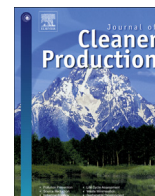




Contents lists available at ScienceDirect

## Journal of Cleaner Production

journal homepage: [www.elsevier.com/locate/jclepro](http://www.elsevier.com/locate/jclepro)

## CeO<sub>2</sub>-based catalysts made by template-precipitation for the DMC synthesis from CO<sub>2</sub> and methanol

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## ARTICLE INFO

## Article history:

Received 18 April 2014

Received in revised form

5 September 2014

Accepted 6 September 2014

Available online xxx

## Keywords:

Carbon dioxide

Dimethyl carbonate

Methanol

Ceria catalysts

## ABSTRACT

This paper mainly describes a novel synthesis of three different ceria catalysts CeO<sub>2</sub>, CeO<sub>2</sub>-SiO<sub>2</sub> and CeO<sub>2</sub>-4A via template-precipitation method. The prepared catalysts were fully characterized by means of temperature-programmed desorption (TPD), X-ray powder diffraction (XRD), BET surface area test, SEM and FTIR. The catalytic performance over these ceria catalysts were examined for the dimethyl carbonate (DMC) synthesis from CO<sub>2</sub> and methanol. The results indicate that CeO<sub>2</sub>-4A exhibits the highest DMC yield, followed by CeO<sub>2</sub>-SiO<sub>2</sub> and CeO<sub>2</sub> catalysts. Under the reaction conditions at 0.6 MPa and 120 °C with space velocity of 300 h<sup>-1</sup>, the highest methanol conversion is 3.97% with DMC selectivity of 81.4%.

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### 1. Introduction

The primary aspect of cleaner production is the reduction of CO<sub>2</sub> massive emission (Rietbergen and Blok, 2013). At present, principal pathways of CO<sub>2</sub> emission reduction are mainly divided into three aspects in industry (Ozalp et al., 2010; Pinto and Soares, 2013). Firstly, industrial structure is adjusted in order to expand enterprises of low emission and low energy consumption. Secondly, industrial energy efficiency should be increased and new clean energy be explored. Thirdly, industrial emissions of CO<sub>2</sub> are separated, sequestered and used via new technologies. The main technology of CO<sub>2</sub> emission reduction is CO<sub>2</sub> capture & separation technology that consists of dissolution method, adsorption method, oxygen-enriched combustion method and membrane separation method. In addition, CO<sub>2</sub> capture & storage (CCS) technology is used to store condensed CO<sub>2</sub> in the depth of the strata. From the perspective of sustainable development, relying solely on carbon emission reduction is bound to affect the normal development of

the social economy. Consequently, how to efficiently use CO<sub>2</sub> has become increasingly worldwide attention (Zhao et al., 2009; Wu et al., 2012). Transformation of CO<sub>2</sub> into useful and value-added chemicals is an important milestone in scientific research due to CO<sub>2</sub> being the most abundant, nontoxic, environmentally and inexpensive acceptable starting material. Direct synthesis of dimethyl carbonate (DMC) from methanol and carbon dioxide is a typical approach of CO<sub>2</sub> resource utilization, which has extremely high atom utilization and non-toxic by-product of water.

Dimethyl carbonate (DMC) is one of the essential chemicals in the chemical, polymer industry and pharmaceutical. Especially in the use of polymer synthesis, fuel additives and solvents, etc., the research and development of DMC is drawing great attention (Wang et al., 2011; Delledonne et al., 2001). DMC is an environmentally benign intermediate that can replace harmful chemicals such as phosgene and dimethyl sulfate for versatile chemical applications (Tundo and Selva, 2002; Sakakura and Kohno, 2009). Moreover, DMC has been widely used as an electrolyte in lithium batteries and an octane booster for gasoline since it has high oxygen content (Pacheco and Marshall, 1997) and high dielectric constant (Wei et al., 2003). The traditional synthesis route of DMC requires highly toxic phosgene as a reagent (Babad and Zeiler, 1973). A palladium catalyst with methyl nitrate promoter (Matsuzaki and Nakamura, 1997) and oxidative carbonylation of

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CH<sub>3</sub>OH with O<sub>2</sub> and CO using a cuprous chloride catalyst (King, 1997) has also been attempted. DMC is mainly synthesized by two-step transesterification from carbon dioxide, methanol and epoxide (Shaikh and Sivaram, 1996; Cui et al., 2004). However, this method needs high energy, large production costs and investment due to the requirement of the intermediate separation. Totally, these processes involve so many disadvantages from an environmental point of view.

