



Research paper

Transformation of CO₂ and glycerol to glycerol carbonate over CeO₂–ZrO₂ solid solution — effect of Zr dopingJiaxiong Liu^a, Yajin Li^a, Huimin Liu^{a,b,**}, Dehua He^{a,*}^a Innovative Catalysis Program, Key Lab of Organic Optoelectronics & Molecular Engineering of Ministry of Education, Department of Chemistry, Tsinghua University, Beijing, 100084, China^b Department of Chemical and Biomolecular Engineering, The University of Sydney, NSW 2006, Australia

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ABSTRACT

Ce_{1-x}Zr_xO₂ (0 ≤ x ≤ 0.2) solid solutions were prepared by hydrothermal method and applied for the synthesis of glycerol carbonate from glycerol and CO₂ in the presence of 2-cyanopyridine (dehydrant) with dimethyl formamide (DMF) as a solvent. The physicochemical properties of the catalysts were characterized by ICP, XRD, BET, H₂-TPR, CO₂/NH₃-TPD, TEM and XPS. The activation route of CO₂ and glycerol were measured by DRIFTS and FT-IR. Compared to pure CeO₂, Ce_{1-x}Zr_xO₂ solid solutions exhibited enhanced activity in the present reaction system, and the improved catalytic activity was associated with the BET surface area and the acid-base properties. DRIFTS results showed that the chelating bidentate carbonate species was the main adsorption pattern for CeO₂ and no striking differences between Ce_{0.98}Zr_{0.02}O₂ and CeO₂. FT-IR spectra of the spent catalysts revealed that glycerol and 2-cyanopyridine could be activated on CeO₂-based catalysts, and an ester intermediate was formed for the production of glycerol carbonate. Thus, a plausible mechanism is proposed for the synthesis of glycerol carbonate from glycerol and CO₂ in the presence of 2-cyanopyridine in DMF solvent over CeO₂-based catalysts. Moreover, the recyclability of Ce_{0.98}Zr_{0.02}O₂ was measured and the catalysts could be regenerated through a simple calcination process at 400 °C for 5 h in air.

1. Introduction

Biodiesel, the mixture of fatty acid methyl esters from the transesterification of vegetable oils with methanol, has gained much industrial attention recently as a renewable environment-friendly energy. However, massive glycerol, produced as a by-product in the biodiesel manufacturing, becomes a serious problem with its increasing stock and dropping price [1]. Consequently, new applications for the surplus glycerol urgently need to be developed. For this purpose, numerous pathways for the conversion of glycerol, including selective hydrolysis, selective oxidation, selective etherification, aqueous-phase reforming and synthesis of glycerol carbonate, have been investigated [2]. Glycerol carbonate, a nonflammable, water-soluble, nontoxic and readily biodegradable green chemical with the potential of various chemical transformations, which has been used in a number of fields such as solvent, personal care and polymer materials [3] is considered as an attractive derivative of glycerol and synthetic procedures from glycerol to glycerol carbonate have been widely studied.

At present, the main methods from glycerol to glycerol carbonate

include indirect catalytic transesterification with carbonate sources such as alkylene carbonate, dialkyl carbonate or urea and direct carbonylation with phosgene, carbon monoxide or carbon dioxide [4]. Various catalysts, such as basic metal oxide catalysts (CaO [5], MgO [6]), Mg–Al hydrotalcite based catalysts [6] and ionic liquids [7] have been proved to be highly effective in the transesterification with dimethyl carbonate or ethylene carbonate. However, the transesterification process showed relatively lower economic advantage and usually required either addition of solvents or uneasily recoverable homogeneous catalysts. Besides, although metal oxide catalysts (MgO, ZnO) [6], gold-supported zeolite ZSM-5 [8] and samarium-exchanged heteropoly tungstate [9] exhibited good catalytic activity for the synthesis of glycerol carbonate from glycerol and urea, the by-product ammonia and the complicated purification process had negative ecological and economical impacts on this method. In addition, phosgene and carbon monoxide routes were obsolete for the toxicity and unsafety of the reagents. Compared with the synthesis methods mentioned above, direct carbonylation of glycerol with CO₂ is an attractive route because on one hand, both glycerol and CO₂ are commercially available at low prices,

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and on the other hand, the atom efficiency of this reaction is 87% [3].

