# Effective and Recoverable Homogeneous Catalysts for the Transesterification of Dimethyl Carbonate with Ethanol: Lanthanide Triflates<sup>1</sup>

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**Abstract**—The catalytic activities of metal triflates were tested for the transesterification of dimethyl carbonate (DMC) with ethanol. It was found that yttrium triflate was the most efficient homogeneous catalyst. When the transesterification reaction was catalyzed by yttrium triflate at 76–80°C, 7 h, ethanol to DMC in 6 : 1 molar ratio, 0.35 mol % of catalyst based on DMC, the conversion of DMC was 89.2%, the selectivities of diethyl carbonate (DEC) and ethyl methyl carbonate (EMC) were 85.1 and 13.6%, respectively. Yttrium triflate was reused 5 times for the transesterification without loss of its catalytic activity.

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In recent years, organic carbonates have been attracted a great attention due to their ubiquitous applications as intermediates for fine chemicals, biological and medicinal reagents, plasticizers, synthetic lubricants, monomers for organic glass [1]. In addition, dimethyl carbonate (**DMC**), ethyl methyl carbonate (**EMC**) and diethyl carbonate (**DEC**) are excellent organic solvents [2–4], and are widely used as additives in lithium batteries [5–7]. Most importantly, DMC and DEC are both considered to be the best alternatives for methyl *tert*-butyl ether (MTBE) as oxygen-containing fuel additive. In comparison with DMC, DEC will reduce emissions from gasoline and diesel engines, and gasoline/water distribution coefficients are more favorable for DEC [8].

The transesterification of DMC with ethanol is considered to be a clean process in which non-toxic DMC is used for the substitution of highly toxic phosgene. In general, transesterification reaction is catalyzed by homogeneous base catalysts such as alkali metal methoxide [9], sodium methoxide/triethanolamine [10]. These catalysts have good activity, but they are toxic, flammable, corrosive and sensitive to air and water. Due to the easy separation from reaction mixture and recovery, many heterogeneous catalysts were developed for the transesterification of DMC with ethanol. Group IIIB metal oxides such as Sm<sub>2</sub>O<sub>3</sub> were used as solid catalysts for the transesterification of DMC with ethanol, but their activities were low [11].  $K_2CO_3$  and modified  $K_2CO_3$  were found to be effective catalysts for this reaction [12, 13]. Zielinska-Nadolska et al. [14] tested a variety of heterogeneous catalysts, and found that two ion-exchange resins, Lewatit K1221 and Nafion SAC-13, had better catalytic activities than other heterogeneous catalysts, but the reaction rate over these catalysts was slow. We found that a *tert*-butyl oxide interlayered Mg-Al hydrotalcite was an effective heterogeneous catalyst for the transesterification of DMC with ethanol, but it was expensive [15].

In terms of activity and life time of the catalysts, both homogeneous and heterogeneous catalysts for transesterification of DMC with ethanol had some kinds of drawbacks. Thus, our aim is to find a catalyst which has both the advantage of homogeneous catalyst with high activity and the advantage of heterogeneous catalyst with easy separation from reaction mixture.

Triflate salts such as lanthanide triflate, copper triflate and zinc triflate are new kinds of Lewis acids which are widely used as catalysts for a variety of organic transformations such as Diels-Alder addition [16–18], Friedel–Crafts reaction [19–21], Michael reaction [22], nitro-aldol (Henry) reaction [23], Mannich and aldol reactions [24], carbon-carbon bondforming reaction [25], cationic copolymerization [26], cycloaddition reactions [27, 28], epoxide ringopening and esterification reactions [29]. In previous study, we found that samarium triflate was active for the transesterification of DMC with phenol to methyl phenyl carbonate and diphenyl carbonate [30]. Triflate salts can be used both in organic and in aqueous medium, and easily recovered from reaction mixture. In the exploration of homogeneous catalysts for the transesterification of DMC with ethanol, we found that lanthanide triflates were efficient homogeneous catalysts for the transesterification of DMC with etha-

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use. ZnO, CuO, Y<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub>, Yb<sub>2</sub>O<sub>3</sub> were purchased from Shanghai Reagent Company. Lanthan ide triflates  $[Ln(CF_3SO_3)_3]$  and  $Y(CF_3SO_3)_3$  were prepared by following method: in aqueous solution of trifluoromethane sulfonic acid, a little excess amount of  $Ln_2O_3$  or  $Y_2O_3$  was added in several times with stirring. The mixture was reacted at 60°C for about half an hour, then filtrated to remove unreacted  $Ln_2O_3$ (or  $Y_2O_3$ ). The mother liquor was evaporated by a

nol. They are stable to air, water and reaction mixture, and reuseable and easy to handle. Lanthanide triflates

could catalyze the transesterification of DMC with

ethanol for a long time without loss of their activities.

