product anisole. In these cases, high yield of anisole was a possible result of strong acidic or basic sites in Al₂O₃ or MgO supports. Among these supports, SiO₂-Al₂O₃ support showed highest MPO and DPO yields. Unfortunately, anisole yield was up to 9.0% and other by-products were also observed in the experiment. In view of the total selectivities to MPO and DPO and yields of MPO and DPO, silica support was regarded as the best.

3.3. Effect of catalyst amount

The effect of the amount of MoO₃/SiO₂ catalyst at 453 K and 2 h was investigated. And the loading amount of Mo was 8%. As shown in Fig. 1, the conversion of DMO was

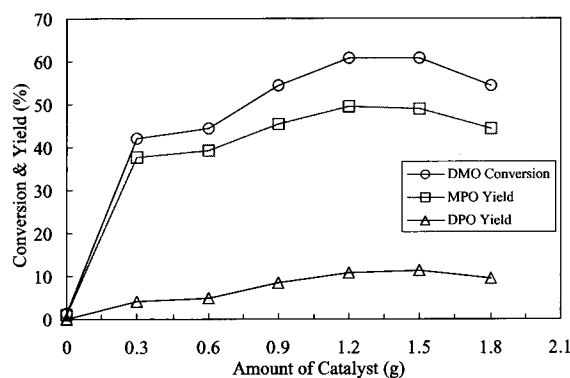


Fig. 1. The effect of catalyst amount on the transesterification of dimethyl oxalate with phenol. Reaction conditions: catalyst, MoO₃/SiO₂ (8% Mo loading), phenol 0.5 mol; PhOH/DMO = 5.0; reaction time 2 h; reaction temperature 453 K.

increased from 42.1 to 60.8% with the increase of catalyst amount from 0.3 to 1.5 g, while the total selectivities to MPO and DPO remained almost constant at around 98–99%. Accordingly, the yield of MPO and DPO was improved. Above 1.5 g, the conversion of DMO was decreased slowly with increasing amount of MoO₃/SiO₂. At 1.5 g catalysts, the conversion of DMO and the yield of MPO and DPO showed the maxima.

3.4. Effect of the amount of Mo loading on silica

Fig. 2 shows the effect of the amount of Mo loading on silica on the transesterification of dimethyl oxalate with phenol to methyl phenyl oxalate and diphenyl oxalate in the Mo loading range 1–16%. When the amount of Mo loading was increased to 8%, the MPO yield with 44.4% was obtained. We found that surface Mo species in the form of a monolayer was dominant when Mo loading was below 1%. And while Mo loading was above 1%, the crystalline MoO₃ was appeared. The crystalline MoO₃ was also active for the transesterification. When Mo loading reached 8%, the activity of crystalline MoO₃ reached the highest. Detailed research for Mo loading is under way.

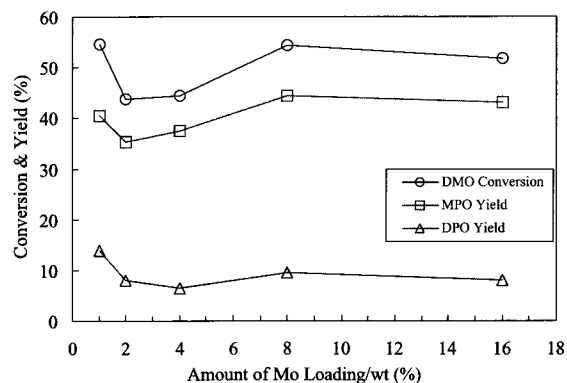


Fig. 2. The effect of Mo loading on SiO₂ on the transesterification of dimethyl oxalate with phenol. Reaction conditions: catalyst 1.8 g; phenol 0.5 mol; PhOH/DMO = 5.0; reaction time 2 h; reaction temperature 453 K.

