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# Gas phase decarbonylation of diethyl oxalate to diethyl carbonate over alkali-containing catalyst

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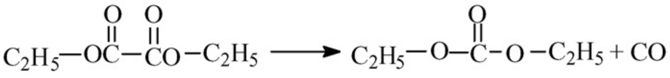
ABSTRACT

A detailed alkali catalytic preparation of diethyl carbonate (DEC) from diethyl oxalate (DEO) via gaseous phase decarbonylation was investigated in the paper. Evaluation results showed that 6 wt% (based on potassium) $K_2CO_3$/AC (activated carbon) catalyst exhibited a relatively high catalytic activity. 54.3% conversion of DEO, 27.8% selectivity to DEC and 300.0 g/(L h) space time yield of DEC were obtained at 513 K and the gas hourly space velocity 1000 $h^{-1}$. A series of characterization approaches were performed to explore the reasons for the decreasing catalytic activity. By means of XRD analysis, it can be concluded that the $K_2CO_3$ with high dispersion on the catalyst surface is favorable for the production of DEC, while the formation of $K_2CO_3$ crystallization results in the decrease of the catalytic activities. The $KHCO_3$ crystallization detected on the catalyst surface after the reaction also leads to the degressive active properties. Moreover, the results of BET, XPS and ICP-OES indicated that the specific surface area and the potassium content of catalysts are closely related with the catalytic activity.

## 1. Introduction

Diethyl carbonate (DEC) has recently attracted increasing attention in the chemical industry as an important raw material for pharmaceutically active compounds, agriculture chemicals, polycarbonates or itself as a solvent. The presence of two ethyl groups and one carbonyl group in its molecule makes DEC a promising alternative to both ethyl halides and phosgene for ethylation and carbonylation processes. In the light of its high oxygen content (40.6 wt%) and more favorable gasoline/water distribution coefficients comparing to dimethyl carbonate (DMC) and ethanol, DEC has been proposed to be an attractive alternative for *tert*-butyl ether as oxygen-containing fuel additive [1]. Furthermore, when released into the environment, DEC slowly biodegrades to carbon dioxide and ethanol with negligible pollution for the environment [2].

Several synthetic routes to DEC have been developed so far, such as the phosgene–ethanol process [3], oxidative carbonylation of ethanol in liquid [4] or gas phase [5,6], transesterification reactions of DMC with ethanol [7], synthesis from carbon dioxide with ethanol [8], reaction of ethanol with urea over organo-tin catalysts [9], and so on. Uchtumi et al. developed a novel way using CO and ethyl nitrite instead of ethanol and oxygen to prepare DEC and diethyl oxalate (DEO) in a single run [10–12]. It related to introducing ethyl nitrite into the reaction system to form the eco-friendly self-recycled route. One key point of this route is that DEO in this reaction system can further be decarbonylated to DEC which is positive for keeping the balance of these two important products according to the market demand. Furthermore, the liquid DEO is advantageous in the view of the reactant input. The main reaction of preparation of DEC from DEO via decarbonylation takes place as shown in reaction (1). The endothermic enthalpy change and the equilibrium constant of the decarbonylation reaction at 533 K are 20.88 kJ/mol and $3.12 \times 10^9$, respectively, which indicates that the direct decarbonylation of DEO to DEC is thermodynamically feasible [13].



$$C_2H_5{-}O\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}O{-}C_2H_5 \longrightarrow C_2H_5{-}O{-}\overset{O}{\overset{\|}{C}}{-}O{-}C_2H_5 + CO \quad (1)$$

There are many reports on the preparation of diaryl carbonate from diaryl oxalate including liquid and gaseous phase reaction via decarbonylation. A variety of compounds can be used as decarbonylation catalysts for the preparation of diphenyl carbonate (DPC) from diphenyl oxalate (DPO) [14–18]. However, there is still long way to go in the pursuit of a good catalyst for the decarbonylation of DEO into DEC. It has been proposed that dialkyl carbonates can be prepared by heating the dialkyl oxalate in a liquid phase at 50–150 °C in the presence of alcoholate catalyst [19]. Honshu [20] reported on the preparation of DMC from dimethyl oxalate (DMO) via decarbonylation over the $Me_4NCl$ catalyst under different reaction conditions. However, the limited selectivity and

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yield together with the complicated separation and recovery procedures makes the process far from satisfaction. In light of these problems, the gaseous decarbonylation including many examples of DMC preparation from DMO via decarbonylation with alkali catalysts supported on activated carbon (AC) was brought forward by Katsumasa [21]. It was reported that both the conversion of DMO and the selectivity to DMC were up to 75% and the gaseous space time yield (STY) of DMC was above 1000 g/(L h). But for DEC preparation via decarbonylation from DEO, there were no detailed reports about the highly active catalyst and the optimum reaction condition. Consequently, this work tried to deal with the alkali catalysts and give some details about its performance in the decarbonylation of DEO for DEC preparation.

