



Transesterification of diethyl oxalate with phenol using $\text{MoO}_3/\text{SiO}_2$ catalyst

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Received 17 September 2004; received in revised form 21 February 2005; accepted 24 February 2005
Available online 22 March 2005

Abstract

Transesterification of diethyl oxalate (DEO) with phenol to form diphenyl oxalate (DPO) has been carried out in liquid phase using $\text{MoO}_3/\text{SiO}_2$ solid acid catalyst with high conversion and 100% selectivity. A series of $\text{MoO}_3/\text{SiO}_2$ catalysts with different Mo loadings (1–20 wt%) were prepared using sol–gel technique and characterized using X-ray diffraction analysis (XRD), BET specific surface area, temperature-programmed desorption (TPD) of ammonia, and FTIR spectroscopic analysis of adsorbed pyridine. XRD analysis revealed the amorphous nature of the catalyst up to 10 wt% MoO_3 loading and the formation of crystalline $\alpha\text{-MoO}_3$ phase on amorphous silica support with higher MoO_3 loading. BET surface area showed high surface area for catalysts prepared by sol–gel technique with lower MoO_3 content; the surface area decreases with increasing MoO_3 loading. Ammonia TPD shows much higher acid strength compared to the catalysts prepared by impregnation technique. Among the series of catalysts prepared, $\text{MoO}_3/\text{SiO}_2$ containing 1 wt% MoO_3 was found to be the most active catalyst for transesterification reaction, with a maximum DEO conversion of 80.9 and 100% selectivity for DPO. The effects of reaction temperature and catalyst concentration on conversion and product selectivity have been investigated.

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Keywords: Transesterification; $\text{MoO}_3/\text{SiO}_2$; Diphenyl oxalate; Diethyl oxalate; Sol–gel technique

1. Introduction

Transesterification is an important organic transformation that provides essential synthons for a large number of applications in organic processes [1] such as synthesis of polycarbonates. Polycarbonates are excellent engineering thermoplastic materials with good mechanical and optical properties as well as electrical and heat resistance properties that are useful in many applications. Aromatic carbonates, mainly diphenyl carbonate (DPC), are an industrially important material used for the production of polycarbonate by melt polymerization process. The present commercial process for polycarbonate synthesis involves interfacial polycondensation of bisphenol-A with phosgene, and thus has major disadvantages of high toxicity and corrosion due to phosgene. It also involves a complex work-up procedure for removal of ionic material and use of a large volume of

water-soluble toxic methylenechloride, which is 10 times the weight of the product [2]. Hence, it is highly desired to develop a safe and environmentally benign process for polycarbonate synthesis. One of the non-phosgene routes for the preparation of polycarbonate involves the synthesis of DPC, followed by transesterification of DPC with bisphenol-A [3]. Various routes are being investigated for the synthesis of DPC. DPC can be prepared by direct transesterification of dimethyl carbonate with phenol using various catalysts [4,5]. One of the attractive synthetic routes for DPC involves decarbonylation of diphenyl oxalate [6–8], which in turn is prepared by transesterification of dialkyl oxalate with phenol. Transesterification of dimethyl oxalate with phenol to form diphenyl oxalate (DPO) has been studied using a variety of catalysts, followed by decarbonylation to obtain DPC. Keigo et al. [6–8] have described transesterification of DMO with phenol in liquid phase using traditional transesterification catalysts such as Lewis acids and soluble organic Pb, Sn, or Ti compounds. However, the selectivity for DPO was poor, and since the system was homogeneous,

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product separation from the reaction mixture was a problem. Various solid acid catalysts mainly metal oxides have been used for transesterification of DMO with phenol [9–13] with very low selectivity for DPO. Predominantly MPO is formed in all the cases, along with anisole in some cases. Maximum DMO conversion of 74.6% with 18% selectivity for DPO and the maximum DPO selectivity of 35% at 2.8% conversions has been reported in all these cases. Similarly, transesterification of dimethyl carbonate with phenol using solid catalysts has been studied. Methyl phenyl carbonate is predominantly formed with lower conversions (<20%); this is further disproportionated to form DPC in the second step using a different catalyst [5,14]. In all the earlier studies, dimethyl oxalate and phenol are used to prepare DPO by transesterification. In the case of transesterification of dimethyl carbonate and diethyl carbonate with different alcohols using a base catalyst, Figueras and Veldurthy [15] have reported considerable differences in the reactivity of diethyl carbonate as compared to dimethyl carbonate. To our knowledge, there are no reports in the open literature on the use of diethyl oxalate for the preparation of DPO. Considering the difference in reactivity of dimethyl oxalate and diethyl oxalate as well as the superior activity of $\text{MoO}_3/\text{SiO}_2$ catalyst prepared by sol–gel techniques, we have investigated the transesterification of diethyl oxalate with phenol. We have prepared $\text{MoO}_3/\text{SiO}_2$ solid acid catalyst by a novel sol–gel technique and used it for transesterification reactions. The results are reported in this paper.

