Synthesis of Diethyl Carbonate from Carbon Dioxide, Propylene Oxide and Ethanol over KNO$_3$-CeO$_2$ and KBr-KNO$_3$-CeO$_2$ Catalysts

Yanlou Wang, Dongdong Jia *, Zhen Zhu and Yongyue Sun

Key Laboratory of Organic Solar Cells and Photochemical Conversion, School of Chemistry & Chemical Engineering, Tianjin University of Technology, Tianjin 300384, China; yanlou1990@126.com (Y.W.); zhu668231@sina.cn (Z.Z.); sunyy1977@hotmail.com (Y.S.)

* Correspondence: dongdonj@tju.edu.cn; Tel.: +86-22-60214259; Fax: +86-22-60214259

Abstract: One-pot syntheses of diethyl carbonate (DEC) from CO$_2$, propylene oxide and ethanol were carried out using different solid catalysts. The supercritical CO$_2$ extraction method was used to separate the liquid products and reactants from the catalysts after reaction. The KNO$_3$-CeO$_2$ and KBr-KNO$_3$-CeO$_2$ were found to be active for the reaction after calcinations. The catalyst was also reusable. The thermodynamic properties of the reaction were also evaluated. The effects of various conditions, such as reaction time, amount of catalysts, molar ratio of the reactants, the composition and calcination temperature of the catalysts on the conversion and yields, were investigated, and the yield of DEC was about 13.0% with a selectivity of 38.5% over KBr-KNO$_3$-CeO$_2$. The yield of DEC was improved about 10-fold by using KBr-KNO$_3$-CeO$_2$ catalyst compared to CeO$_2$.

1. Introduction

The synthesis of chemicals using CO$_2$ as a raw material is characterized at present by increasing industrial and academic efforts to use this carbon renewable [1]. The production of carbonates [2,3], carbamates [4], methanol [5], formic acid and its derivatives could be synthesized from CO$_2$ [6,7]. Diethyl carbonate (DEC) is one of the most important green chemicals among carbonate esters. It is an excellent solvent and an intermediate for various pharmaceuticals, such as antibiotics and phenobarbital [8]. DEC has also been proposed as a replacement for MTBE as an attractive oxygen-containing fuel additive for its high oxygen content (40.6 wt. %) compared to MTBE (18.2 wt. %) [9,10].

Since the conventional methodologies for the DEC synthesis, including ethanol phosgenation [11], ethanol oxidative carbonylation [12] and the reaction of ethanol with urea [13], have many problems, such as the toxicity of phosgene, corrosion and low production rates [14], the novel technology for DEC synthesis starting from CO$_2$ and ethanol is a promising route. However, the reaction hardly occurs spontaneously, even under harsh conditions, due to the thermodynamic limitations (yield of less than 0.5%) [8]. To address this issue, chemical dehydration reagent was usually involved to shift the reaction forward to the carbonate side. In the similar reaction of the synthesis dimethyl carbonate (DMC), acetals [15] and orthoesters [16] were used as the organic dehydrants, respectively, and both the DMC yields could be effectively improved above 20-fold. However, the high cost of acetals and orthoesters makes them difficult for industrial production. Acetonitrile [17] and amines [18] were also reported as being used as the dehydrants for the DEC synthesis, but their co-products were complex. Recently, butylene oxide was also used as the dehydrant for the direct synthesis of the DEC over CeO$_2$ catalyst [8,19]. According to the results, the yield of DEC had a nine-fold

enhancement compared to that over CeO_2 without dehydrant, but it was still not high enough (only 1.5%) in this system and needed to be improved. Besides, CeO_2 with 2-cyanopyridine was also used as the carboxylation/hydration cascade catalyst by Tomishige group [20] for the propylene carbonate synthesis from CO_2 and 1,2-propanediol, and the yield was much higher (>99%), which might be a landmark in carbonate synthesis using CeO_2 catalysis.

In addition, the one-pot synthesis of DEC from carbon dioxide, ethylene oxide (EO) and ethanol on the KI and sodium ethoxide binary homogeneous catalyst was also researched by Wang *et al.* [21], and the yield of DEC was improved. However, KI and sodium ethoxide are dissolved in ethanol and cannot be separated easily.

On the other hand, the synthesis of cyclic carbonate from epoxide and CO_2 was well established in industrial manufacturing. Furthermore, the transesterification of cyclic carbonate with ethanol to produce DEC was also proven to be feasible [22] However, from views of energy consumption, productivity and investment, the one-pot reaction directly from CO_2 was undoubtedly superior to the two-step separate reaction. Thus, the development of a more effective one-pot reaction to improve the productivity of DEC directly from CO_2 is highly desired.

