



Original article

Enhancements of dimethyl carbonate synthesis from methanol and carbon dioxide: The *in situ* hydrolysis of 2-cyanopyridine and crystal face effect of ceria



Sheng-Ping Wang*, Jing-Jie Zhou, Shu-Yang Zhao, Yu-Jun Zhao, Xin-Bin Ma

Key Laboratory for Green Chemical Technology, School of Chemical Engineering and Technology, Collaborative Innovation Center of Chemical Science and Engineering, Tianjin University, Tianjin 300072, China

ARTICLE INFO

Article history:

Received 2 April 2015

Received in revised form 14 April 2015

Accepted 27 April 2015

Available online 15 May 2015

Keywords:

Dimethyl carbonate

CeO₂

Hydrolysis

2-Cyanopyridine

Crystal face

ABSTRACT

This paper describes the effect of the *in situ* hydrolysis of 2-cyanopyridine and its derivatives on the synthesis of dimethyl carbonate (DMC) from CO₂ and methanol over CeO₂. 2-Cyanopyridine, with the highest electronic charge number of the carbon in the cyanogroup, is the most effective agent to accelerate the desired reaction by a decrease of water. CeO₂ (1 1 0) planes are active for the hydrolysis of 2-cyanopyridine, further enhancing the DMC formation by *in situ* removal of water effectively. The DMC yield is improved drastically up to 378.5 mmol g cat⁻¹ from 12.8 mmol g cat⁻¹ with the *in situ* hydrolysis of 2-cyanopyridine over rod-CeO₂ (1 1 0) catalyst.

© 2015 Chinese Chemical Society and Institute of Materia Medica, Chinese Academy of Medical Sciences. Published by Elsevier B.V. All rights reserved.

1. Introduction

Dimethyl carbonate (DMC) has attracted much attention in the chemical field as an environmentally benign and biodegradable chemical in recent years [1–4]. The applications of DMC have covered a variety of fields [5,6]. As reported previously, several reaction routes have been presented for DMC formation [7,8]. The direct synthesis of DMC from methanol and CO₂ is highly favorable since such a method is environmentally benign by nature [9]. A great many catalysts have been employed in the direct synthesis of carbonic ester over recent decades, such as Cu based catalysts [10,11], cerium-based catalysts [12–14], and zirconia-based catalysts [1,15]. Among them, nanoceria has shown the favorable catalytic performance for the reaction of methanol and CO₂ [16].

However, the DMC yield is far from satisfactory because of the thermodynamic limitation of the direct synthesis of DMC reaction. *In situ* removal of water coproduced in the reaction system is an important strategy to effectively improve the yield of DMC. Several dehydration agents have been applied to remove H₂O from the reaction system [17]. It is convenient to add physical drying agents to decrease H₂O because there is no other product coproduced in

the reaction system, but it is extremely difficult for physical drying agents to absorb water from the mixture of methanol and CO₂ at high temperature [18]. Therefore, a variety of chemical dehydrated reagents, such as butylene oxide [19], CH₃I [20] and acetonitrile [21], have been exploited for *in situ* removal of water, which has the advantage of working even far above 100 °C. Compared with other dehydration agents, 2-cyanopyridine is easy to hydrolyze and regenerate by dehydration very conveniently, especially, the hydrolysis of 2-cyanopyridine which also can be catalyzed by CeO₂ [22]. This is more favorable for a co-existed reaction system using the same catalyst for DMC formation. Therefore, the DMC yield improved effectively using 2-cyanopyridine as the dehydrated agent over CeO₂ catalyst [23,24]. CeO₂ possesses three crystal faces (1 1 0), (1 1 1), and (1 0 0). The theoretical simulations have indicated that the different crystal faces exhibit different properties, further influencing the catalytic activity [25]. Our preliminary studies have shown that rod-CeO₂ with the most (1 1 0) crystal face showed more favorable catalytic performance than cube-CeO₂ (1 0 0) and octahedron-CeO₂ (1 1 1) for the direct synthesis of DMC [26]. It is therefore necessary to study the effect of the crystal face of CeO₂ on the hydrolysis of 2-cyanopyridine, and its further influence on DMC formation.

On the other hand, the hydrolysis performance of the derivatives of 2-cyanopyridine is likely to be different because the derivatives of 2-cyanopyridine with a similar structure possess

* Corresponding author.

E-mail address: spwang@tju.edu.cn (S.-P. Wang).

Table 1

The yield of DMC with different dehydration agents.

Dehydration agent	2-Cyano pyridine	2-Cyano furan	2-Cyano-5-fluorpyridine	5-Chloro-2-cyanopyridine	5-Bromo-2-cyanopyridine
DMC/mmol g cat ⁻¹	350.7	231.9	333.8	163.2	59.4

Reaction conditions: Amorphous CeO₂ catalyst $m_{\text{cat}} = 0.1$ g, $V_{\text{methanol}} = 15$ mL, $P_{\text{CO}_2} = 5$ MPa, $t = 3$ h, $n_{\text{dehydration}} = 50$ mmol, $T = 140$ °C.

a different electron charge of the carbon in the cyanogroup. Thus, it is essential to evaluate the influence of the derivatives of 2-cyanopyridine with the different substituents on DMC formation. This paper reports the effective synthesis of DMC from methanol and CO₂ with the co-existed hydrolysis reaction of 2-cyanopyridine and its derivatives over CeO₂ catalysts. The electronic charge number of the carbon in the cyano group of the 2-cyanopyridine and its derivatives with different substitute atoms and heterocyclic ring atoms were evaluated through DFT calculations. The influence of morphologies of CeO₂ with different crystal faces (1 1 0), (1 0 0) and (1 1 1) on the hydrolysis of the 2-cyanopyridine was carried out to determine the active crystal face for the hydrolysis reaction and co-existed formation of DMC.

