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Enhanced yields of diethyl carbonate via one-pot synthesis from ethanol, carbon dioxide and butylene oxide over cerium (IV) oxide

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ABSTRACT

There is a considerable industrial interest towards short-chain dialkylcarbonate production technologies due to their attractive properties and apparent commercial applications. Over the years, dimethyl carbonate (DMC), in contrast to diethyl carbonate (DEC), was mainly explored in seeking novel synthesis ideas in academic investigations. Therefore, this work has been devoted to the synthesis of diethyl carbonate. The preliminary results showed that the formation of DEC via direct route starting from ethanol and carbon dioxide (CO_2) is limited by the reaction equilibrium and therefore thermodynamics of the reaction has been estimated. Consecutively, butylene oxide was introduced to the reaction system as a dehydrating agent in order to overcome thermodynamic constrains and shift the equilibrium towards diethyl carbonate production. The underlying reason for choosing a longer chain epoxide (i.e. butyl instead of e.g. propyl) was the acute toxicity of short-chain epoxides. A 9-fold enhancement in DEC yield compared to the method without any water removal was achieved over cerium (IV) oxide (CeO_2) in the presence of butylene oxide at 180 °C and 9 MPa of total final pressure unequivocally indicating that butylene oxide is an efficient chemical water trap. The highest obtained yield of diethyl carbonate was 2.5 mmol, corresponding to ethanol conversion of 15.6% and selectivity to DEC 10% on ethanol basis. Moreover, kinetic studies were conducted facilitating understanding of the reaction pathway and influence of various parameters on the reaction.

1. Introduction

Diethyl carbonate, the second homologue in the dialkylcarbonate family, is one of the most important green chemicals among carbonate esters. It is a colorless, transparent liquid under the normal conditions and has a mild toxicology profile [1]. Due to the presence of two ethyl groups in its structure, as well as one carbonyl group, it is considered as a promising alternative to both ethyl halides and phosgene for ethylation and carbonylation processes. When released into the environment DEC slowly biodegrades to carbon dioxide and ethanol [2,3], a fact rendering it a significant advantage over other fuel oxygenates such as methyl *tert*-butyl ether (MTBE). Because of its high oxygen content (40.6 wt%) compared to MTBE (18.2 wt%) DEC has been proposed as a replacement for MTBE as an attractive oxygen-containing fuel additive [4]. Furthermore, DEC finds applications as a raw material for manufacturing of polycarbonates, as an excellent solvent and an intermediate for various pharmaceuticals such as antibiotics and phenobarbital [5,6].

Several conventional methodologies exist for diethyl carbonate synthesis, such as phosgenation of ethanol, which is the oldest DEC production method developed in 1941 [7], oxidative carbonylation of ethanol [8,2], carbonylation of ethyl nitrite [9,10,3] and reaction of ethanol with urea [11]. However, each of the aforementioned processes raise problems, such as toxicity of phosgene, corrosion and low production rates. Thus, the novel technology for DEC synthesis via a direct route (Eq. (1)), starting from cheap, easy to handle and non-toxic carbon dioxide and ethanol has recently attracted great interest – also due to the carbon dioxide utilization aspect, that is considered as one of the most prominent greenhouse gases responsible for global warming. Moreover, direct synthesis of diethyl carbonate allows CO_2 to be viewed as a valuable renewable feedstock.

$$2C_2H_5OH + CO_2 \rightleftharpoons (C_2H_5O)_2CO + H_2O \qquad (1)$$

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Nevertheless, direct synthesis of DEC from ethanol and CO_2 has not been under intensive study so far and only few reports exist about this topic [12–15]. Although the selectivity of DEC over CeO_2–ZrO_2 with varied Ce/Zr ratios was very high (ca. 100%) in all cases under the reported reaction conditions, the amount of DEC produced remained very low (ca. 0.4 mmol) due to the hydrolysis of DEC caused by co-produced water (Eq. (1)). Therefore, it is of the great interest to develop novel, safe and environmentally acceptable catalytic systems coupled to efficient water removal in order to improve the productivity of diethyl carbonate via the direct route.

In this work, first an effort has been directed to the straightforward synthesis of DEC from ethanol and CO_2 over cerium (IV) oxide. However, the results showed that the reaction is limited by the reaction equilibrium and therefore the thermodynamics of the reaction was evaluated. Subsequently butylene oxide(1,2-epoxybutane) was introduced to the reaction system as a dehydrating agent aiming for enhanced yields of DEC by disrupting the thermodynamic limitations and thereby shifting the equilibrium towards carbonate production. Undoubtedly, the advantage of this method is the use of butylene oxide as a chemical water trap, which is found to be less hazardous or detrimental to human health and exhibits a higher reactivity towards alcohols and CO_2, compared to e.g. ethylene or propylene oxide [16]. Moreover, the kinetic tests of DEC synthesis from ethanol, CO_2 and butylene oxide were carried out for the first time in order to reveal the reaction network and to determine the maximum yield of DEC.