2. Results and Discussion

The one-pot reaction in DEC synthesis might be composed of two steps, the cycloaddition reaction and subsequent transesterification reaction. The mechanisms of the reaction have been studied and proven by many researchers [21,23]. As analyzed by the GC-MS method in this work, the main products in the one-pot reaction from CO_2, ethanol and PO were 1,2-propanediol (PG), DEC and propylene carbonate (PC) with the side-product 1-ethoxy-2-propanol (EP). The EP might be formed from propylene oxide by ethanolysis [23,24] in the basic catalytic environment. The possible equations of these reactions are presented as follows (Scheme 1).
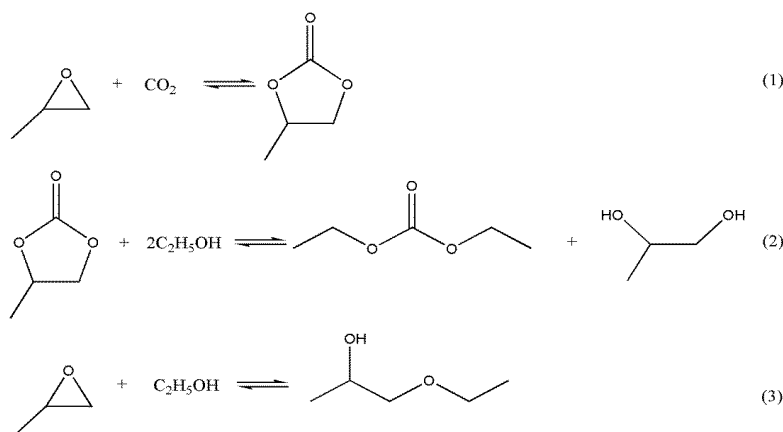
Scheme 1. The reaction schemes.

2.1. The One-Pot Synthesis of DEC over KNO₃-CeO₂ Catalyst

As reviewed in the literature [8], the heterogeneous catalyst CeO_2 has catalytic activity for the one-pot reaction in DEC synthesis. In order to improve the catalytic activity in DEC synthesis, the strong base of KOH and several typical alkali and alkaline-earth metal salts, which might be necessary to meet the requirement for catalyzing the transesterification reaction combined with CeO_2, were researched. Several metal oxides, such as γ-Al_2O_3, ZrO_2, SiO_2 and La_2O_3, were also tested. In the typical reaction, the molar ratio of CO_2, ethanol and PO was fixed as 0.29:0.17:0.14; the reaction temperature was 150 °C; the initial pressure was 5 MPa; and during the reaction, the pressure could reach 9 MPa, which is higher than the critical pressure of CO_2. The results are summarized in Table 1, Runs 1–12.

Table 1. Effects of different catalysts on the one-pot reaction. DEC, diethyl carbonate; PG, 1,2-propanediol; EP, 1-ethoxy-2-propanol.

| Run	Catalyst	Specific surface area/m^2/g	Ethanol conversion/%	DEC yield/%	Selectivity/%		
					DEC	PG	EP
1	CeO_2	-	1.5	1.3	84.0	-	-
2	$NaNO_3$-CeO_2	-	12.6	3.6	28.3	24.1	19.3
3	$Ba(NO_3)_2$-CeO_2	-	8.1	0.9	12.6	10.2	16.6
4	$Mg(NO_3)_2$-CeO_2	-	15.9	2.2	13.0	15.9	17.4
5	$Ca(NO_3)_2$-CeO_2	-	6.6	1.3	22.3	16.7	19.8
6	KOH-CeO_2	-	13.4	3.6	28.0	20.1	33.6
7	K_2CO_3-CeO_2	-	9.1	1.8	19.0	17.6	25.1
8	KNO_3-CeO_2	30.5	34.0	11.2	33.3	23.7	23.5
9	KNO_3-γ-Al_2O_3	102	46.8	11.5	24.5	23.1	16.5
10	KNO_3-ZrO_2	22.9	23.7	6.3	27	24.4	22.9
11	KNO_3-SiO_2	78.1	12.3	3.1	25.3	26.1	18.8
12	KNO_3-La_2O_3	31.8	0.6	0.4	69.1	20.7	10.9
13	KI-CeO_2 [A]	-	18.0	0.9	6.3	6.4	10.3
14	KI-CeO_2 [B]	-	9.0	1.3	14.4	17.4	12.8
15	KI-KNO_3-CeO_2 [A]	-	17.1	0.9	5.8	4.9	7.7
16	KI-KNO_3-CeO_2 [B]	-	9.6	0.4	7.5	7.9	7.2
17	KCl-KNO_3-CeO_2 [A]	-	14.4	2.7	17.4	14.4	5.7
18	KCl-KNO_3-CeO_2 [B]	-	39.9	10.3	25.9	22.3	5.9
19	KBr-KNO_3-CeO_2 [A]	-	23.1	9.4	40.8	30.5	7.6
20	KBr-KNO_3-CeO_2 [B]	-	33.9	13.0	38.5	27.7	7.5