## 2. Experimental

### 2.1. Catalysts preparation

#### 2.1.1. Supports preparation

Zirconium was obtained by the precipitation of zirconium oxychloride solution with the necessary amount of ammonia to reach a constant pH of 10. The precipitated material was filtrated and washed with deionized water until it was free from chlorine ions, as determined by the silver nitrate test. The product was then dried at 393 K for 4 h and calcined at 923 K for 5 h to get a white zirconia dioxide powder. Finally, the powder was shaped under 25 MPa and crashed into 20–40 meshes for further use.

Magnesium oxide was synthesized following the similar procedures proposed by Cosimo and co-workers [22]. 20 g commercial magnesium oxide was added to 200 mL deionized water at room temperature in a stirred glass reactor. The slurry was stirred for 4 h after the temperature was raised to 353 K. Then, the sample was dried at 358 K overnight. The obtained $Mg(OH)_2$ was thermally decomposed in $N_2$ at 30 mL/min (STP) at 623 K for 2 h and then at 773 K for another 8 h. Finally, the MgO powder was shaped and crashed into 20–40 meshes.

The 20–40 meshes AC were treated in 0.1 mol/L KOH solution followed by 0.1 mol/L $HNO_3$ solution, and finally washed with deionized water in order to remove the adhering ash on the surface. Then the sample was dried at 393 K for 24 h and stored in a desiccator.

Prior to impregnation, the commercial $SiO_2$ and $Al_2O_3$ were treated in deionized water for 5 h, followed by desiccation at 393 K for 24 h.

Commercial HZSM-5 was calcined at 773 K for 12 h to eliminate the water presented as humidity or bonded to the crystals before impregnation [23].

#### 2.1.2. Supported alkali catalysts preparation

Three impregnation methods were investigated in the supported alkali catalysts preparation as follows:

(I) *Dipping impregnation*. 1.062 g $K_2CO_3$ was dissolved in 50 mL water and 10 g support was added. The mixture was placed under a reduced pressure of 0.09 MPa to impregnate for 3 h and then heated from room temperature to 353 K to evaporate water gradually in a rotary evaporator. Thereafter, the residual mixture was dried at 393 K for 24 h to prepare a solid catalyst. The total loading of the catalyst in terms of metallic potassium was 6 wt%.

(II) *Incipient wetness impregnation*. The prepared support was added to the necessary amount of solution to fill the pore volume of the support for 24 h at room temperature and atmospheric pressure, followed by desiccation in an oven at 393 K for 24 h.

(III) *Supersonic impregnation*. The beaker with potassium containing aqueous solution and prepared support mixture was placed in the supersonic container followed by impregnating for 30 min, then dried at 393 K for 24 h under atmospheric pressure.

### 2.2. Decarbonylation of DEO to DEC

The decarbonylation of DEO over alkali catalysts was conducted at atmospheric pressure in a continuous flow fixed-bed reactor. The reactor (400 mm long, 13 mm inner diameter stainless tube placed coaxially in a Ø 400 mm thermostated furnace) was loaded with the catalyst. The reactant was pumped (Lab Alliance Series II Pump) into a preheater and carried by an inert $N_2$ stream into the reactor.

The liquid mixture caught in the condensator was analyzed by an Agilent 4890D gas chromatograph (GC) equipped with an HP-5 capillary column (Hewlett–Packard Company, 15 m × 0.53 mm × 1.5 μm) and a flame ionization detector (FID). The analysis of the gaseous products collected at the reactor outlet was performed by SP3420 GC provided with a thermal conductivity detector (TCD) and a molecular sieve 5 A column. The qualitative analysis of the products was confirmed on an Agilent HP5971 gas chromatograph-mass spectroscopy (GC–MS) in the DEC preparation from DEO via decarbonylation. The catalytic activity was expressed by the conversion of DEO, the selectivity and the STY of DEC.