2. Experimental

2.1. Catalyst

Cerium (IV) oxide (<25 μm particle size) was purchased from Sigma–Aldrich. Prior to the experiment the catalyst was calcined for 3 h at 600 °C in the air. The specific surface area of the catalyst was determined by measuring the nitrogen adsorption–desorption isotherms (Sorptomatic 1900, Carlo Erba) in liquid nitrogen. Before each measurement, the samples were outgassed for 3 h at 150 °C to a residual pressure below 0.01 Pa. The total surface area was calculated according to the B.E.T. equation. The structural properties of CeO_2 were investigated by X-ray diffraction (XRD) (Philips, X'Pert Pro MPD) using CuKα (40 kV, 50 mA) radiation with 2θ ranging from 23° to 83° at a scanning speed 0.04°/3 s.

2.2. Catalytic test

All experiments were carried out in a laboratory scale stainless steel autoclave (Parr Inc.) with an inner volume of 300 ml equipped with a stirrer and an electric heater. In a standard procedure 1 g of catalyst, 314 mmol (18.3 ml) of ethanol (Etax, Aa, 99.5%) and 19 mmol (1.6 ml) of dehydrating agent 1,2-epoxybutane (Fluka, ≥99.0%) were charged into the autoclave and the reactor was purged and pressurized to 4.5 MPa with CO_2 (AGA 99.99%) at room temperature. The reactor was heated and mechanically stirred constantly at the desired temperature during the reaction. The stirring rate was ca.700 rpm suppressing external diffusion. The reaction was carried in the kinetic regime [17] as internal mass transfer was eliminated because of the catalyst particle size <25 μm. After the reaction, the reactor was cooled to about 5 °C and depressurized. During the kinetics studies, the autoclave setup was modified by addition of a sampling line made of stainless steel equipped with a system of valves at the inlet and outlet. The sample (ca. 100 μl) trapped in the sampling line was cooled and collected slowly in a glass tube. An important issue in the performed kinetic experiments was the total CO_2 pressure drop observed during the sampling which in turn had an impact on the final yield of diethyl carbonate (Fig. 1).

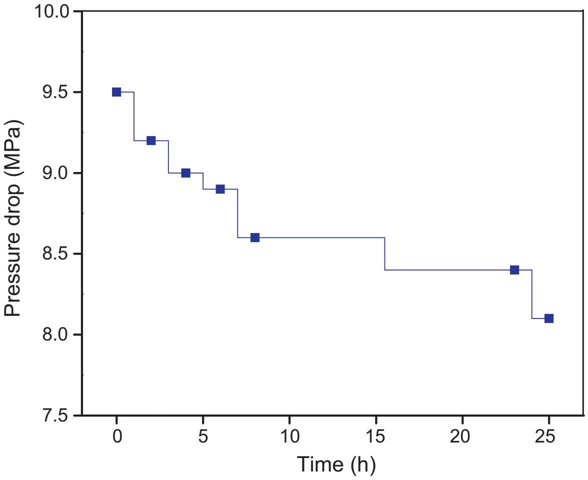

Fig. 1. The total pressure as a function of time during kinetic experiments.

The products in the liquid phase were analyzed by gas chromatography (Agilent Technologies, 6890N) using a capillary columns (HP-Wax 30 m × 250 μm × 0.25 μm and DB-Petro 100 m × 250 μm × 0.5 μm) and the products in the gas phase using a capillary column (HP-Plot Q + HP-Molsiv 5A 60 m × 530 μm × 33 μm) equipped with a FID detector. Reliability of the results has been confirmed by analyzing each sample twice. The peaks in the chromatogram were identified with the following reference substances: diethyl carbonate (Sigma, 99%), ethanol (Etax, Aa, 99.5%), 1,2-epoxybutane (Fluka, ≥99.0%), 1,2-butanediol (Fluka, 98%), diethyl ether (Merck, 99.5%) and a gas mixture (AGA containing ethane 1%, propene 0.983%, butene-1 0.961%, butane – ISO 0.977%, helium 96.1%). The products were also identified by means of GC–MS (Agilent Technologies, 6890N) using capillary column (DB-Petro 50 m × 200 μm × 0.5 μm).

3. Results and discussion

3.1. Catalyst characterization

Cerium (IV) oxide, due to its unique properties such as its ability to reversibly store oxygen is a readily accessible redox couple. Also, due to its acido-basic characteristics, it has been shown to be a very potent catalyst, catalyst support or promoter in various reactions of industrial importance [18,19]. Fig. 2 presents the XRD patterns of non-calcined CeO_2, calcined at 600 °C and 800 °C.

The main CeO_2 peaks are shown at 2θ of about 28.6° and 33.1° which is an evidence of a typical cubic fluorite structure of CeO_2 [20]. In agreement with the literature [21,22], eight peaks were identified as a characteristic peaks for cerium oxide ([1 1 1], [2 0 0], [2 2 0], [3 1 1], [2 2 2], [4 0 0], [3 3 1], [4 2 0]). The fluorite structure of cerium oxide was not affected by the calcination temperature. However, the degree of crystallinity increased with the calcination temperature, simultaneously with a decrease in the specific surface area (Table 1). The XRD patterns became sharper for the samples calcined at higher temperature, indicating that the crystal growth of CeO_2 proceeded more significantly at higher calcination temperatures.