**EXPERIMENTAL** 

Catalyst Preparation

tilled and stored over molecular sieves (4 Å) prior to

DMC was analytic grade. It was fractionally dis-

rotation evaporator to remove water.  $Cu(CF_3SO_3)_3$ ,  $Zn(CF_3SO_3)_2$  were prepared according to literature [31]. The other reagents were used as received. The hydrated H<sub>2</sub>O in metal triflates was removed by refluxing with toluene (dehydrating reagent) using a Dean-Stark apparatus.

## General Procedure for Transesterification Reaction

The experiments were done in a thermostatted three-neck flask equipped with a magnetic stirrer, a thermometer, a tube for sample withdrawal and a rectification column which was filled with small cylinder cerams. Thus, a reactive distillation under atmospheric pressure was used to remove the by-product methanol to shift the equilibrium to the direction of products.

In a typical experiment, DMC 18.0 g (0.2 mol), ethanol 55.2 g (1.2 mol), 0.35 mol % of catalyst based on DMC were introduced into the flask, and heated to desired temperature. At certain intervals, samples of reacting mixture were collected and analyzed by gas chromatography (GC). The catalytic activity of catalyst was assessed based on the yield and selectivity of DEC and EMC.

# **RESULTS AND DISCUSSION**

## Thermodynamical Analysis

The transesterification of DMC with ethanol to DEC is a two-stage process:

$$\begin{array}{c} O & O \\ H_3CO-C-OCH_3 + C_2H_5 - OH \rightleftharpoons H_3CO-C-OC_2H_5 + CH_3 - OH, \\ DMC & EMC \end{array}$$
(I)

$$O \qquad O \\ \parallel \\ H_3CO-C-OCH_5 + C_2H_5 - OH \implies H_5C_2O-C-OC_2H_5 + CH_3 - OH.$$
(II)  
EMC DEC (II)

The stoichiometric equation for the transesterification of DMC with ethanol to DEC is presented as reaction (III):

$$\begin{array}{c} O & O \\ \parallel \\ H_2 CO - C - O CH_3 + 2C_2 H_5 - O H \rightleftharpoons H_5 C_2 O - C - O C_2 H_5 + 2 C H_3 - O H. \end{array}$$
(III)

On the basis of literatures [30, 32, 33], the reaction enthalpy and Gibbs free energy at 298 K, 101325 Pa for reaction (III) were calculated as  $\Delta_r H_m^0$  =  $-3.4 \text{ kJ/mol}, \Delta_r G_m^0 = +12.6 \text{ kJ/mol}.$  It is obvious that the transesterification of DMC with ethanol to DEC is a thermodynamically unfavorable reaction. In order to shift the reaction to the direction of EMC and DEC, methanol must be removed from reaction system. But part of DMC was distilled out of flask simultaneously with methanol during reaction because DMC and methanol could form azeotrope system. Since the reaction enthalpy for reaction (III) is very small, the effect of temperature on this reaction should be small. This conclusion was verified by Luo and Xiao [12] when modified  $K_2CO_3$  was used as catalyst for this reaction. Theoretically, the reaction temperature is manipulated to continuously remove boiling azeotrope. In this experiment, the temperature was controlled at 76–80°C when ethanol was used in excess.

### The Catalytic Activity of Metal Oxides and Metal Triflates

The catalytic activities of metal oxides and metal triflates for the transesterification of DMC with ethanol are presented in Table 1.

