



Transformation of CO₂ with glycerol to glycerol carbonate by a novel ZnWO₄-ZnO catalyst

Jiaxiong Liu, Dehua He*

Innovative Catalysis Program, Key Lab of Organic Optoelectronics & Molecular Engineering of Ministry of Education, Department of Chemistry, Tsinghua University, Beijing 100084, China



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ABSTRACT

ZnWO₄-ZnO catalysts with different W content were prepared by conventional hydrothermal and wet impregnation methods and applied in the direct synthesis of glycerol carbonate from CO₂ and glycerol. The crystallite structure, texture property, morphology, redox and acid-base properties and the surface chemical situation of the catalysts were characterized by XRD, BET, TEM, H₂-TPR, NH₃/CO₂-TPD and XPS. The possible activation routes of CO₂ and glycerol were analyzed with DRIFTS and FTIR. ZnWO₄-ZnO composite catalysts showed better catalytic performances with respect to ZnO in the carbonylation of glycerol with CO₂. The improved activity of ZnWO₄-ZnO catalysts was associated with the formation of ZnWO₄, the interaction between ZnWO₄ and ZnO, and the enhanced moderate acidic property. DRIFTS results showed that chelating bidentate carbonate species was the main adsorption pattern for CO₂ on ZnO, while the introduction of W led to the bridged bidentate carbonate, which became the main adsorption pattern on ZnWO₄-ZnO. As for the activation of glycerol, zinc glycerolate played an important role in the reaction process. Based on the reaction and characterization results, a plausible reaction route involved a seven-membered ring esters intermediate was suggested for the reaction of CO₂ and glycerol over ZnWO₄-ZnO catalysts.

1. Introduction

Carbon dioxide, as a major component of greenhouse gas which contributing to the global warming and climate change, is also an abundant, nonflammable, nontoxic and renewable C1 resource for the production of value-added organic compounds, such as alcohols, esters, amides, carboxylic acids, aldehydes, carbonates and carbamates [1]. Nevertheless, it is a great challenge to convert CO₂ into fine chemicals due to its inert nature and low reactivity [2]. As a matter of fact, harsh reaction conditions such as high reaction temperature or high CO₂ pressure as well as stoichiometric amount of catalysts were often required for the efficient chemical fixation of CO₂ [3]. Therefore, the development of newly efficient catalytic systems for the transformation of CO₂ is of great interest to researchers from academia and industry.

Five-membered cyclic carbonates are momentous heterocyclic compounds which could be applied as precursors of polycarbonates and polyurethanes, aprotic polar solvents, electrolytes and material for producing drugs [4]. Among these cyclic carbonate, glycerol carbonate is particularly attractive for the consumption of glycerol, the surplus byproduct of biodiesel manufacturing, in the synthesis of glycerol carbonate. The carbonyl sources for the production of glycerol carbonate

from glycerol include linear carbonate such as alkylene carbonate, dialkyl carbonate or urea, phosgene, carbon monoxide and carbon dioxide [5]. Synthesizing glycerol carbonate by coupling CO₂ and glycerol is a green and economical process conforming to the sustainable development strategy because the atom economy of this reaction is 87% and the only side product is H₂O [6]. However, this synthetic route is severely limited by the thermodynamics [7], thus the yield of glycerol carbonate is usually not high.

Homogeneous [8,9] and heterogeneous catalysts [10–14] were both applied in the direct carbonylation of glycerol with CO₂ to glycerol carbonate. Since the homogeneous catalysts were suffered from recovery difficulties, heterogeneous catalysts, especially metallic oxides, were investigated for their potential catalytic activity in the transformation of CO₂ with glycerol due to the surface adsorption and activation of CO₂ [4,10]. Ozorio et al. [11] prepared metal-impregnated zeolite Y catalysts which were evaluated in the transformation of CO₂ with glycerol at 180 °C and 100 Bar for 3 h. The parent NaY zeolite showed no activity in the reaction, while the calcined Ag(Zn or Sn)-Y zeolites, as well as the calcined metal salt precursor, were able to promote the production of glycerol carbonate. The yields of glycerol carbonate were 5.6%, 5.8% and 5.1% over AgY, ZnY and SnY zeolites,

* Corresponding author.