Both of the volumes of ethanol and PO were 10 mL; the reaction temperature was 150 °C; the initial pressure was 5 MPa. [A] Catalysts prepared by the impregnation method; [B] catalysts prepared by the solid mixed method.

As seen in Table 1, when KNO_3-CeO_2 was used as the catalyst, the yield of DEC was effectively improved about 10-fold, compared to that using CeO_2 catalyst. The KNO_3-CeO_2 had better catalytic activity than KOH and other alkali and alkaline-earth metal salts loading on CeO_2, such as KOH-CeO_2, K_2CO_3-CeO_2, $NaNO_3$-CeO_2, $Ba(NO_3)_2$-CeO_2, $Mg(NO_3)_2$-CeO_2 and $Ca(NO_3)_2$-CeO_2. Then, KNO_3 with other metal oxides, including γ-Al_2O_3, ZrO_2, La_2O_3 and SiO_2, was evaluated. The results indicate that the oxides with acid-base properties, especially ZrO_2, γ-Al_2O_3 and CeO_2 combined with KNO_3, are more active for DEC synthesis. The basicity of the catalysts KNO_3-γ-Al_2O_3, KNO_3-CeO_2 and CeO_2 were analyzed by the CO_2-TPD method (Figure 1). The desorption peaks at about 280 °C–340 °C could be observed for KNO_3-γ-Al_2O_3 and KNO_3-CeO_2, which had better catalytic activities. It is indicated that the addition of a small amount of a moderate base is more effective for enhancing the activity of the catalyst. Considering the KNO_3-CeO_2 catalyst obtaining the better yield and selectivity for DEC, it was finally selected for the following reactions. The XRD spectrums of KNO_3-CeO_2 and CeO_2 are shown in Figure 2. By comparison, the characteristic peaks of KNO_3 cannot be found, and the diffraction peaks of KNO_3-CeO_2 are stronger than CeO_2. It is indicated that the KNO_3 might be well dispersed and caused no considerable distortion in the structure of CeO_2 [25].
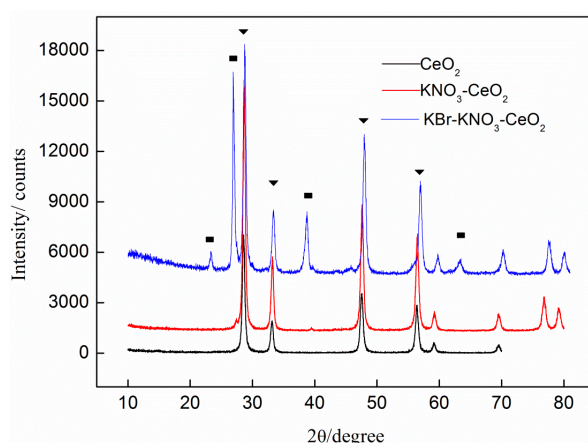
The preparation conditions for KNO_3-CeO_2 including the load of KNO_3 and the calcination temperature were optimized. The results are shown in Figure 3a,b. It is indicated that the KNO_3-CeO_2 with n(Ce)/n(K) = 1:0.4 has better catalytic activity (Figure 3a). And the DEC yield reaches higher level (Figure 3b) at the calcination temperature of 500 °C. According to the TG-DTG analysis of KNO_3 (Figure 4), the decomposition temperature of KNO_3 is 520 °C. When the temperature is higher than 520 °C, the KNO_3 will be decomposed to K_2O, and the catalytic activity will decrease.