So far, many attempts for synthesizing glycerol carbonate from glycerol and CO₂ have been carried out. Vieville et al. [10] investigated the catalytic performance of zeolites and basic ion-exchange resins in the carbonylation of glycerol with supercritical CO₂, and the yield of glycerol carbonate reached 32%. However, no evidence could prove the direct insertion of CO₂ since glycerol carbonate was formed only when 63% mol fraction of ethylene carbonate was introduced and the formation of glycerol carbonate might be the result of a transesterification process. Direct reactions of glycerol with subcritical CO₂ were conducted by Aresta et al. using ¹¹⁹SnO and ¹¹⁹Sn(OMe)₂ [11], or CeO₂/Al₂O₃ and CeO₂/Nb₂O₅ [12] as catalysts, but the conversion of glycerol came to only 2.5% and 2.3% (453 K, 5 MPa, 6 h), respectively. Such low conversion of glycerol was mostly due to the severe thermodynamic limitation of this reaction for which the reaction equilibrium constant *K* is only 1.506×10^{-3} at the condition of 453 K and 5 MPa [13]. So dehydrant or couplant was necessary to shift the chemical equilibrium. Recently, acetonitrile was employed as a coupling agent for this purpose. Li et al. investigated the transformation of glycerol and CO₂ into glycerol carbonate over La₂O₂CO₃–ZnO catalysts [14] and Zn/Al/La/M (M = Li, Mg, Zr) hydrotalcite-like catalysts [15] in the presence of acetonitrile and achieved enhanced results. The peak conversions of glycerol were 30.3% and 35.7%, and the yields of glycerol carbonate were 14.3% and 15.1% (170 °C, 4.0 MPa, 12 h), respectively. Synergism between ZnO and La₂O₂CO₃, and large specific surface area as well as high density of moderately basic sites of the modified Zn/Al/La catalysts were reported to be responsible for the good catalytic activity of these two types of catalysts. Cu-based catalysts [16,17] were also studied for the synthesis of glycerol carbonate using acetonitrile as the solvent and dehydrant. The conversion of glycerol could reach 33.4% over 2.3%Cu/La₂O₃ catalyst at 150 °C and 7.0 MPa. Cu sizes and basic sites of the catalysts showed significant effect on the conversion and selectivity in the reaction. Even though acetonitrile could break the thermodynamic limit of the carbonylation of glycerol with CO₂, the selectivity of glycerol carbonate was commonly lower than 50% owing to the production of monoacetin and diacetin, which were the by-products produced via the hydrolysis product (acetic acid) reacting with glycerol. Recently, we took an attempt to produce glycerol carbonate over CeO₂ catalysts in the presence of 2-cyanopyridine [18]. The results showed that 2-cyanopyridine was an excellent dehydration agent, and the selectivity of glycerol could be higher than 95%. The high catalytic activity of CeO₂ could be somewhat related to the redox and/or acid-base properties of CeO₂.

It was reported that compared to CeO₂, Ce_xZr_{1-x}O₂ solid solution showed improved catalytic performances resulted from the higher concentration of acid-base sites, oxygen storage capacity, good redox property, and greater thermal stability [19–24]. Especially the acid-base properties, which consist of the coordinatively unsaturated metal cations M⁴⁺ (Lewis acid sites as electron acceptor), oxide anion O²⁻ (Lewis base sites as electron donor) and hydroxyl groups (Brønsted base centers) played an important role in the formation of carbonate species [25]. Honda et al. [26] proposed the reaction mechanism for the direct synthesis of propylene carbonate from 1,2-propanediol and CO₂ over CeO₂, which started with the activation of 1,2-propanediol through the adsorption of one OH group to Lewis acid sites of CeO₂ to form cerium alkoxide adspecies. In addition, the amount of the oxygen defect sites and the Lewis base sites were proved to have a good correlation with the activity of CeO₂ in the hydration of 2-cyanopyridine [27].