E-mail address: hedehe@mails.tsinghua.edu.cn (D. He).

respectively, which were higher than those over calcined AgNO₃(3.5%), Zn(NO₃)₂(2.7%) and SnCl₂(2.6%). The reason for the better activity of the metal-impregnated zeolites was associated with the highly dispersed metal oxide phase on the external surface of zeolites. Zn/Al/La/M (M = Li, Mg, Zr, F, Cl, Br) mixed oxides [12,13], La₂O₃ impregnated with Cu [14] and CeO₂ nanomaterials [10] were also evaluated for the transformation of CO₂ and glycerol with acetonitrile or 2-cyanopyridine as dehydrating agent, and yielded 15.1%, 15.2% or 78.9% glycerol carbonate for Zn/Al/La/Li, 2.3%Cu/La₂O₃ or CeO₂ nanorods, respectively, on different reaction conditions. The basic sites amount of the catalysts showed significant effect on the production of glycerol carbonate. The use of dehydrants could shift the chemical equilibrium to glycerol carbonate side. However, the introduction of other reactants led to undesired byproducts and complicated constituent system which suffered from complex and expensive purification process.

Recently, monocomponent metal oxides (ZnO, SnO₂, Fe₂O₃, CeO₂, La₂O₃) were employed for accelerating the reaction rate for the direct carbonylation of glycerol with CO₂ without addition of any dehydrating agents [4]. Among them, ZnO showed good activity on the condition of 180 °C, 150 Bar and 12 h. Since metal oxides are able to activate glycerol and CO₂ [4,11,12], the potential of searching for more active mono or mixed oxides is very promising.

In the present work, a series of mono- and bi-component oxides were investigated as the catalyst for the formation of glycerol carbonate from glycerol and CO₂ without the presence of dehydrant. The yields of glycerol carbonate on ZnO, WO₃, CeO₂, TiO₂, La₂O₃, Mo₂O₃, ZrO₂, ZnWO₄, CeO₂-ZrO₂, ZnWO₄-ZnO, V-Zn-O, Sn-Zn-O, CuO/WO₃, CuO/ZnO and CeO₂-TiO₂ were in the range of 0%~6.5%, as shown in Table S1. With comparison to others, ZnWO₄-ZnO exhibited the better catalytic performance towards the reaction of glycerol with CO₂. Thus, we chose W-Zn composites for further investigation. ZnWO₄-ZnO samples with different W content were prepared by hydrothermal and wet impregnation methods, and tested in the direct carbonylation of glycerol with CO₂ without any addition of dehydrating agent. The effect of the loading amounts of tungsten component on the structure, texture property and acid-base properties of the catalysts were investigated. The interface interaction between tungsten and zinc oxide as well as the structure-activity relationship were also discussed. The results showed that the catalytic activity were highly associated with the physicochemical properties of ZnWO₄-ZnO.

2. Experimental

2.1. Materials

Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, AR), sodium carbonate (Na₂CO₃, AR), ammonium metatungstate ((NH₄)₆H₂W₁₂O₄₀, 99.5%) and diethylene glycol monomethyl ether (DEGME, 99%) were obtained from Aladdin. Glycerol (HPLC) was supplied by Alfa Aesar Company. *N,N*-dimethylformamide (DMF, 99.5%) was purchased from Sinopharm chemical reagent company. CO₂ with a high purity of 99.999% was purchased from Beijing HTJK gas Chemical Company. All the reagents were used as received.

2.2. Catalyst preparation

ZnO was prepared by hydrothermal method. A typical procedure was as follows. That is, 3.26 g Zn(NO₃)₂·6H₂O was dissolved in 40 mL deionized water at room temperature, then the salt solution was added dropwise into 20 mL Na₂CO₃ solution (3 mol/L) in a Teflon bottle under vigorous stirring, and the formed suspension was kept stirred for 20 min. Subsequently, the mixture was hydrothermally treated at 120 °C for 24 h. After cooling down to room temperature, the obtained precipitate was washed thoroughly with deionized water for 4 times, then dried at 110 °C in an oven overnight. After calcinations at 400 °C for 3 h, ZnO powder was obtained.