The transesterification is almost not carried out without catalysts. Zinc triflate and copper triflate show moderate catalytic activity for transesterification. When four metal oxides are used as heterogeneous catalysts for the transesterification reaction, the conversion of DMC is low, and EMC is the main product. For four metal trifaltes, the conversion of DMC is high, and DEC is the main product. The transesterification selectivities (DEC selectivity plus EMC selec-

| Catalyst                       | DMC con-<br>version, % | DEC selectiv-<br>ity,* % | EMC selec-<br>tivity,* % |
|--------------------------------|------------------------|--------------------------|--------------------------|
| No                             | 2.4                    | 66.7                     | 33.3                     |
| $Zn(CF_3SO_3)_2$               | 30.0                   | 59.7                     | 36.3                     |
| $Cu(CF_3SO_3)_2$               | 50.0                   | 25.8                     | 70.6                     |
| $Y(CF_3SO_3)_3$                | 91.6                   | 80.7                     | 16.8                     |
| $La(CF_3SO_3)_3$               | 83.2                   | 76.6                     | 22.6                     |
| $Sm(CF_3SO_3)_3$               | 86.5                   | 80.9                     | 11.9                     |
| $Yb(CF_3SO_3)_3$               | 88.2                   | 70.2                     | 6.0                      |
| $Y_2O_3$                       | 25.0                   | 8.8                      | 85.2                     |
| La <sub>2</sub> O <sub>3</sub> | 20.8                   | 21.2                     | 78.8                     |
| $Sm_2O_3$                      | 44.0                   | 42.9                     | 52.3                     |
| $Yb_2O_3$                      | 28.0                   | 44.6                     | 51.1                     |

Table 1. The catalytic activity of metal triflates

Note: Reaction conditions: DMC (18.0 g, 0.2 mol), ethanol (55.2 g, 1.2 mol), 1.4 mol % of catalyst based on DMC, temperature (76–80°C), time (7 h).

\* Based on DMC conversion.

Table 2. The effect of the amount of yttrium triflate

| Catalyst,* mol % | DMC<br>conversion, % | DEC selec-<br>tivity, % | EMC selec-<br>tivity, % |
|------------------|----------------------|-------------------------|-------------------------|
| 0.175            | 84.0                 | 62.5                    | 27.6                    |
| 0.35             | 89.2                 | 85.1                    | 13.6                    |
| 0.7              | 86.6                 | 84.1                    | 15.8                    |
| 1.4              | 91.6                 | 80.7                    | 16.8                    |

Note: Reaction conditions: DMC (18.0 g, 0.2 mol), ethanol (55.2 g, 1.2 mol), temperature (76–80°C), time (7 h).

\* Based on DMC.

Table 3. The effect of reaction time

| Time, h | DMC conversion, % | DEC selectivi-<br>ty, % | EMC selectivi-<br>ty, % |
|---------|-------------------|-------------------------|-------------------------|
| 3       | 90.2              | 75.8                    | 22.8                    |
| 5       | 89.3              | 80.4                    | 16.2                    |
| 7       | 89.2              | 85.1                    | 13.6                    |
| 9       | 87.4              | 86.0                    | 12.4                    |

Note: Reaction conditions: DMC (18.0 g, 0.2 mol), ethanol (55.2 g, 1.2 mol), yttrium triflate (0.375 g, 0.7 mmol), temperature (76–80°C).

tivity) of  $Y(CF_3SO_3)_3$  and  $La(CF_3SO_3)_3$  are higher than those of  $Sm(CF_3SO_3)_3$  and  $Yb(CF_3SO_3)_3$ . Especially for  $Yb(CF_3SO_3)_3$ , a considerable amount of ethers such as diethyl ether and dimethyl ether was detected. This can be explained that  $Yb(CF_3SO_3)_3$  is the strongest Lewis acid among four metal triflates, and it catalyzes the decomposition of DMC and DEC to dimethyl ether and diethyl ether. Fu [34] demonstrated that strong solid acids and bases could catalyze the thermal decomposition of DMC to mainly give dimethyl ether. In consideration of both the conversion and transeterification selectivity,  $Y(CF_3SO_3)_3$  is the best homogeneous catalyst among all catalysts tested for the transesterification reaction.

#### The Effect of the Amount of Yttrium Triflate

The effect of the amount of yttrium triflate on the transesterification of DMC with ethanol is shown in Table 2.

The results in Table 2 show that the increase of DEC selectivity and the decrease of EMC selectivity are obvious when yttrium triflate is used in a dose from 0.175 to 0.35 mol %. When the amount of yttrium triflate is greater than 0.35 mol %, DMC conversion, DEC and EMC selectivities change very little. Therefore, 0.35 mol % of yttrium triflate is chosen as the optimal catalyst loading for the transesterification reaction.

## The Effect of Reaction Time Using Yttrium Triflate as Catalyst

Because the transesterification of DMC with ethanol is a thermodynamically unfavorable reaction, the conversion of DMC is very small even with increasing temperature at a long time without catalyst. The effect of reaction time on the transesterification of DMC with ethanol using yttrium triflate as catalyst is given in Table 3.