2. Experimental

2.1. Catalyst preparation

A series of $\text{MoO}_3/\text{SiO}_2$ catalysts with varying molybdenum concentrations (1–20 wt%) were prepared by a sol–gel technique. Ammonium molybdate and ethyl silicate-40 (CAS registry no. 18945-71-7) were used as molybdenum and silica source, respectively. In a typical synthesis of 1% $\text{MoO}_3/\text{SiO}_2$, 0.353 g ammonium molybdate was dissolved in 20 ml water at 80 °C. This hot solution was added dropwise to the dry isopropyl alcohol solution (20 ml) of ethyl silicate-40 (29.7 g) with constant stirring. The resultant greenish gel was air dried and calcined at 500 °C in air in a muffle furnace for 8 h. Similarly catalysts with 5, 10, 15, and 20 wt% molybdenum loading were prepared.

Pure silica catalyst was prepared by adding 52 g of ethyl silicate-40 to 30 g dry isopropyl alcohol; to this mixture 0.02 g ammonia solution (25%) was added with constant stirring. The transparent white gel thus obtained was air-dried and calcined in a muffle furnace at 500 °C for 8 h.

2.2. Catalyst characterization

The X-ray diffraction analysis was carried out using a Rigaku X-ray diffractometer (Model DMAX IIIVC) with Cu

$\text{K}\alpha$ (1.542 Å) radiation. Temperature programmed desorption of ammonia (TPD- NH_3) was carried out using a Micromeritics Autocue 2910. BET surface area was determined using NOVA 1200 Quanta chrome.

The acidity of the samples was determined by pyridine adsorption studies using a Shimadzu 8000 series FTIR spectrometer arranged for DRIFT technique. The sample was placed in the DRIFT cell and heated to 400 °C in flow of inert gas (N_2) for 2 h. It was then cooled to 100 °C and pyridine was adsorbed on the sample in N_2 flow. The physisorbed pyridine was removed by flushing the cell with N_2 for 45 min at the same temperature and the spectrum was recorded. Then pyridine was desorbed for 45 min at 200, 300, and 400 °C and spectra were recorded at each temperature. The spectrum of the neat catalyst (before pyridine adsorption) at 100 °C was subtracted from all the spectra.

2.3. Catalytic activity

In a typical transesterification reaction, a 50 ml two-necked flask was fitted with a distillation apparatus and a thermometer. The temperature of the distillation condenser was maintained at 80 °C to remove the ethanol formed during the reaction to accelerate the reaction to form the desired product. The flask was charged with diethyl oxalate, phenol and catalyst. The flask was flushed with nitrogen for 10 min to remove the air from the reaction system. The reaction mixture was heated to 180 °C. The ethanol formed during the reaction was distilled out. The reaction was stopped after 5 h and the reaction mixture was analyzed using GC, Perkin-Elmer autosystem XL equipped with a capillary column PE-1 (30 m length, 0.25 mm internal diameter and 1 µm film thickness) with flame ionization detector as well as with a HP6890 equipped with FFAP column (50 m length, 0.25 mm internal diameter and 1 µm film thickness). The product was confirmed using GC–MS (Model GC Agilent 6890N with HP5 MS 30 m capillary column, MS Agilent 5973 Network MSD, MS data of DPO, M/Z : 242 (M^+), 214 ($M^+ - \text{CO}$), 77 (Ph)) and GC–IR (Perkin-Elmer Spectrum 2001, column DB-1, 25 m length, 0.32 mm internal diameter, IR bands of DPO, cm^{-1} : 1020.5 w, 1132.7 s, 1164.8 m, 1194.0 s ($-\text{O}=\text{C}-\text{O}-\text{C}-$), 1768.1 m, br, 1800.2 sh, ($\text{C}=\text{O}$)).

