Applied Catalysis A: General 433–434 (2012) 229–235

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Synthesis of diethyl carbonate from ethyl carbamate and ethanol over ZnO-PbO catalyst

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ARTICLE INFO

Article history:
Received 21 December 2011
Received in revised form 11 May 2012
Accepted 17 May 2012
Available online 24 May 2012

Keywords:
Diethyl carbonate
Ethyl carbamate
Ethanol
Urea
ZnO-PbO

ABSTRACT

The synthesis of diethyl carbonate (DEC) from ethyl carbamate and ethanol was investigated over a series of double metal oxides. Among the catalysts, ZnO-PbO showed the best catalytic activity and the highest DEC yield was 20.6%. Furthermore, ZnO-PbO had an excellent reusability. According to the results of XRD measurement, IR and element analysis, ZnO and PbO in ZnO-PbO catalyst were separately converted to $Zn(NCO)_2(NH_3)_2$ and metal Pb during the reaction, indicating that the mixture of $Zn(NCO)_2(NH_3)_2$ and metal Pb may be the real active composition for DEC synthesis and ZnO-PbO is the precursor. In addition, a possible reaction mechanism for DEC synthesis was proposed.

1. Introduction

Diethyl carbonate (DEC) is not only an important organic intermediate but also an attractive alternative oxygen-containing fuel additive. The processes for the synthesis of DEC mainly include phosgenation of ethanol [1], transesterification of organic carbonates [2], oxidative carbonylation of ethanol [3,4], ethanolysis of CO_2 [5] and ethanolysis of urea [6]. Among them, the ethanolysis of urea exhibits great advantages such as available raw materials and simple product separation. In such an approach, the intermediate ethyl carbamate (EC) is first produced from urea and ethanol and then further converted to DEC by consecutive reaction with ethanol. The reaction of EC with ethanol to DEC is the rate-control step. Several kinds of catalysts such as organometallic compounds, metal salts and metal oxides have been tested toward the reaction of urea and alcohols [7–9]. Among them, metal oxide catalysts have drawn much more attention because they can overcome the drawbacks in the separation of product and the recovery of the homogeneous catalysts [10,11].

In our previous work, lead oxide was found to be the most active catalyst for the reaction of EC and ethanol to DEC among a series of single metal oxides but DEC yield was still unsatisfactory [12]. Furthermore, it was found that the addition of a little lead oxide into some metal oxides could promote their catalytic performance. Therefore, in the present work, a series of double metal oxides containing lead oxide were prepared and the activity evaluation results revealed that ZnO-PbO presented the highest catalytic activity. The effect of preparation conditions and DEC synthesis reaction parameters on the catalytic performance of ZnO-PbO was studied, and the catalysis and reusability of ZnO-PbO were discussed, and a possible reaction mechanism for DEC synthesis was proposed.

2. Experimental

2.1. Preparation of double metal oxides

All of double metal oxide catalyst samples were prepared by calcinating their corresponding metal compounds. The preparation process was as follows: the metal compounds were mixed and ground first and then calcined at a certain temperature for a period of time in air. For example, for the preparation of ZnO-PbO with PbO weight percentage of 10%, $Zn_2(OH)_2CO_3$ (41.3 g) and $PbCO_3$ (4.0 g) were mixed and then ground in a mortar by hand for about 3 min and finally calcined at 500 °C for 4 h in air.

2.2. DEC synthesis reaction

DEC synthesis reaction was carried out in a 500 mL stainless steel autoclave with a packed column and a back-pressure valve for ammonia gas removal. In a typical process, 30.5 g EC, 158 g ethanol and 1.9 g catalyst were introduced into the autoclave first, and then the mixture was rapidly heated to 180 °C under stirring and kept for 7 h. After the completion of reaction, the autoclave was cooled to room temperature and the product mixture was weighed and

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http://dx.doi.org/10.1016/j.apcata.2012.05.023

Table 1
Catalytic performance of the double metal oxides.

Catalyst	Precursor	Calcination temperature/°C	Conversion of EC (%)	Yield of DEC (%)	Selectivity of DEC (%)
MgO-PbO	$Mg(NO_3)_2·6H_2O$	500	18.8	4.7	25.0
CaO-PbO	$CaCO_3$	900	37.4	9.4	25.1
SrO-PbO	$Sr(NO_3)_2$	1100	18.9	1.6	8.5
BaO-PbO	$Ba(NO_3)_2$	700	23.1	3.7	16.0
ZnO-PbO	$Zn_2(OH)_2CO_3$	500	33.9	13.8	40.7
ZrO_2-PbO	$Zr(NO_3)_4·5H_2O$	500	26.5	5.4	20.4
Al_2O_3-PbO	$Al(NO_3)_3·9H_2O$	500	20.1	1.4	7.0
Fe_2O_3-PbO	$Fe (NO_3)_3·9H_2O$	500	26.1	5.8	22.2
CuO-PbO	$CuCO_3·Cu(OH)_2·2H_2O$	300	42.6	5.9	13.8
NiO-PbO	$NiCO_3·2Ni(OH)_2·4H_2O$	300	26.2	4.5	17.2
TiO_2-PbO	$TiO(OH)_2$	500	14.0	0.28	2.0
La_2O_3 -PbO	$La(NO_3)_3·6H_2O$	800	20.8	5.0	24.0
None			1.7	0.5	29.4