Then, the reaction conditions, including the amount of catalyst, reaction time and volume ratio of ethanol and PO, were studied. The results are shown in Figure 3c–e. As seen in Figure 3c, the DEC yield first increases and then decreases with the increase of catalyst amounts. The DEC yield reaches the peak value when the amount of KNO_3-CeO_2 is 0.3 g (Figure 4c). Figure 4d shows the dependence of DEC yield on reaction time. The reaction reaches equilibrium in 2 h. Figure 3e shows that the DEC
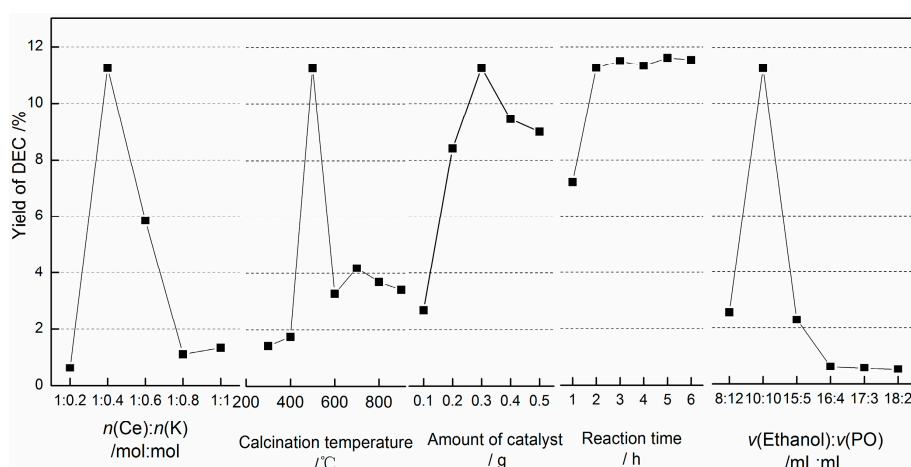
yield reaches the higher level, when both of the volumes of ethanol and PO are 10 mL (0.17 mol and 0.14 mol, respectively) and the CO_2 amount is fixed as 0.25 mol.
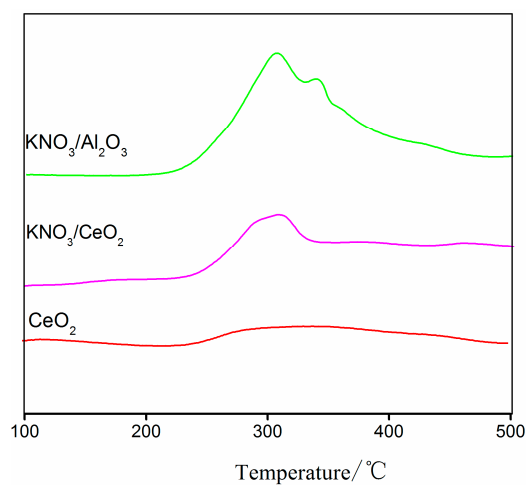
Figure 1. CO_2-temperature-programmed desorption (TPD) analysis for the catalysts.

Figure 2. XRD patterns of CeO_2, KNO_3-CeO_2 and KBr-KNO_3-CeO_2 (KBr, CeO_2).

Figure 3. Optimization of the conditions for the catalyst preparation and the DEC synthesis. The ethanol volume was fixed as 10 mL; the reaction temperature was 150 °C; and the initial pressure was 5 MPa.
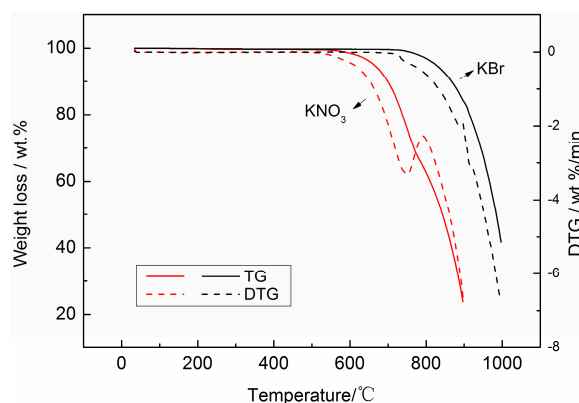
Figure 4. TG-DTG analysis for KNO_3 and KBr.

2.2. The One-Pot Synthesis of DEC over KBr-KNO_3-CeO_2 Catalyst

As potassium halides (KI, KBr and KCl) were proven to be conducive to the cycloaddition reaction [15]; the KI, KBr and KCl were added in the KNO_3-CeO_2 catalyst for the one-pot synthesis of DEC. The addition methods for potassium halides, including solid mixed and impregnation methods, were compared.