2. Experimental

2.1. Catalyst preparation

Amorphous CeO₂ was prepared by calcinating the Ce(NO₃)₃·6H₂O at 600 °C for 3 h. This kind of catalyst was used to optimize the dehydration agents.

CeO₂ catalysts with the different morphologies were prepared by the hydrothermal method. For the octahedron-CeO₂, 4 mmol Ce(NO₃)₃·6H₂O and 0.04 mmol Na₃PO₄·12H₂O were dissolved in distilled water, respectively with 80 mL of distilled water. After being stirred at room temperature for 1 h, the solution was put into the 100 mL Teflon-lined stainless autoclave. Subsequently, the autoclave was transferred to the drying oven and heated for 12 h at 160 °C. The precipitates were obtained by filtration, washed with ethanol and deionized water several times, and then dried at 80 °C for 12 h and calcined at 600 °C for 5 h to get octahedron CeO₂.

A hydrothermal process was adopted to obtain rod-CeO₂ and cube-CeO₂. 480 mmol NaOH and 4 mmol Ce(NO₃)₃·6H₂O were dissolved in 10 and 70 mL of deionized water, respectively. After being stirred at room temperature for 30 min, the purple slurry was transferred into a 100 mL Teflon-lined stainless autoclave and heated at 90 °C (170 °C) for 24 h to obtain rod-CeO₂ (cube-CeO₂). After the hydrothermal treatment, the precipitates were separated by filtration, washed with deionized water and ethanol several times. After drying at 80 °C for 24 h, the products were calcined at 600 °C for 5 h.

2.2. Catalyst characterization

The morphology micrographs of the CeO₂ samples were taken by both a JEM-2100F transmission electron microscope (TEM) and a high resolution transmission electron microscopy (HRTEM) by using an accelerating voltage of 200 kV. The CeO₂ samples were characterized by a scan electron microscope (SEM) conducted under high vacuum on a Hitachi S-4800.

2.3. The synthesis of DMC from CH₃OH and CO₂ with 2-cyanopyridine and its derivatives

The reaction was carried out in a stainless steel autoclave reactor with an inner volume of 100 mL. In a typical procedure, 15 mL CH₃OH, 50 mmol 2-cyanopyridine or its derivatives and 0.1 g catalyst were transferred into the autoclave before the reactor

was purged with CO₂. After that, the autoclave was pressured with CO₂ to 5 MPa and heated to 140 °C for 3 h with mechanical stirring.

2.4. The DFT calculation of the 2-cyanopyridine and its derivatives

The stable structure of the 2-cyanopyridine and its derivatives was optimized by the DFT/B3LYP/DNP. All the atoms in the stable structure were further conducted by a population analysis.

2.5. The hydrolysis of 2-cyanopyridine over CeO₂ with a different morphology

In a typical procedure for the hydrolysis of 2-cyanopyridine to 2-picolinamide, 0.1 g 2-cyanopyridine, 3 g H₂O, and 0.03 g CeO₂ with different morphologies were added into the autoclave. The resulting mixture was vigorously stirred at 140 °C. After the reaction, the mixture was extracted with CHCl₃ three times.

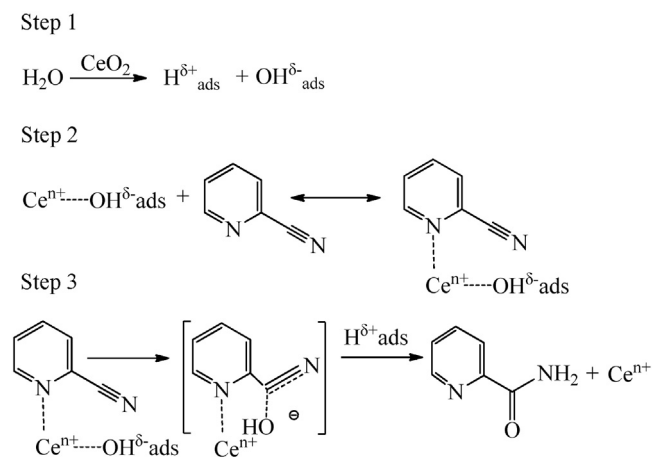
3. Results and discussion

In the absence of 2-cyanopyridine, the yield of DMC is only 8.6 mmol g cat⁻¹ in the direct synthesis reaction from methanol and CO₂ over amorphous CeO₂ catalyst. It is noticeable that the maximal production of the DMC reached 350.7 mmol g cat⁻¹ with the addition of 50 mmol 2-cyanopyridine. It is a much higher yield than that obtained in the presence of 2,2-dimethoxypropane by using CeO₂-ZrO₂ as a catalyst, which reported that the DMC yield increased from 1.6 mmol g cat⁻¹ to 14.0 mmol g cat⁻¹ [27]. Therefore, it is quite effective for the promotion of DMC formation by using the *in situ* hydrolysis of 2-cyanopyridine over a CeO₂ catalyst.

3.1. Effect of a different dehydration agent

Table 1 illustrates the dependence of DMC formation in the direct synthesis reaction of DMC over amorphous CeO₂ with different dehydration agent. As Table 1 shows, the highest yield of DMC, 350.7 mmol g cat⁻¹, was obtained with the addition of 2-cyanopyridine.

According to the reaction path reported previously (shown in Fig. 1) [22], the nitrile hydration by CeO₂ starts with the

**Fig. 1.** The mechanism of 2-cyanopyridine hydrolysis [22].

Download English Version:

<https://daneshyari.com/en/article/1254673>

Download Persian Version:

<https://daneshyari.com/article/1254673>

[Daneshyari.com](https://daneshyari.com)