In this work, we described the enhanced catalytic performance of Zr doped CeO₂ for the synthesis of glycerol carbonate in the presence of 2-cyanopyridine. Efforts have been made to investigate the influence of molar ratio of Ce:Zr on the crystallite structure, redox property, surface composition, acid-base property, as well as the relation of the physico-chemical properties with the catalytic performance.

2. Experimental

2.1. Materials

Cerium nitrate (Ce(NO₃)₃·6H₂O, AR), zirconium nitrate (Zr(NO₃)₄·5H₂O, AR), sodium hydroxide (NaOH, AR) and *N,N*-dimethylformamide (DMF, 99.5%) were obtained from Sinopharm chemical reagent company. Glycerol (HPLC) was purchased from Alfa Aesar Company. 2-cyanopyridine was supplied by J&K Scientific. Diethylene glycol monomethyl ether (DEGME, 99%) was purchased from Aladdin. CO₂ and Ar with a high purity of 99.999% were purchased from Beijing htjkgas Chemical Company. All the reagents were used as received.

2.2. Catalyst preparation

Ce–Zr mixed oxides with different Ce:Zr atomic ratios were prepared by hydrothermal method. Typically, a salt solution (20 mL, 0.3 mol/L) of Ce(NO₃)₃·6H₂O and Zr(NO₃)₄·5H₂O was added dropwise into 40 mL of 1 mol/L NaOH solution with vigorous stirring in a Teflon bottle, and the mixture was kept stirred for 20 min. Subsequently, the suspension was hydrothermally treated in a Teflon stainless steel autoclave at 120 °C for 24 h. The obtained precipitate was thoroughly washed with deionized water, dried at 60 °C in air for 24 h, and calcined at 400 °C for 5 h. The catalysts were denoted as Ce_{1-x}Zr_xO₂, where *x* represents the molar fraction of Zr (0, 0.01, 0.02, 0.05, 0.1 and 0.2).

2.3. Catalyst characterization

The surface areas and pore volumes of the catalysts were determined by low-temperature nitrogen adsorption-desorption using a Micromeritics TriStar II 3020 M instrument. The specific surface areas were calculated with the Brunauer-Emmett-Teller (BET) equation, and pore volumes with pore size distributions were received from the desorption branch of the isotherm by the Barrett-Joyner-Halenda (BJH) method. Prior to the measurements, Samples were degassed at 200 °C for 1 h under vacuum.

The X-ray diffraction (XRD) measurements were carried out on a Rigaku D/Max-2500 diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$, 40 kV, 200 mA) and a nickel filter within the range of 20–90°. The mean crystallite size (*d*) was calculated based on the (111) plane of CeO₂ with the Scherrer equation $d = K\lambda/\beta\cos\theta$, where λ is the wavelength of X-ray, *K* is Scherrer constant taken as 0.89, β is determined as the width of the peak at half maximum height, and θ is the diffraction angle. The peak position and lattice parameter were determined by fitting profiles with the Marquardt-Levenberg algorithm.

The Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) was conducted on a VARIN VISTA-MPX instrument to determine the actual elemental composition of the samples. Samples were dissolved by aqua regia and hydrofluoric acid before measurement.

The X-ray photoelectron spectroscopy (XPS) was performed on a PHI Quantera Scanning X-ray Microprobe of ULVAC-PHI Inc with monochromatic Al K α radiation. The binding energy was referenced with respect to the carbonaceous C1s line at 284.8 eV.

The images of transmission electron microscopy (TEM) were recorded on a Hitachi HT-7700 microscope operating at 100 kV. Previous to the measurement, the samples were ultrasonically dispersed in 30 mL ethanol for 30 min, and subsequently, one drop of the suspension was dried on a copper grid in room temperature.

The Fourier Transform Infrared (FTIR) spectra were recorded on a Bruker VERTEX70 instrument over the wave number range from 600 cm⁻¹–4000 cm⁻¹ with a resolution of 4 cm⁻¹. The Diffuse Reflection Infrared Fourier Transform Spectroscopy (DRIFTS) experiments were also conducted on the Bruker VERTEX70 instrument equipped with a heat chamber and a DiffusIR™ diffuse reflectance accessory from PIKE TECHNOLOGIES to explore the adsorption of CO₂.

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