### 2.3. Catalysts characterization

Powder X-ray diffraction crystalline phases were recorded at room temperature by using an X-ray powder diffraction (XRD). A PANalytical X' Pert Highscore (Holland) diffractometer, equipped with Co Kα radiation anode ($k$ = 1.78901 Å, 40 kV and 40 mA), was used for these measurements. Intensity data were measured by step scanning in the $2\theta$ ranges with a scanning rate of $12^\circ\,\text{min}^{-1}$ from $2\theta = 10^\circ$ to $80^\circ$.

The specific surface areas of the catalysts were measured on an adsorption apparatus (Micromeritics Gemini V) by the $N_2$-BET method at the liquid nitrogen temperature. The point surface area was determined at $P/P_0 = 0.1, 0.2, 0.3$.

The surface composition of catalyst was studied by X-ray photoelectron spectroscopy (XPS) in a PerkinElmer PHI 1600 ESCA system with Mg Kα 1253.6 eV radiation as the excitation source. The samples were mounted on the specimen holder by means of double-sided adhesive tape. Spectra were recorded in steps of 0.15 eV. The C1s peak (284.5 eV) was used as the internal standard for binding-energy calibration. An estimated error of ±0.1 eV can be assumed for all the measurements. The scanning of the spectra was done at pressures less than $10^{-8}$ Torr and the temperature was approximately 293 K.

Further elemental analysis of catalysts was performed by an inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Varian VISTA-MPX) at the frequency emission power of 1.2 kW, plasma air flow of 15.0 L/min and $\lambda_K = 766.491$ nm.

## 3. Results and discussion

### 3.1. Qualitative analysis of the products in the reaction

The qualitative analysis of products in the preparation of DEC from DEO by decarbonylation over $K_2CO_3$/AC was performed by Agilent HP5971 gas chromatography-mass spectroscopy. DEC, DEO, ethanol, ethyl formate, and 1,1-diethoxyethane were identified, respectively [24].

**Table 1**
Comparison of various alkali catalysts[a] on the catalytic performance for the preparation of diethyl carbonate from diethyl oxalate via decarbonylation[b].

| Catalyst | Conversion of DEO (%) | Selectivity to DEC (%) | STY of DEC (g/(L h)) |
|---|---|---|---|
| $K_2C_2O_4$ | 45.1 | 19.1 | 165.0 |
| $CH_3COOK$ | 53.0 | 16.5 | 163.6 |
| $K_2CO_3$ | 54.3 | 27.8 | 300.0 |
| $K_2CO_3$–$K_3PO_4$ | 52.0 | 28.2 | 291.4 |

[a] Potassium loading = 6 wt%; support: activated carbon (AC); preparation method: incipient wetness impregnation.

[b] Reaction condition: $T = 513$ K, $GHSV = 1000\ h^{-1}$, $N_2 = 25$ mL/min, reaction time = 1 h.

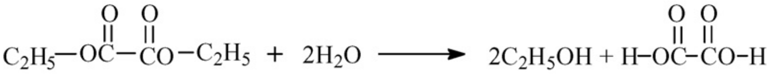
**Table 2**
Effect of supports on the catalytic performance of catalysts[a] for the preparation of diethyl carbonate from diethyl oxalate via decarbonylation[b].

| Support | Conversion of DEO (%) | Selectivity to DEC (%) | STY of DEC (g/(L h)) |
|---|---|---|---|
| $SiO_2$ | 22.0 | 2.4 | 10.4 |
| $Al_3O_3$ | 38.8 | 17.3 | 133.3 |
| H-ZSM-5 | 23.4 | 2.1 | 9.73 |
| $ZrO_2$ | 33.8 | 15.6 | 105.3 |
| AC | 54.3 | 27.8 | 300.0 |
| MgO | 33.8 | 1.7 | 11.4 |

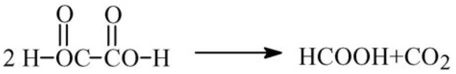
[a] $K_2CO_3$ catalysts, potassium loading = 6 wt%; preparation method: incipient wetness impregnation.