ZnWO₄-ZnO catalysts were prepared by wet impregnation method. In a typical procedure, a certain amount of ammonium metatungstate (The exact employed amounts were shown in Table S2) was dissolved in 30 mL deionized water at room temperature. Then, 2 g of ZnO powder was added into the above solution with stirring for 12 h. After the impregnation process, a vacuum rotary evaporation was carried out at 60 °C to remove the excess water. The solid samples were dried at 110 °C for 12 h and calcined at 400 °C for 3 h in air. The obtained ZnWO₄-ZnO catalysts were labeled as xW-Zn, where x represented the mass percentage of loading amount of WO₃ in ZnWO₄-ZnO (x = 1%, 2%, 5%, 10%, 15%, 20%, 50%). For comparison, WO₃ was prepared by calcinations of ammonium metatungstate at 400 °C for 3 h in air. Partial xW-Zn precursors were calcined at different temperatures from 300 °C to 800 °C, and the obtained catalysts were denoted as xW-Zn-T, where T represented the calcinations temperature (T = 300, 400, 500, 600, 700, 800).

2.3. Catalyst characterization

The crystallite structures of xW-Zn samples were characterized by powder X-ray diffraction (XRD) 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 with a scan rate of 10°/min.

Surface areas and pore volumes were measured by low-temperature nitrogen physisorption on a Micromeritics TriStar II 3020 M instrument. The specific surface area was calculated by Brunauer-Emmett-Teller (BET) equation using the adsorption branch, and the pressure range and *c* constant used for the calculations are listed in the Table S3. The pore size distribution was calculated by Barrett-Joyner-Halenda equation using the desorption branch of the isotherm.

The morphology and crystallite size of the catalysts were measured by transmission electron microscopy (TEM) on a Hitachi HT-7700 microscope operating at 100 kV. Prior to the measurement, the samples were dispersed in ethanol ultrasonically, and then one drop of the suspension was dried on a copper grid naturally.

The X-ray photoelectron spectroscopy (XPS) measurement was conducted on a PHI Quantera Scanning X-ray Microprobe of ULVAC-PHI Inc with monochromatic Al K α radiation.

All Fourier Transform Infrared (FTIR) spectra were recorded on a Bruker VERTEX70 instrument with a resolution of 4 cm⁻¹. The adsorption of carbon dioxide on the catalyst samples was also recorded on the Bruker VERTEX70 instrument equipped with a DiffusIR™ diffuse reflectance accessory as well as a heat chamber.

H₂ temperature-programmed reduction (H₂-TPR) was performed on a CHEMBET 3000 TPR/TPD of Quantachrome Instrument. Typically, 0.1 g catalyst samples were placed into a U-shape quartz reactor and pretreated at 400 °C in Ar for 30 min to remove the surface contaminants. After cooling down, the TPR process was carried out from 50 °C to 930 °C with a gas of 5.01% H₂/Ar (40 mL/min), and the spectra of H₂ consumption was monitored by a TCD detector.

Surface basic and acidic properties of W-Zn catalysts were probed by temperature-programmed desorption of CO₂ (CO₂-TPD) and NH₃ (NH₃-TPD), respectively, on a Cat-Lab instrument (BEL-A, Japan) equipped with a GAM 200 mass spectrometer of Inprocess Instruments. A typical procedure included sample pretreatment at 400 °C in Ar, adsorption of 20.1% CO₂/Ar (40 mL/min) or 2.00% NH₃/Ar at 100 °C (40 mL/min), desorption and detection from 100 °C to 800 °C, and quantification of the desorbed gases.

2.4. Catalytic reaction

The direct carbonylation of glycerol with CO₂ over xW-Zn catalysts was carried out in a 100 mL stainless-steel autoclave. A typical procedure was as follows: 0.92 g glycerol, 0.5 g catalyst and 20 mL DMF (solvent) were added into the autoclave. Then the sealed reactor was initially cooled in an ice-water bath, and the air inside was replaced

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