3. Results and discussion

The XRD patterns of all the $\text{MoO}_3/\text{SiO}_2$ catalysts prepared by sol–gel technique are shown in Fig. 1. For comparison, the XRD pattern of pure silica is also included in the Fig. 1a. The patterns show the amorphous nature of the material at lower Mo loading (Fig. 1b–d). Catalysts with 15 and 20% Mo loading (Fig. 1e and f) show highly crystalline nature with intense peaks at $2\theta = 12.9^\circ$, 23.4° , 25.8° , and 27.4° corresponding to α - MoO_3 in the orthorhombic phase. No β - MoO_3 phase is observed in the structure because the

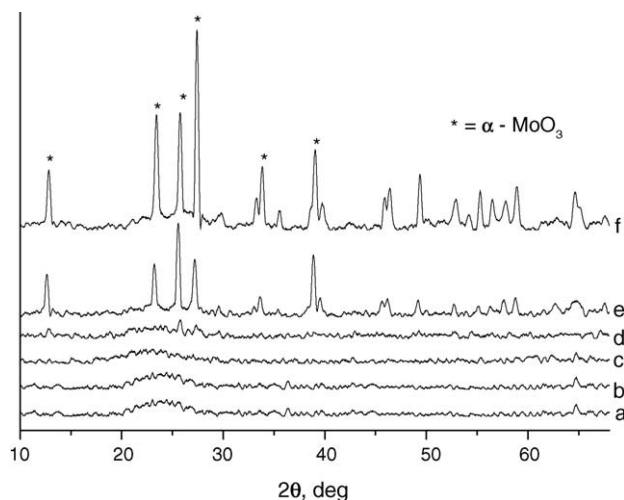


Fig. 1. XRD of (a) silica and MoO₃/SiO₂ with (b) 1% MoO₃ loading, (c) 5% MoO₃ loading, (d) 10% MoO₃ loading, (e) 15% MoO₃ loading, and (f) 20% MoO₃ loading.

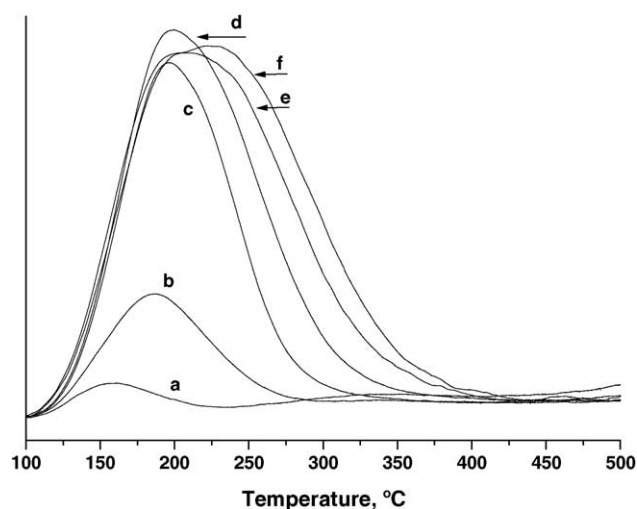


Fig. 2. NH₃-TPD of (a) silica and MoO₃/SiO₂ with (b) 1% MoO₃ loading, (c) 5% MoO₃ loading, (d) 10% MoO₃ loading, (e) 15% MoO₃ loading, and (f) 20% MoO₃ loading.

Table 1
Surface area and acidity of the catalysts

Catalyst	Surface area (m ² /g)	NH ₃ desorbed (mmol/g)
Silica	606	0.0317
1% MoO ₃ /SiO ₂	583	0.1830
5% MoO ₃ /SiO ₂	432	0.5562
10% MoO ₃ /SiO ₂	284	0.7056
15% MoO ₃ /SiO ₂	275	0.863
20% MoO ₃ /SiO ₂	106	0.937

samples were calcined at 500 °C, a temperature at which β-MoO₃ phase is not stable [16]. It is interesting to note that even though the MoO₃ is in the crystalline form at higher Mo loading, the silica support still retains its amorphous nature, leading to the high surface area of the catalysts.