[b] Reaction condition: $T = 513$ K, $GHSV = 1000\ h^{-1}$, $N_2 = 25$ mL/min, reaction time = 1 h.

From the qualitative results, ethanol and ethyl formate are considered as the main by-products. It is supposed that the initial by-products oxalic acid and ethanol were obtained on account of the hydrolysis of DEO, followed by the decomposition of oxalic acid to $CO_2$ and formic acid at high temperature. And then, ethyl formate was formed by partial formic acid and ethanol. At the same time, formic acid continues to decompose to CO and $H_2O$ due to its instability at high temperature [25]. Unfortunately, the product $H_2O$ here would further accelerate the hydrolysis of DEO, resulting in the production of ethanol, which leads to a limited selectivity of the aimed product. In order to eliminate the negative effect of $H_2O$ introduced via inlet on the yield of DEC, 3 A molecular sieve was employed to the reactant DEO and the inert $N_2$ to eliminate the $H_2O$ before feeding into the reactor. It was revealed that the selectivity of DMC was increased to some extent after the treatment. In light of this, the control of the amount of $H_2O$ in the reaction system is considered to be one of the key points in the decarbonylation process. The existence of trace $H_2O$ in the reaction system could be the main reason for the formation of by-products. In addition, it is feasible for the dehydrogenation of ethanol to acetaldehyde over the alkali catalyst. Thus, the 1,1-diethoxyethane is considered as the product of ethanol with the acetaldehyde by aldol reaction. The equations about by-products formation were exhibited as follows:



$$C_2H_5{-}O\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}O{-}C_2H_5 + 2H_2O \longrightarrow 2C_2H_5OH + H{-}O\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}O{-}H \tag{2}$$



$$2\ H{-}O\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}O{-}H \longrightarrow HCOOH + CO_2 \tag{3}$$

$$HCOOH + C_2H_5OH \rightarrow HCOOC_2H_5 \tag{4}$$

$$HCOOH \rightarrow CO + H_2O \tag{5}$$

$$C_2H_5OH \xrightarrow{K_2CO_3/AC} CH_3CHO + H_2 \tag{6}$$

$$CH_3CHO + C_2H_5OH \rightarrow (C_2H_5O)(CH_3)CH(OC_2H_5) + 2CO_2 + H_2O \tag{7}$$

## 3.2. Performance of catalysts

### 3.2.1. Catalytic activity comparison of various alkali catalysts

It has been reported that the supported alkali catalysts such as $K_2CO_3$/AC, $K_3PO_4$/AC, $K_2C_2O_4$/AC etc. showed high catalytic activity in the synthesis of DMC from DMO via decarbonylation [21]. Here in this paper, three AC supported alkali catalysts, i.e. $K_2CO_3$/AC, $K_2C_2O_4$/AC and $CH_3COOK$/AC, were studied in the DEC preparation via decarbonylation. The $K_2CO_3$/AC catalyst exhibits a relatively high activity as shown in Table 1, which gives 54.3% conversion of DEO, 27.8% selectivity to DEC and 300.0 g/(L h) STY of DEC. $K_2C_2O_4$/AC and $CH_3COOK$/AC catalysts are not beneficial for the selectivity to DEC and the main by-product is ethanol. Obviously, they are more favorable for the hydrolysis of the reactant to ethanol. In addition, it has been indicated that a rather high conversion of DMO was obtained over the $K_2CO_3$/AC catalyst and an excellent selectivity to DMC was obtained over the $K_3PO_4$/AC catalyst [21]. In view of this, the $K_2CO_3$–$K_3PO_4$/AC catalyst was also investigated for the production of DEC. However, the conversion of DEO and the selectivity to DEC over $K_2CO_3$–$K_3PO_4$/AC was nearly equal with those over $K_2CO_3$/AC. Therefore, the single component $K_2CO_3$/AC catalyst was selected for the further experiments in the preparation of DEC.

### 3.2.2. Supports screen

It is well-known that support plays an important role in the structure and activity of the supported catalysts. The alkali metal compound deposited on different kinds of supports such as AC, silica, $Al_2O_3$, magnesia, zirconia, molecular sieves etc. were studied in the preparation of DMC from DMO via decarbonylation [21]. Thus, a series of supports was investigated for the preparation of DEC. The effect of the support on the catalytic activity of the supported $K_2CO_3$ catalysts for the preparation of DEC from DEO via decarbonylation was displayed in Table 2. Higher selectivity to DEC was obtained with AC as the support likely due to its large specific surface area, which is beneficial for the loading of active components, while other supports were not so effective for the DEC production. In the case of silica, the neutralization of the active component $K_2CO_3$ with the acid sites on the silica is referred to the poor activity.