If ethanol is used in excess, DMC can quickly react with ethanol and upon catalysis by yttrium triflate produce EMC. Because DMC can form boiling azeotrope with the produced methanol, the unreacted DMC is distilled out of flask with methanol. This leads to exhaustion of DMC. Thus, the conversion of DMC changes little after 3 h, while the yield of DEC increases and the yield of EMC decreases with increase of time. This result indicates that reaction (I) proceeds quickly before 3 h. After 3 h, reaction (II) is rate-determining stage for whole reaction of transesterification. Because the selectivities of DEC and EMC change little after 7 h, the optimal reaction time is set at 7 h.

## The Effect of Molar Ratio of Ethanol to DMC

The effect of molar ratio of ethanol to DMC on the transesterification of DMC with ethanol was tested using yttrium triflate.

It is observed that the selectivities of DEC and EMC depend on the molar ratio of ethanol to DMC. When DMC and ethanol were used in equimolar ratio or in excess of DMC, the transesterification of DMC

| <i>n</i> (EtOH) :<br><i>n</i> (DMC) | DMC conver-<br>sion, % | DEC selectivi-<br>ty, % | EMC selectivi-<br>ty, % |
|-------------------------------------|------------------------|-------------------------|-------------------------|
| 1:3*                                | 43.5                   | 14.9                    | 83.4                    |
| 1:1                                 | 71.3                   | 34.5                    | 61.3                    |
| 3:1                                 | 85.8                   | 53.1                    | 40.4                    |
| 5:1                                 | 87.4                   | 79.7                    | 19.2                    |
| 6:1                                 | 89.2                   | 85.1                    | 13.6                    |
| 7:1                                 | 87.9                   | 83.0                    | 15.6                    |
| 8:1                                 | 89.2                   | 85.1                    | 13.9                    |

Table 4. The effect of molar ratio of ethanol to DMC

Note: Reaction conditions: 0.35 mol % of catalyst based on DMC, temperature (76–80°C), time (7 h).

\* 0.35 mol % of catalyst based on ethanol.

| Times | DMC conver-<br>sion, % | DEC selectivity,<br>% | EMC selectivity,<br>% |
|-------|------------------------|-----------------------|-----------------------|
| 1     | 89.2                   | 85.1                  | 13.6                  |
| 2     | 89.0                   | 80.9                  | 15.2                  |
| 3     | 88.0                   | 84.1                  | 6.3                   |
| 4     | 86.0                   | 87.2                  | 6.5                   |
| 5     | 86.2                   | 86.7                  | 7.0                   |

**Table 5.** The catalytic activity of the recovered yttrium triflate

Note: Reaction conditions: DMC (18.0 g, 0.2 mol), ethanol (55.2 g, 1.2 mol), yttrium triflate (0.375 g, 0.7 mmol), temperature (76–80°C), time (7 h).

with ethanol is carried out to obtain EMC as a main product. If ethanol is used in excess, the two-step transesterification proceeds and the final amount of DEC is dominant. When the molar ratio of ethanol to DMC reaches to 6 : 1, all the parameters change little. Thus, this ratio was chosen for the transesterification reaction. The results in Table 4 also demonstrate that the goal product (DEC or EMC) can be obtained by adjusting the molar ratio of ethanol to DMC when using yttrium triflate as catalyst.

## The Catalytic Activity of Recovered Yttrium Triflate

In order to assess the duration of catalytic activity, the catalyst was recovered by distillation of the components of reaction mixture and it was used with fresh portion of DMC and ethanol. The results are shown in Table 5.

The results in Table 5 show that yttrium triflate is an efficient homogeneous catalyst for the transesterification of DMC with ethanol. After being used for 5 times, its activity remains practically unaltered. Due

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to its long duration and good activity, yttrium triflate may be of great potential for commercial application for the transesterification of DMC with ethanol.

In summary, yttrium triflate was proved to be active homogeneous catalysts for the transesterification of DMC with ethanol. It can be easily regenerated without loss of its activity. The transesterification of DMC with ethanol over yttrium triflate proceeds fast. Even when a very small amount of yttrium triflate (0.35 mol %) is used, its catalytic activity is high. The excellent performance of yttrium triflate makes it potential for commercial application in the transesterification of DMC with ethanol.

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