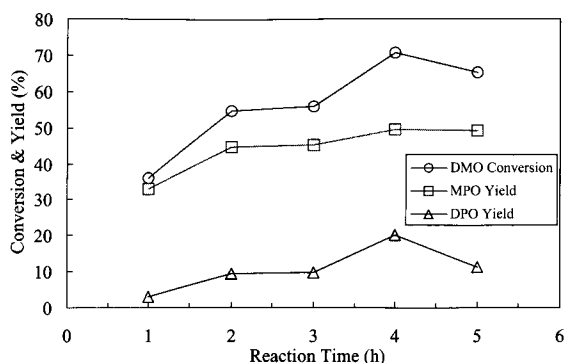
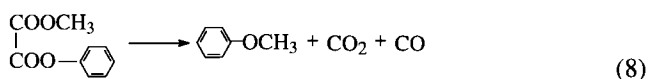
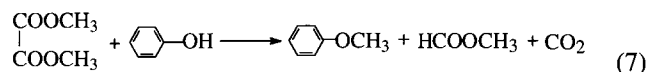


Fig. 3. The effect of reaction time on the transesterification of dimethyl oxalate with phenol. Reaction conditions: catalyst, $\text{MoO}_3/\text{SiO}_2$ (8% Mo loading) 1.8 g; phenol 0.5 mol; $\text{PhOH}/\text{DMO} = 5.0$; reaction temperature 453 K.

3.5. Effect of reaction time

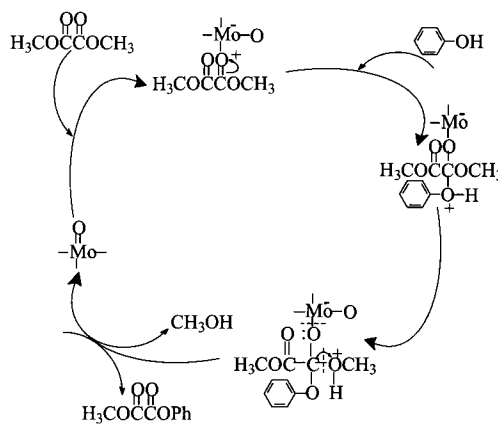
The effect of reaction time on the transesterification of dimethyl oxalate with phenol was studied in the presence of $\text{MoO}_3/\text{SiO}_2$ (8% Mo loading, 1.8 g) at 453 K. The reaction time was varied in the range 1–5 h, and the results are shown in Fig. 3. The yield of DPO increased constantly in the reaction time range between 1 and 4 h, and thereafter decrease in DPO yield was observed. The selectivities to anisole, MPO and DPO were 2.1, 75.3, and 17.5%, respectively, at 5 h of the reaction time. The decrease in DPO yield at reaction time more than 4 h can be rationalized by assuming that the synergetic effect of the methylation of phenol [11] (Eq. (7)) and decarboxylation of methyl phenyl oxalate [21] (Eq. (8)) made the DPO yield decreased and the selectivity to anisole improved.



The maximum DPO yield was found to be 17.3% at 4 h reaction time and total selectivities to MPO and DPO were up to 98%, indicating that our catalyst system comprising MoO_3 and SiO_2 is more active than traditional ester exchange catalysts (Table 1).

3.6. Proposed reaction mechanism

Based on the experimental results, the mechanism of the transesterification of dimethyl oxalate with phenol to methyl phenyl oxalate and diphenyl oxalate by $\text{MoO}_3/\text{SiO}_2$ is proposed in Scheme 1. In the presence of the active species, MoO_3 , the reaction course is according to cleavage of acyloxy bond. The carbonyl in DMO molecule is not easy to be attacked by weak nucleophilic reagent, phenol, because of its low activity. And the charges between carbon atom



Scheme 1. A plausible reaction mechanism.

in carbonyl and oxygen atom are not distributed evenly. So MoO_3 combines with negative charged oxygen atom, which makes the subsequent carbonyl translated into carbenium ion. Thereout, carbon atom in carbonyl possesses higher positive charge, which is propitious to attacking of phenol. Finally, ester exchange is completed along with formation of methanol and methyl phenyl oxalate.

4. Conclusions

From the studies on the transesterification of DMO with phenol over $\text{MoO}_3/\text{SiO}_2$, the following conclusions may be derived. The accomplishment of this study is the high yields of methyl phenyl oxalate and diphenyl oxalate over $\text{MoO}_3/\text{SiO}_2$ which can be employed effectively to transesterify dimethyl oxalate to diphenyl oxalate. At the experimental conditions, the Mo loading 8% in weight, 4 h and 453 K, the yield of diphenyl oxalate reaches 17.3%. In comparison to other conventional catalysts, $\text{MoO}_3/\text{SiO}_2$ gives higher total selectivities to methyl phenyl oxalate and diphenyl oxalate, up to 98%, and can be utilized in benign reaction conditions. A tentative mechanism for the transesterification over $\text{MoO}_3/\text{SiO}_2$ has also been proposed. Further detailed optimization research of this catalyst is in progress in this laboratory.

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