The surface areas of all the catalysts determined using BET method are given in Table 1. As expected, a very high surface area of 606 m²/g has been observed in case of pure silica because of sol–gel synthesis using ethyl silicate-40 as the silica source. Ethyl silicate-40 is a polymeric form (trimeric and tetrameric) of tetraethyl orthosilicate monomer, which on controlled hydrolysis yields the silica of a very high surface area [17]. On controlled hydrolysis of ethyl silicate-40, the trimeric and tetrameric species form corresponding trimeric and tetrameric silica structure. The trimeric and tetrameric silica structures restrict the growth of large particles. The surface area was found to decrease with increase in MoO₃ loading. During the sol–gel synthesis, an aqueous solution of ammonium molybdate is added to ethyl silicate-40, which hydrolyzes ethyl silicate-40. However, the control of the rate of hydrolysis is difficult, because of the use of excess water for dissolving ammonium molybdate, which leads to a decrease in the surface area. The highly basic pH of the solution also leads to the formation of the product with lower surface area. It is expected that, as MoO₃ loading is increased, the crystalline molybdenum oxide

clusters are formed that cover the amorphous silica support, reducing the total surface area of the catalyst. However, the catalysts prepared by sol–gel techniques show a very high surface area as compared to the catalysts prepared by impregnation method. For 1% Mo loading, the catalyst prepared by sol–gel technique shows surface area of 583 m²/g whereas the catalyst prepared by impregnation method shows a surface area of only 155 m²/g [11].

Ammonia-TPD experiments were carried out to determine the acid strength of the catalysts. The results are shown in Fig. 2 and amount of NH₃ desorbed is given in Table 1. The pure silica catalyst shows the lowest acidity, with 0.0317 mmol/g of ammonia desorbed at comparatively lower temperature, indicating the presence of few weaker acid sites. Addition of 1% MoO₃ to the silica support by sol–gel increases the acidity almost six times (0.183 mmol/g) with respect to the number of acid sites as well as the acid strength. The temperature for total desorption of ammonia increases (275–400 °C) with increase in MoO₃ loading showing the increase in acid strength as well as in the number of acid sites. The catalyst with 20% Mo loading shows maximum number of acid sites (NH₃ desorbed: 0.937 mmol/g) as well as the highest acid strength.

Pyridine adsorption studies for the determination of the nature of acidity reveal the presence of Lewis acidity in all the catalysts. Fig. 3 shows the IR spectra of adsorbed pyridine on the catalyst surface. The spectrum of pure silica (Fig. 3a) shows the presence of only Lewis acidity (peak at 1450 cm⁻¹) with low acidity; the 1% MoO₃/SiO₂ sample (Fig. 3b) shows increase in Lewis acidity as well as acid strength. As the MoO₃ loading is further increased, the samples show the presence of both Brønsted (peak at 1540 cm⁻¹) as well as Lewis acid sites (Fig. 3c–f). The generation of Brønsted acidity may be correlated to the formation of polymolybdate Keggin structures [18]. The IR spectra of the catalyst in the framework region show the

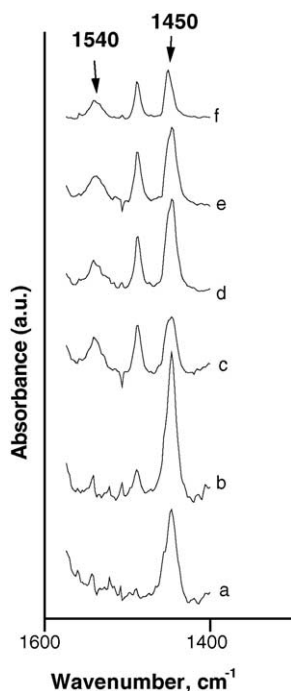


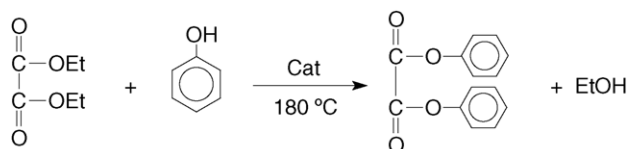
Fig. 3. Pyridine adsorption spectra of (a) silica, MoO₃/SiO₂ with (b) 1% Mo loading, (c) 5% Mo loading, (d) 10% Mo loading, (e) 15% Mo loading, and (f) 20% Mo loading.