The results are shown in Table 1, Runs 13–20. As seen in Table 1, when KI-CeO_2 is used as the catalyst, the ethanol conversion increases, but the yield of DEC is not improved compared to CeO_2 alone. In addition, when KBr or KCl is added to KNO_3-CeO_2, the ethanol conversion decreases, but the selectivity of DEC is effectively improved. Additionally, the catalysts prepared by the solid mixed method give a higher DEC yield and selectivity. However, when KI-KNO_3-CeO_2 is used as the catalyst, the DEC yield seriously decreases. This might be because that KI, with a stronger reduction property, is oxidized by KNO_3, which causes deactivation.

The molar ratio of KBr and KNO_3 was evaluated with fixed $n(CeO_2)/n(KNO_3)$ = 1:0.4. The results are shown in Figure 5. The XRD patterns of KBr-KNO_3-CeO_2 are presented in Figure 4, and the characteristic peaks of KBr are labeled. The yield and the selectivity of DEC are improved with the addition of KBr into the catalyst. When the molar ration is $n(KBr)/n(KNO_3)$ = 6:4, that is $n(CeO_2)/n(KNO_3)/n(KBr)$ = 1:0.4:0.6, the yield of DEC reaches 13.0% with a selectivity of 38.5% on the ethanol basis. Both the yield and selectivity of DEC are much higher than reported in Leino's research [8] by using butylene oxide as the dehydration agent and CeO_2 as the catalyst. In their results, the highest obtained yield of DEC was 1.5%, and selectivity to DEC was 10% on the ethanol basis.
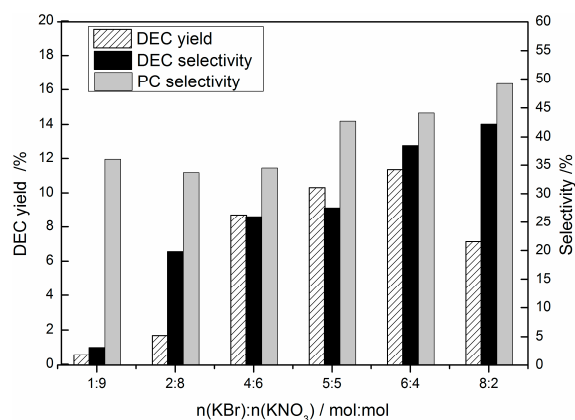

Figure 5. Effects of the molar ratio of KBr and KNO_3 on the products (both of the volumes of ethanol and PO were 10 mL; the reaction temperature was 150 °C; the initial pressure was 5 MPa). PC, propylene carbonate.

The formation kinetics of DEC were also studied, and the dependence of DEC yield on reaction time at 150 °C in 180 min is shown in Figure 6. It is also indicated that the reaction can reach equilibrium in 100 min. The reaction time was selected as 120 min.
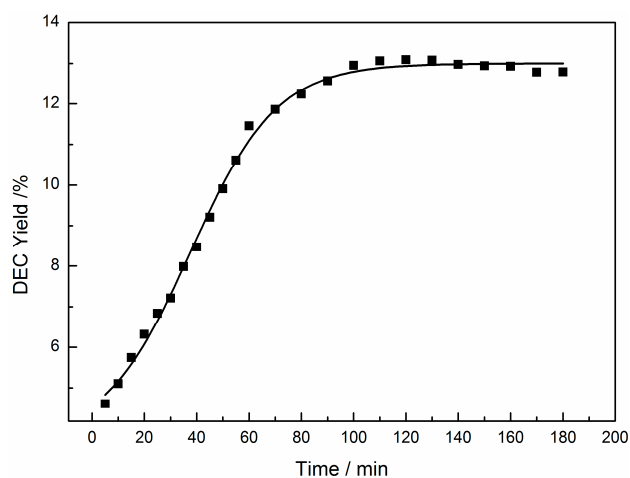
Figure 6. The relationship between the reaction time and yield of DEC at 150 °C for 180 min. (both of the volumes of ethanol and PO were 10 mL; the initial pressure was 5 MPa).