### 3.2.3. Effect of the potassium loading

Fig. 1 reveals the effect of the potassium loading on the catalytic performance of $K_2CO_3$/AC catalyst for the preparation of DEC from DEO via decarbonylation in the range of 2–10 wt%. As shown in Fig. 1, the STY of DEC increases with the increase of the potassium loading and thereafter sharply decreases when the potassium loading is above 6 wt%. In the view of the selectivity to DEC, there is almost no change with the further increased potassium loading. Therefore, under the reaction condition, 6 wt% was considered as the optimum potassium loading of the decarbonylation catalyst. It is suggested that the inactive potassium species might be produced under the excessive high potassium loading, as explained further in the catalysts characterization section.

### 3.2.4. Effect of the preparation method of the catalyst

Catalysts prepared by different preparation methods may show a remarkable difference in the activity in spite of the same amount of active component and the same support. Dipping impregnation and incipient wetness impregnation are the most common methods

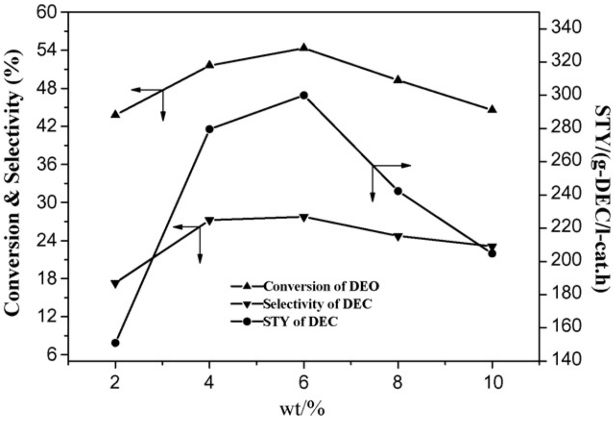


**Fig. 1.** Effect of the potassium loading on the catalytic performance of $K_2CO_3$/AC catalysts for the preparation of diethyl carbonate from diethyl oxalate via decarbonylation. Reaction condition: $T = 513$ K, *GHSV* = 1000 h$^{-1}$, $N_2 = 25$ mL/min, reaction time = 1 h.

in the supported catalysts preparation. In order to obtain the fine dispersion of active component on the support, supersonic impregnation was also investigated in this study. Effect of the catalyst preparation method on the catalytic performance for the preparation of DEC from DEO via decarbonylation was illustrated in Table 3. It is found that the incipient wetness impregnation highlights a better catalytic activity compared with the other two methods, of which 32.2% conversion of DEO, 25.3% selectivity to DEC and 359.5 g/(L h) STY of DEC were obtained. Supersonic impregnation is disadvantageous to the selectivity to DEC and the dipping impregnation presents a relatively lower conversion of DEO and also the selectivity to DEC. In view of its simple operation process and the flexibility to control the amount of potassium loading, the incipient wetness impregnation was selected as the preparation method.

### 3.2.5. *Effect of the reaction temperature*

The effect of the reaction temperature in the range of 473–573 K on the catalytic performance of $K_2CO_3$/AC catalyst for the preparation of DEC from DEO via decarbonylation at atmospheric pressure is plotted in Fig. 2. As expected, higher temperature is favorable for the preparation of DEC from DEO via decarbonylation, which is consistent with the thermodynamic results studied previously. A higher equilibrium constant is obtained at the higher reaction temperature [13]. However, the selectivity to DEC shows a rapid decrease with the further increase of the reaction temperature and the STY of DEC reaches to the summit at temperature around 513 K. Accelerated hydrolysis of the reactant DEO under the extremely high temperature forming by-product ethanol is responsible for the decrease of the catalytic activity.