Recently, direct synthesis of DMC from methanol and carbon dioxide has attracted more and more attention as an environmentally benign chemical process (Tomishige et al., 2000; Sjølie, 2012; Zhang et al., 2013; Cao and Li, 2014; Fang and Fujimoto, 1996). According to the mechanism for the direct synthesis of DMC from carbon dioxide and methanol, carbon dioxide adsorbs on the base sites of the catalyst and methanol is activated to methyl species and methoxy species on the acid and base sites of the catalyst. Thereafter, methoxy carbonate anion is formed by the reaction of methoxy species with carbon dioxide. Finally, methoxy carbonate anion further reacts with methyl species on the acid sites of the catalyst to produce DMC. Because of the thermodynamic equilibrium limitation, DMC yield in the direct synthesis reaction still remains very low. It has been reported that this problem can be solved by shifting the equilibrium through adding effective dehydrating agents and pressurizing carbon dioxide agents (Keller et al., 2010).

Various catalysts have been investigated for the conversion of CO<sub>2</sub> and methanol into DMC. Most of the catalysts can be divided into two categories, that is metallic oxide catalysts and copper based catalysts. The typical catalysts and their catalytic properties are summarized in Table 1. For comparison purpose, the data reported in literature are converted into maximum DMC yield. For the metallic oxide catalysts, the maximum DMC yield ranges from 0.42% to 1.79%. While the maximum DMC yield of copper based catalysts ranges from 3.45% to 7.62%. Compared to metallic oxide catalysts, copper based catalysts have a better catalytic activity. However, Cu based catalysts need to be reduced by dangerous hydrogen and the reduced (activated) catalyst is poisoned and loses its catalytic activity in a short period of time. What's more, copper based catalysts are easily to be oxidized by O<sub>2</sub> in air. Therefore, they are very difficult to be stored. Conversely, metallic oxide catalysts are easily to be stored because the real active components of the catalysts are stable metallic oxide rather than zero valent metal.

In this paper, we report the synthesis of three different CeO<sub>2</sub>-based catalysts by a simple method of template-precipitation. These catalysts were applied to synthesize the DMC synthesis from CO<sub>2</sub> and methanol. Among these catalysts, CeO<sub>2</sub>-4A was found to show the highest catalytic activity with methanol conversion of 3.97% and DMC selectivity of 81.4%. We have also investigated the

relationship between the surface acid-base properties of the catalysts and their catalytic performance.

## 2. Experimental

### 2.1. Materials

Cerium(III) chloride heptahydrate CeCl<sub>3</sub>·7H<sub>2</sub>O(99.9%, AR), sodium dodecyl sulfate CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>OSO<sub>3</sub>Na(92%, USP), sodium hydroxide NaOH(97%, GR), SiO<sub>2</sub>(99.8%, AR, HL-380), and 4A molecular sieve Na<sub>12</sub>[(AlO<sub>2</sub>)<sub>12</sub>(SiO<sub>2</sub>)<sub>12</sub>] (2 mm–3 mm) were all purchased from Aladdin Co., Ltd(Shanghai China). Methanol (99.5%, AR) was obtained from Guangdong Guanghua Sci-Tech Co., Ltd (Guangzhou, China).