presence of peaks at 959 and 914 cm⁻¹, which corresponds to polymolybdate Keggin structures which is reported to exhibit Brønsted acidity. At temperatures of about 500 °C transformation of hexagonal form of molybdenum trioxide into its orthorhombic form takes place. The oxide becomes hydrated and subsequently converted into polymolybdenic trimers [19,20]. Such structural units are expected to show Brønsted acidity. The ratio of Brønsted to Lewis (B/L) acidity increases with increase in Mo loading. Though the Lewis acidity is found to decrease with increase in Mo loading, the Brønsted acidity observed at higher Mo loading contributes to overall increase in the total acidity, which is seen by NH₃-TPD. The MoO₃/SiO₂ catalysts prepared by impregnation technique are reported to show the presence of only Lewis acid sites without any Brønsted acidity. The NH₃ desorption in case of impregnated catalyst takes place at much lower temperature (<250 °C) indicating presence of weak acidity [11].

3.1. Catalytic reactions

Formation of DPO by transesterification of diethyl oxalate (DEO) with phenol is shown in Scheme 1. Transesterification of DEO with phenol was carried out at 180 °C using a series of MoO₃/SiO₂ catalysts; the results are given in Table 2.

The results clearly show 100% selectivity for DPO with high conversions. DEO conversion decreases with increasing Mo loading. The reaction with pure silica was also carried out and it showed a very low DEO conversion



Scheme 1. Formation of diphenyl oxalate.

Table 2
Results of transesterification of DEO with phenol

Catalyst	DEO conversion (%)	DPO selectivity (%)	DPO yield ^a (%)
–	22.9	100	22.9
SiO ₂	21.6	100	21.6
1% MoO ₃ /SiO ₂	80.9	100	80.9
5% MoO ₃ /SiO ₂	73.6	100	73.6
10% MoO ₃ /SiO ₂	55.9	100	55.9
15% MoO ₃ /SiO ₂	55.6	100	55.6
20% MoO ₃ /SiO ₂	54.0	100	54.0

Reaction conditions: DEO 0.035 mol, PhOH 0.175 mol, catalyst 0.750 g, temperature 180 °C, time on stream 5 h.

^a Yields based on GC.

(21.6%), which is comparable with that of the reaction without catalyst (22.9%). In case of 1% Mo loading the conversion increased to 80.9% with 100% selectivity for DPO. In case of 5% Mo loading, the conversion is marginally decreased to 73.6% without decrease in DPO selectivity. In the case of higher Mo loading, the conversion is further decreased to almost 55%; however, the selectivity for DPO remained constant. In case of 1% MoO₃/SiO₂ catalyst, the maximum DEO conversion may be attributed to the maximum number of weak Lewis acid sites. The decrease in DEO conversion with increase in Mo loading may be attributed to increase in B/L ratio. From these results it is clear that weak Lewis acid sites are responsible for the transesterification of DEO.

Since the catalyst with 1% Mo loading has shown maximum catalytic efficiency, the effects of reaction temperature and catalyst concentration on DEO conversion and DPO selectivity were studied using this catalyst. The results of temperature and catalyst concentration variation are given in Table 3. There was no reaction at 160 °C; however, at 180 °C 80.8% conversion was observed, which shows that 180 °C is the threshold temperature for transesterification of DEO with phenol. As expected DEO conversion increased with increase in the reaction temperature. Maximum DEO conversion of 84.7% was obtained at 220 °C with 100% selectivity for DPO. Temperature variation studies showed no effect of temperature on DPO selectivity; at all the studied temperatures, 100% selectivity for DPO was retained.

Studies of the effect of catalyst concentration on DEO conversion and DPO selectivity showed that 15 wt% catalyst concentration with respect to DEO is the optimum concentration for this reaction. At this concentration, maximum conversion (80.9%) and selectivity (100%) have been obtained. The conversion decreased at higher as well as at lower catalyst concentrations. At lower catalyst con-

Table 3
Effect of temperature and catalyst concentration on conversion and selectivity

Catalyst concentration (wt%)	Temperature (°C)	DEO conversion (%)	DPO selectivity (%)	DPO yield (%)
10	180	51.7	100	51.7
15	160	0	0	0
	180	80.9	100	80.9
	200	81.3	100	81.3
	220	84.7	100	84.7
20	180	78.3	100	78.3
30	180	62.5	71.3 ^a	44.6

Reaction conditions: DEO 0.035 mol, PhOH 0.175 mol, time on stream 5 h.