### 3.2.6. *Influence of the gas hourly space velocity*

**Table 3**
Effect of catalyst[a] preparation method on the catalytic performance for the preparation of diethyl carbonate from diethyl oxalate via decarbonylation[b].

| Catalyst preparation method | Conversion of DEO (%) | Selectivity to DEC (%) | STY of DEC (g/(L h)) |
|---|---|---|---|
| Dipping impregnation | 25.6 | 25.4 | 287.1 |
| Incipient wetness impregnation | 32.2 | 25.3 | 359.5 |
| Supersonic impregnation | 38.1 | 19.4 | 326.0 |

[a] $K_2CO_3$/AC catalyst, potassium loading = 6 wt%; preparation method: incipient wetness impregnation.

[b] Reaction condition: $T = 533$ K, *GHSV* = 2000 h$^{-1}$, $N_2 = 50$ mL/min, reaction time = 1 h.

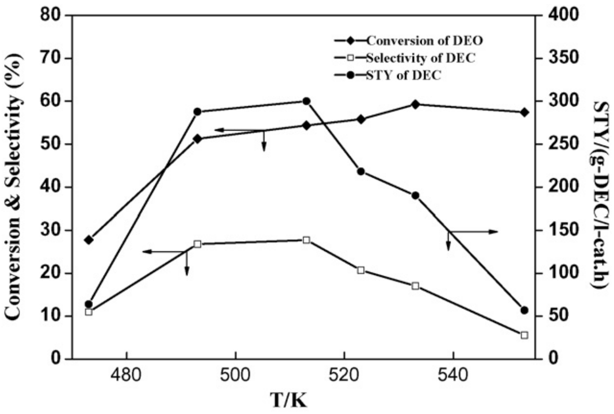


**Fig. 2.** Effect of the reaction temperature on the catalytic performance of 6 wt% $K_2CO_3$/AC catalysts for the preparation of diethyl carbonate from diethyl oxalate via decarbonylation. Reaction condition: *GHSV* = 1000 h$^{-1}$, $N_2 = 25$ mL/min, reaction time = 1 h.

Fig. 3 indicates the influence of the gas hourly space velocity (*GHSV*) on the catalytic performance of $K_2CO_3$/AC catalyst for the preparation of DEC from DEO via decarbonylation between 500 and 1400 h$^{-1}$. There is an obvious increase in the STY of DEC as the *GHSV* increases. The STY of DEC is enhanced from 23.6 to 300.0 g/(L h) with the increase of *GHSV* from 500 to 1000 h$^{-1}$. The conversion of DEO keeps at a relatively high level when the *GHSV* varies from 500 to 800 h$^{-1}$ and thereafter descends sharply when above 800 h$^{-1}$, under which the reactant could left off the catalyst bed quickly without reacting on the catalyst efficiently. The selectivity to DEC inclines with the increase of the *GHSV* from 500 to 1000 h$^{-1}$ and then keeps a steady state.

## 3.3. *Catalysts characterization*

### 3.3.1. *X-ray powder diffraction analysis*

The XRD analysis was undertaken to determine the bulk structure of the active component on $K_2CO_3$/AC. XRD patterns plotted in Fig. 4 were performed on the $K_2CO_3$/AC catalysts with different potassium loading before and after the reaction. Obviously, for those catalysts before the reaction, there are no characteristic diffraction peaks of crystalline $K_2CO_3$ on the AC when the potassium loading is below 6 wt%, which indicates that $K_2CO_3$ was highly dispersed on the AC. However, partial characteristic peaks of crystalline $K_2CO_3$ appear when the potassium loading is 8 wt%. As shown in Fig. 1, 6 wt% potassium loading catalyst exhibits the highest performance for the preparation of DEC with the varying potassium loading. Combining the above results, it is inferred that

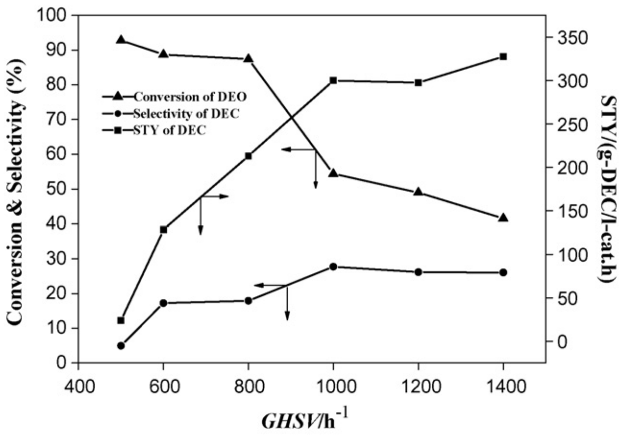


**Fig. 3.** Effect of the gas hourly space velocity on the catalytic performance of 6 wt% $K_2CO_3$/AC catalyst for the preparation of diethyl carbonate from diethyl oxalate via decarbonylation. Reaction condition: $T = 513$ K, $N_2 = 25$ mL/min, reaction time = 1 h.