2.3. Recycling Experiments

The recycling experiment results of the KBr-KNO$_3$-CeO$_2$ catalyst are listed in Figure 7. After three times reuse, the catalyst still keeps good catalytic activity, and the DEC yield is above 90%, as in the primary reaction. The XRD patterns of fresh KBr-KNO$_3$-CeO$_2$ and the catalyst after using three times were also compared. The calcination temperature KBr-KNO$_3$-CeO$_2$ was also set as 500 °C. Additionally, the KBr was not decomposed according to the TG-DTG analysis (Figure 4). As seen in Figure 7, the characteristic peaks do not change after three runs. This indicates that the active species of KBr and KNO$_3$ do not leach from the catalyst. The reason might be that CO$_2$ was the main reactant in this reaction, and the reactants and products were extracted by Sc-CO$_2$ after the reaction, while the catalyst was not soluble in Sc-CO$_2$ and left in the reactor, which avoided the loss of catalyst. This is one of the advantages of separating the products by Sc-CO$_2$.
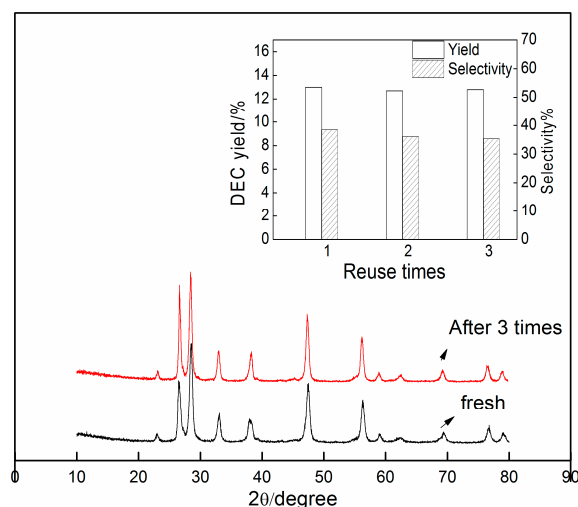
Figure 7. Recycling experiment results of the KBr-KNO$_3$-CeO$_2$ (both of the volumes of ethanol and PO were 10 mL; the reaction temperature was 150 °C; the initial pressure was 5 MPa).

2.4. Thermodynamic Evaluation of the One-Pot Synthesis of DEC

In order to perform the thermodynamics evaluations, which are important in seeking novel synthesis ideas, the thermodynamic data of various substances, such as ethanol, CO_2, PO, DEC and PG, involved in the reaction are tabulated in Table 2.

Table 2. Thermodynamic data of various substances in the reaction [26].

Substance	$\Delta_f H^\theta_{298k}/\text{kJ}\cdot\text{mol}^{-1}$	$S^\theta_{298k}/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$C^{id}_{p\,298k}/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
C_2H_5OH	−235.10	282.70	112.6
CO_2	−393.509	213.74	37.13
DEC	−637.9	412.94 [a]	211
H_2O	−241.82	188.82	33.58
PO	−94.68	281.15	72.55
PG	−421.29	288 [a]	189.9

[a] Calculated by the Constantinous-Gani (CG) group contribution method [27].

The enthalpy and the entropy of the reaction at 298 K estimated from the $\Delta_f H^\theta_{298k}$ and S^θ_{298k} values amounted to $\Delta_r H^\theta_{298k} = -101.4\,\text{KJ}\cdot\text{mol}^{-1}$ and $\Delta_r S^\theta_{298k} = -357.22\,\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. The Gibbs energy at 298 K and 100 KPa could be calculated by Equation (1) and has a value $\Delta_r G^\theta_{298k} = 5.10\,\text{KJ}\cdot\text{mol}^{-1}$.

$$\Delta_r G^\theta_{298k} = \Delta_r H^\theta_{298k} + T\Delta_r S^\theta_{298k} \tag{1}$$

Based on the obtained values, it can be concluded that the reaction is exothermic ($\Delta_r H^\theta_{298k} = -101.4\,\text{KJ}\cdot\text{mol}^{-1} < 0$) and does not occur spontaneously at room temperature $\Delta_r G^\theta_{298k} = 5.10\,\text{KJ}\cdot\text{mol}^{-1} > 0$.

The relative pattern of the reaction heat with the temperature is expressed by Kirchhoff's law (Equation (2)), whereas the Gibbs energy of the reaction, at different temperatures, can be given by the Gibbs–Helmholtz equation (Equation (3)) [8]. Gibbs energy values of this reaction at different temperatures were calculated. The results are shown in Figure 8. The value of $\Delta_r G^\theta_T$ increases with the reaction temperature, and the increase in the temperature is disadvantageous to the formation of DEC.