The weight percentage of lead oxide in double metal oxides was 10% and the calcination time was 4 h.
Catalytic activity evaluation conditions: catalyst weight percentage 1%, molar ratio of ethanol: EC = 10:1, 180 °C, and 7 h.

filtrated. The filtrate was analyzed by a SP 2100 gas chromatograph with a FID and a PEG-20 M capillary column using cyclohexanol as the internal standard. The yield and selectivity of DEC were calculated based on EC:

$$\text{DEC yield}(\%) = \frac{\text{moles of DEC formed}}{\text{moles of EC charged}} \times 100$$

$$\text{DEC selectivity}\,(\%) = \frac{\text{moles of DEC formed}}{\text{moles of EC converted}} \times 100$$

2.3. Catalyst characterization

XRD analysis of the catalyst was performed on a D/MAX-2500 diffractometer with Cu Kα radiation operated at 40 kV and 100 mA. IR spectroscopic spectrum of the catalyst was recorded on a Bruker Vector 22 FT-IR spectrophotometer in the 4000–400 cm^{-1} range. TG of the precursors ($Zn_2(OH)_2CO_3$ and $PbCO_3$) was carried out on a SDT Q600 simultaneous DSC-TGA instrument at a heating rate of 10 °C/min under a flow of air. Element analysis of the recovered catalyst was determined by a Flash EA1112 elemental analyzer.

3. Results and discussion

3.1. Screening for catalysts

As shown in Table 1, ZnO-PbO exhibits the highest activity among the prepared double metal oxide catalysts and the yield and selectivity of DEC are 13.8% and 40.7%, respectively. So it is necessary to study the effect of preparation conditions and DEC synthesis reaction parameters on the catalytic performance of ZnO-PbO catalyst.

3.2. Effect of preparation conditions

Reaction conditions for evaluating the catalytic performance of ZnO-PbO sample were as follows: molar ratio of ethanol/EC of 10:1, catalyst weight percentage of 1%, 180 °C, and 7 h.

3.2.1. Effect of precursor

The catalytic performance of ZnO-PbO samples prepared from different precursor is listed in Table 2. As a result, ZnO-PbO sample prepared with $Zn_2(OH)_2CO_3$ and $PbCO_3$ as the precursors shows the highest activity; the yield and selectivity of DEC are 13.8% and 40.7%, respectively. Hence, $Zn_2(OH)_2CO_3$ and $PbCO_3$ are selected as the precursors of ZnO-PbO catalyst.

3.2.2. Effect of calcination temperature

The effect of calcination temperature on the catalytic performance of ZnO-PbO is illustrated in Table 3. It can be seen that DEC selectivity reaches the maximum 40.7% at the calcination temperature of 500 °C (DEC yield 13.8%) while DEC yield attains the maximum 13.9% at the calcination temperature of 300 °C (DEC selectivity 38.2%). From the viewpoint of full use of reactants, the suitable calcination temperature is determined as 500 °C.

ZnO-PbO samples calcined between 300 °C and 600 °C were analyzed by XRD and the result is shown in Fig. 1. The diffraction peaks of ZnO in different samples can be indexed to hexagonal structured ZnO but lead oxides with different valence states and crystal forms can be observed at different calcination temperature. Tetragonal PbO is obtained from the samples prepared at 300 °C and 400 °C

Table 2
Catalytic performance of ZnO-PbO prepared from different precursor.

Precursor of zinc oxide	Precursor of lead oxide	Calcination temperature/°C	Conversion of EC (%)	Yield of DEC (%)	Selectivity of DEC (%)
$Zn_2(OH)_2CO_3$	$PbCO_3$	500	33.9	13.8	40.7
$Zn_2(OH)_2CO_3$	$Pb(NO_3)_2$	500	21.6	9.5	44.0
$Zn_2(OH)_2CO_3$	$Pb(CH_3COO)_2$	500	27.1	9.7	35.8
$Zn(NO_3)_2$	$PbCO_3$	400	19.8	7.1	35.9
$Zn(NO_3)_2$	$Pb(NO_3)_2$	400	19.4	4.6	23.7
$Zn(NO_3)_2$	$Pb(CH_3COO)_2$	400	17.8	6.9	38.8
$Zn(CH_3CO_2)_2$	$PbCO_3$	400	29.7	11.0	37.0
$Zn(CH_3CO_2)_2$	$Pb(NO_3)_2$	400	23.4	7.0	29.9
$Zn(CH_3CO_2)_2$	$Pb(CH_3COO)_2$	400	24.9	6.8	27.3
$Zn(OH)_2$	$PbCO_3$	500	27.8	10.9	39.2
$Zn(OH)_2$	$Pb(NO_3)_2$	500	19.6	5.6	28.6
$Zn(OH)_2$	$Pb(CH_3COO)_2$	500	26.3	9.8	37.3

The weight percentage of lead oxide in double metal oxides was 10% and the calcination time was 4 h.
Catalytic activity evaluation conditions: catalyst weight percentage 1%, molar ratio of ethanol: EC = 10:1, 180 °C, and 7 h.