### 2.2. Catalysts preparation

Cerium (III) chloride heptahydrate CeCl<sub>3</sub>·7H<sub>2</sub>O and sodium dodecyl sulfate CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>OSO<sub>3</sub>Na were dissolved in distilled water. Then, the solution was stirred at room temperature for 30 min. This solution was labeled as solution I. To this solution SiO<sub>2</sub> (HL-380) was charged to get solution II. 4A molecular sieve was ground to fine power and put into solution I labeled as solution III. NaOH was dissolved in deionized water and then dropped into solution I, II and III separately to get solution I', II' and III'. Thereafter, solution I', II' and III' were stirred 6 h and aged for 8 h at 90 °C. The precipitates of three solutions were collected by washing with distilled water several times and filtration, then dried at 100 °C for 12 h and calcined at 500 °C for 6 h to get CeO<sub>2</sub>, CeO<sub>2</sub>-SiO<sub>2</sub>(CeO<sub>2</sub> wt% = 20%) and CeO<sub>2</sub>-4A(CeO<sub>2</sub> wt% = 30%). CeCl<sub>3</sub>·7H<sub>2</sub>O:SDS (sodium dodecyl sulfate): NaOH: SiO<sub>2</sub>: 4A: H<sub>2</sub>O = 1: 2.7: 4.3: 11.5: 0.2355: 1100 (molar ratio).

### 2.3. Catalyst characterization

#### 2.3.1. Powder X-ray diffraction (XRD)

The X-ray powder diffraction was acquired on Rigaku Dmax 2200 diffractometer with graphite monochromatized Cu Kα radiation (λ = 0.154178 nm) at 40 kV and 30 mA. The sample was scanned from 10° to 80° at a rate of 4°/min. The crystallite sizes of the particles were calculated from the XRD peaks using the Scherrer equation.

#### 2.3.2. Temperature programmed desorption (TPD)

Temperature programmed desorption (TPD) was measured on Quantachrom Chem-BET 3000 apparatus to determine the surface acid-base properties of catalysts. Before adsorption experiments, 100 mg of the samples were pretreated at 200 °C in a quartz U-tube in an nitrogen flow with a flow rate of 100 mL per minute for 1 h to remove absorbed water. Upon cooling to room temperature, the samples were saturated with 10%CO<sub>2</sub>/90%N<sub>2</sub>, 10%NH<sub>3</sub>/90%N<sub>2</sub> or CH<sub>3</sub>OH gas/N<sub>2</sub>(Nitrogen flows into methanol solution and then mixed gas is obtained) for 30 min. Then the physical adsorbed CO<sub>2</sub>, NH<sub>3</sub> or CH<sub>3</sub>OH were removed by streaming with 30%N<sub>2</sub>/70% He for 2 h under a flow rate of 60 mL/min. The samples were then heated up to 600 °C at a heating rate of 8 °C/min in N<sub>2</sub>/He under a flow rate of 50 mL/min.

#### 2.3.3. Specific surface area measurement

Sample was measured by Quantachrom CHEM-BET 3000. 50 mg of the sample was pretreated at 200 °C in a quartz U-tube in a nitrogen flow with a flow rate of 100 mL per minute for 1hr. When cooling to 25 °C, sample in U-tube was in 70%He/N<sub>2</sub> under a flow rate of 110 mL/min. Then, the sample adsorbed in liquid nitrogen and desorbed in room temperature water.

**Table 1**

Various catalysts for the direct synthesis of DMC from methanol and CO<sub>2</sub> reported in literature.

Entry	Catalysts	Max DMC yield/%	Literature
1	Metallic oxide catalysts	H <sub>3</sub> PO <sub>4</sub> /ZrO <sub>2</sub>	0.42 Ikeda et al., 2000
2		Al <sub>2</sub> O <sub>3</sub> /CeO <sub>2</sub>	0.45 Aresta et al., 2008
3		5Ga <sub>2</sub> O <sub>3</sub> /Ce <sub>0.6</sub> Zr <sub>0.4</sub> O <sub>2</sub>	0.47 Lee et al., 2011
4		CeO <sub>2</sub>	0.73 Yoshida et al., 2006
5		CeO <sub>2</sub> -ZrO <sub>2</sub>	0.76 Tomishige and Kunimori, 2002
6	ZrO <sub>2</sub>		Tomishige et al., 1999
7		H <sub>3</sub> PO <sub>4</sub> /V <sub>2</sub> O <sub>5</sub>	1.79 Wu et al., 2005
8		Cu (Ni, V, O)	3.45 Wang et al., 2007
9	Cu based catalysts	Cu-Fe/SiO <sub>2</sub>	4.61 Zhou et al., 2012
10		Cu-Ni/GNS	7.62 Bian et al., 2011

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