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

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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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