$$\Delta_r H^\theta_T = \Delta_r H^\theta_{298k} + \Delta C_p\,(T - 298) \tag{2}$$

$$d\left(\frac{\Delta_r G^\theta_T}{T}\right) = \left(-\frac{\Delta_r H^\theta_T}{T^2}\right)d\text{T} \tag{3}$$
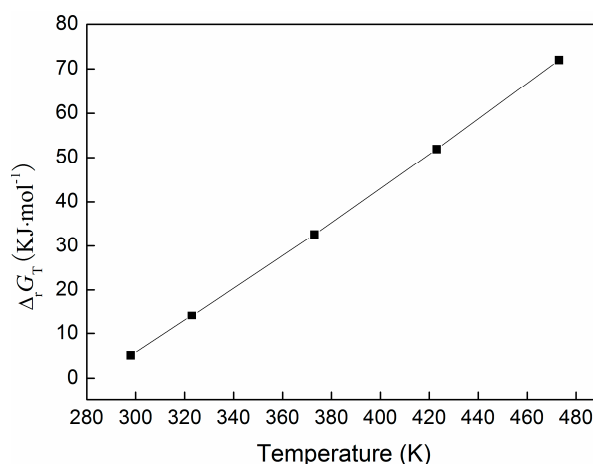
Figure 8. Dependence of temperature on the Gibbs energy of DEC synthesis from ethanol, CO_2 and PO.

When the temperature is fixed at 423 K, the Gibbs energy of the reaction is a function of pressure and can be written as follows [8]:

$$\Delta_r G_P = \Delta_r G^\theta - RT\ln\left(\frac{p}{p^\theta}\right) \tag{4}$$

The equilibrium constant K was determined from the Gibbs energy according to Equation (5):

$$\Delta_r G_T = -RT\ln K \tag{5}$$

$$K = \frac{[DEC]\,[PG]}{[C_2H_5OH]^2\,[PO]\,[CO_2]} \tag{6}$$

In this work, the reaction temperature and pressure are 423 K and 9 MPa; the $\Delta_r G_P$ calculated by Equation (4) is 36.07 kJ·mol^{-1} > 0; and the equilibrium constant K calculated by Equation (5) is 3.5×10^{-5}. When the amounts of CO_2, ethanol and PO are 0.29, 0.17 and 0.14 mol, respectively, and assuming that the reaction is in the gas phase, the equilibrium yield of DEC at 423 K and 9 MPa calculated by Equation (6) is about 14.2% based on ethanol. It is indicated that the yield of DEC in the experiment (13.0%) is close to the equilibrium yield calculated.

3. Experimental Section

3.1. Material

Ethanol (99.8%, analytical grade) was dehydrated by adding spherical 3A molecular sieves before the reactions. Propylene oxide (PO), n-propanol, $Ce(NO_3)_3 \cdot 6H_2O$, KNO_3, KOH, $NaNO_3$, $Mg(NO_3)_2 \cdot 6H_2O$, $Ba(NO_3)_2$, $Ca(NO_3)_2 \cdot 4H_2O$, KBr, KCl, KI, ammonium hydroxide ($NH_3 \cdot H_2O$, 28%) and spherical 3A molecular sieves were purchased from Jiangtian Chemical Reagent Co., Ltd., Tianjin, China. All of the chemicals were of analytical grade and used without further purification. CO_2 (99.99%) was purchased from Lianbo Gas Co., Ltd., Tianjin, China.

3.2. Catalyst Preparation and Characterization

CeO_2 was prepared by the precipitation method. The 6.5 g of cerium (III) nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$) were firstly dissolved in 50 mL water. Then, the precipitating solution of ammonium hydroxide of 50% (v/v) was slowly added into the well-stirred cerium nitrate aqueous solution. The pH of the solution was controlled at 10 throughout the synthesis process. The resulting precipitate was filtrated, washed with deionized water and then dried overnight at 100 °C and calcined at 500 °C for 2 h in air.

KNO_3-CeO_2 was prepared by the incipient impregnation method. The slurry ($n(Ce)/n(K)$ = 1:0.2, 1:0.4, 1:0.6, 1:0.8 or 1:1) was kept in a static state for 24 h and dried at 110 °C for 5 h. The dried samples were calcined at 500 °C for 3 h. Similar methods were used for the preparation of $NaNO_3$-CeO_2, KOH-CeO_2, $Ca(NO_3)_2$-CeO_2, $Mg(NO_3)_2$-CeO_2 and $Ba(NO_3)_2$-CeO_2.

KBr-KNO_3-CeO_2 was prepared by both the impregnation method and solid mixed method. The impregnation method was performed as in the KNO_3-CeO_2 preparation. For the solid mixed method, the dried solids of KBr and KNO_3-CeO_2 were mixed evenly and then calcined at 500 °C for 3 h.

The specific surface area was measured by using nitrogen adsorption (Sorptometer 1900, Carlo Erba Instruments, Milan, Italy). The sample was out gassed at 150 °C for 3 h prior to the measurement of the surface area. For calculating the surface area, the BET equation was used.