^a Unidentified byproducts.

centration (10 wt%), the conversion is decreased to 51.7% without decrease in the DPO selectivity. At slightly higher concentration (20 wt%), the conversion is decreased marginally from 80.9 to 78.3% without decrease in the selectivity; at still higher concentration (30 wt%), the conversion decreased to 62.5% with a drastic decrease in DPO selectivity (71.3%).

It is interesting to note that the formation of mono transesterified product (ethyl phenyl oxalate EPO) was not observed during these reactions. The samples were analyzed each hour during the course of reaction and no EPO was detected in GC even in the beginning of the reaction. This clearly indicates that DPO formation does not proceed stepwise through formation of EPO. Hence, the mechanism suggested by Ma and co-workers for stepwise formation of DPO through formation of MPO does not operate in this case [12]. One possible mechanism for selective formation of diphenyl oxalate is shown in Scheme 2. In the proposed mechanism, both the carbonyl oxygen atoms of DEO form five-membered chelates with molybdenum, thus activating both the carbonyl groups at the same time. First, one phenol molecule attacks one carbonyl group, liberating one ethanol

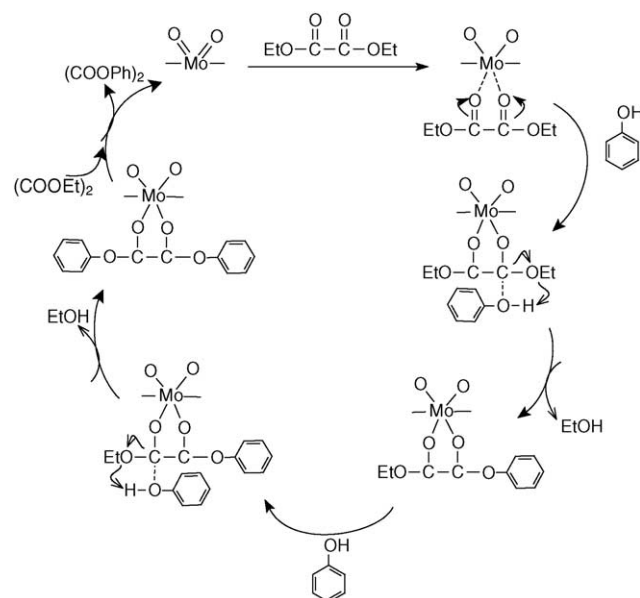
molecule. In the next step, the second phenol molecule attacks a second carbonyl carbon, liberating a second ethanol molecule forming diphenyl oxalate. According to this mechanism, there is no free ethyl phenyl oxalate formed at any stage, explaining the selective formation of diphenyl oxalate. In this case, the starting material used, i.e. diethyl oxalate, is playing a crucial role in selective (100%) formation of DPO instead of the monotraneesterified product. In the case of transesterification of dimethyl carbonate and diethyl carbonate with different alcohols using a base catalyst, Figueras and Veldurthy [15] have reported considerable differences in the reactivity of diethyl carbonate as compared to dimethyl carbonate. The ethoxy group is a better leaving group as compared to methoxy group; this leads to the selective formation of diphenyl oxalate instead of ethyl phenyl oxalate. Hence, it can be concluded that diethyl oxalate is a much better and more cost-effective starting material for production of DPO with very high selectivity and high conversion level by transesterification with phenol.

4. Conclusions

Silica-supported molybdenum oxide catalysts with varying Mo loadings prepared by sol-gel technique were found to be very active catalysts for transesterification of DEO with phenol, giving 100% selectivity for DPO. High DEO conversions of up to 84.7% were obtained with 1% MoO₃ loading. The higher conversion and selectivity can be attributed to the weaker Lewis acidity of the catalyst, the higher dispersion of molybdenum oxide on high surface area silica support and the higher reactivity of diethyl oxalate compared to that of dimethyl oxalate. In this system, no EPO formation was observed at any stage of the reaction, suggesting that DPO is not formed stepwise through EPO formation.

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Scheme 2. Possible mechanism of transesterification of DEO with phenol.

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