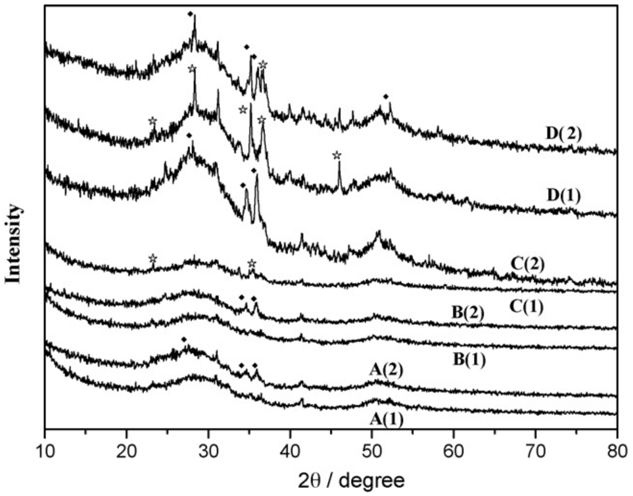


**Fig. 4.** XRD spectra of different amount of K loading catalysts [$K_2CO_3$/AC catalyst; preparation method: incipient wetness] before (1) and after (2) reaction for the synthesis of diethyl carbonate from diethyl oxalate via decarbonylation. A, 4 wt%; B, 6 wt%; C, 8 wt%; D, 10 wt%; (♦) $KHCO_3$; (☆) $K_2CO_3$.

the $K_2CO_3$ with high dispersion on the catalyst surfaces is favorable for the production of DEC, while the formation of crystalline $K_2CO_3$ leads to the decrease of the catalyst activities. In other words, the crystalline $K_2CO_3$ is less active for the yield of DEC. Moreover, from the XRD patterns of the catalysts after the reaction, it is notable that the characteristic diffraction peaks of crystalline $KHCO_3$ appear on the 8 wt% potassium loading catalyst. It is referred that the crystalline $KHCO_3$ is mainly obtained from the reaction of $K_2CO_3$ with $CO_2$ and $H_2O$, which was produced via the decomposition of the oxalic acid and the formic acid in the by-products formation cycle, respectively. Moreover, the characteristic diffraction peak of crystalline $KHCO_3$ enhances with the increase of the potassium loading. Fig. 4 provided the strong evidence for the conclusion that the 6 wt% potassium loading is the optimum amount for DEC preparation. Inactive crystalline $K_2CO_3$ holds back the production of DEC. At the same time, it also indicates that the formation of $KHCO_3$ in the reaction is one of the possible reasons for the degressive catalytic activity.

### 3.3.2. Specific surface area analysis

Comparative results of the specific surface area of $K_2CO_3$/AC obtained from different AC sources before and after the reaction for preparing DEC from DEO via decarbonylation were presented in Table 4. The specific surface areas of all catalysts exhibit a great decrease after the reaction. For the AC of Kunshan, specific surface area gives a reduction from 950 to 80 $m^2$/g. Results in Table 4 indicate clearly that the larger surface of the catalyst makes for more STY of DEC. Remarkable decrease of the catalysts specific surface may be one of the main reasons for the diminished active behavior of catalysts. Unfortunately, the exact reasons for the great decrease of the specific surface area have not been understood fully in this work. The detailed demonstrations will be made in the further research.

**Table 4**
Comparison of the specific surface area before and after reaction of activated carbon from different sources for the preparation of diethyl carbonate from diethyl oxalate via decarbonylation.

| Catalysts[a]/no. | Specific surface area ($m^2$/g) | | |
|---|---|---|---|
| | Original | Before reaction | After reaction |
| 1 | 1380 | 950 | 80 |
| 2 | 882 | 452 | 46 |
| 3 | 845 | 412 | 76 |
| 4 | 718 | 400 | 17 |

[a] Potassium loading = 6 wt%; catalysts preparation method: incipient wetness. 1, Kunshan carbon; 2, Ningde carbon; 3, Zhengzhou carbon; 4, Tangshan carbon.