The structural properties of the catalysts were investigated by X-ray diffraction (XRD) (X'Pert Pro MPD, PANalytical, Lelyweg, The Netherlands) using CuKα (40 kV, 50 mA) radiation with 2θ ranging from 0° to 80° at a scanning speed 0.04°/3 s.

Thermogravimetric (TG) analysis was carried out on a thermogravimetric analyzer (TG209, Netzsch Co., Wittelsbacherstr, Germany) under a N_2 stream of 40 mL min^{-1}. The temperature was raised at a heating rate of 10 °C min^{-1}.

Temperature-programmed desorption (TPD) of CO_2 was carried out using the Micromeritics Instrument (Auto Chem 2910, Micromeritics Instrument Co., Norcross, GA, USA). Zero-point-one gram of catalyst was placed in a quartz-made U-shaped tube. The catalyst was firstly treated in a flow of helium (50 mL· min^{-1}) at 200 °C for 2 h to remove any physisorbed organic molecules. The sample was then saturated by adsorption of CO_2 (50 mL· min^{-1}) at 60 °C for 30 min. Physisorbed CO_2 was flushed at 150 °C for 1 h. After the sample was cooled, the furnace temperature was increased from 60 °C to 800 °C at a heating rate of 5 °C· min^{-1} under a flow of helium (30 mL· min^{-1}). The desorbed CO_2 was detected by using a TCD (thermal conductivity detector).

3.3. Catalytic Test

All experiments were carried out in a laboratory-scale stainless steel autoclave (Weihai Chemical Machinery Co., Ltd., Weihai, China) with an inner volume of 100 mL equipped with a stirrer and an electric heater. In a standard procedure, 0.3–0.5 g of catalyst, 170 mmol (10 mL) of ethanol and 140 mmol (10 mL) propylene oxide were introduced into the autoclave. The reactor was purged with CO_2 at room temperature. Then, the reaction system was pressurized to the predetermined initial pressure with CO_2 by a pump (Model SFC-24, SSI/LabAlliance, State College, PA, USA). The amount of CO_2 was calculated from measuring the weight difference of the CO_2 cylinder before and after charging the CO_2. After the reaction, the reactor was cooled to about 50 °C. The CO_2 was released slowly through a receiving flask with methanol as the absorbent. Then, the liquid chemicals in the reactor were extracted *in situ* by supercritical CO_2 at 12 MPa and 50 °C. All of the reactants and products were collected using methanol in a flask. The catalyst was left in the reactor. About 240 g CO_2 were required to extract all liquid chemicals. For the recycling experiments, the catalyst was used directly after the extraction process by repeating the procedures above.

$$\text{Yield of product } Y_i\,(\%) = \frac{\text{mole of product i}}{0.5 \times \text{mole of ethanol charged}} \times 100\%$$

$$\text{Selectivity } S_i\,(\%) = \frac{\text{mole of product i}}{0.5 \times \text{mole of ethanol convered}} \times 100\%$$

3.4. Analysis Method

The products were analyzed by gas chromatography (GC) with an FID detector (6890N, Agilent Co., Santa Clara, CA, USA) and GC–MS (HP 6890 gas chromatograph coupled with mass detector HP 5973N, Agilent Co., Santa Clara, CA, USA) using an HP-5MS (30 m × 0.25 mm × 0.25 μm, Agilent Co., Santa Clara, CA, USA) fused silica capillary column. n-Propanol was used as the internal standard. The chromatography conditions were the same as our previous studies [14].

4. Conclusions

The direct synthesis of DEC from carbon dioxide, ethanol and PO was developed over KNO_3-CeO_2 and KBr-KNO_3-CeO_2 catalyst. Supercritical CO_2 was used to extract the products and reactants in site, and the catalysts could be reused. In comparison with the direct synthesis of DEC from CO_2 and ethanol, the involvement of PO could improve the formation of DEC, simultaneously with the important chemicals of glycol coproduced. The yield of DEC was improved about 10-fold compared to that using single CeO_2 as the catalyst. The yield of DEC was about 13.0% with a selectivity of 38.5% under the optimized conditions with KBr-KNO_3-CeO_2 as the catalyst, which was close to the equilibrium yield calculated in this work.

Author Contributions: Zhen Zhu synthesized the catalysts and performed most of the catalytic reactions, while Yongyue Sun performed some of the charaterisation. The initial draft of the paper was written by Yanlou Wang; while the final copy and corrections made at various stages of this paper was done by the corresponding author, Dongdong Jia.

Conflicts of Interest: The authors declare no conflict of interest.

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