**Table 5**
Comparison of surface composition of $K_2CO_3$/AC catalysts[a] before and after reaction for the preparation of diethyl carbonate from diethyl oxalate via decarbonylation.

| Catalyst | Surface composition (atomic %) | | | | |
|---|---|---|---|---|---|
| | C | O | N | K | S |
| $K_2CO_3$/AC | | | | | |
| Before reaction | 81.6 | 16.1 | 2.3 | 0 | 0 |
| After reaction | 81.2 | 16.6 | 1.2 | 0.5 | 0.4 |

[a] Amount of potassium loading: 6 wt%; preparation method: incipient wetness.

**Table 6**
Comparison of the potassium content before and after reaction of different amount of potassium loading catalysts[a] for the preparation of diethyl carbonate from diethyl oxalate via decarbonylation.

| Theoretical potassium loading (wt%) | Practical potassium loading (wt%) | |
|---|---|---|
| | Before reaction | After reaction |
| 4 | 3.7 | 2.4 |
| 6 | 3.8 | 3.2 |
| 8 | 6.3 | 5.0 |
| 10 | 6.8 | 6.0 |

[a] $K_2CO_3$/AC catalyst; preparation method: incipient wetness impregnation.

### 3.3.3. X-ray photoelectron spectroscopy analysis

The investigation of binding energy and intensity of surface elements by XPS gives the information of the chemical states and relative quantities of the outermost surface compounds. In order to obtain the surface information of the $K_2CO_3$/AC catalysts, the XPS characterization was carried out. Comparison of surface composition of 6 wt% $K_2CO_3$/AC catalyst before and after the reaction for the preparation of DEC from DEO via decarbonylation was shown in Table 5. It is visible that the content of potassium element increases from 0 to 5% after the reaction. Detection of potassium on the catalyst surface after the reaction by XPS indicates that potassium initially seems to be concentrated onto the surface and gradually leached out during the course of reaction. The migration or the loss of potassium content of catalysts may suppress the catalytic activity. So, further research of element content of potassium was performed by ICP-OES.

### 3.3.4. Inductively coupled plasma-optical emission spectroscopy analysis

Element content of potassium on different potassium loading of $K_2CO_3$/AC catalysts before and after the reaction was measured by ICP-OES. According to the ICP experimental results shown in Table 6, it is evident that the amount of potassium contained in all samples after the reaction is less than that of fresh ones. Therefore, loss of the active potassium component took place during the course of reaction, which is consistent with the results in the XPS. Thus, the decrease of the potassium content of the catalyst must be one of the reasons for the fall in the activity of the catalyst.

## 4. Conclusions

The detailed preparation of diethyl carbonate from diethyl oxalate via gaseous decarbonylation with alkali catalysts was studied in this paper. $K_2CO_3$/AC catalyst prepared by the incipient wetness impregnation shows the favorable catalytic performance, and the optimum potassium loading is 6 wt%. The catalyst has a better activity with 54.3% DEO conversion, 27.8% selectivity to DEC and 300.0 g/(L h) space time yield of DEC at 513 K and gas hourly space velocity 1000 $h^{-1}$. Measurement of specific surface area, the analysis of XRD, XPS and ICP-OES conducted on the catalysts before and after the reaction was performed in order to explain the reasons for the decrease of catalytic activities. From the analysis of XRD, it can be found that the catalytic activity of the supported $K_2CO_3$ catalyst is mainly due to the high dispersion of $K_2CO_3$ on the support, and the increased loading amount of $K_2CO_3$ leads to the formation of the $K_2CO_3$ crystallization, accordingly, decreases the catalytic activity. On the other hand, the $KHCO_3$ crystallization was detected on the catalyst surface after the reaction due to the reaction of $K_2CO_3$ with $CO_2$ and $H_2O$. So, the formation of $KHCO_3$ crystallization during the reaction is one of important reasons for the decreased catalytic activity. Moreover, by means of the measurement of catalysts specific surface area and element content by BET, XPS and ICP-OES, it is possible to assess that the specific surface area and potassium content are two important factors of the catalytic performance in DEC preparation.

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