



Greener synthesis of propylene carbonate using graphene-inorganic nanocomposite catalysts



Adegboyega Isaac Adeleye^a, Suela Kellici^a, Tobias Heil^b, David Morgan^c, Martin Vickers^d, Basudeb Saha^{a,*}

^a Centre for Green Process Engineering, School of Engineering, London South Bank University, 103 Borough Road, London SE1 0AA, UK

^b Nanoinvestigation Centre at Liverpool, 1–3 Brownlow Street, Liverpool L69 3GL, UK

^c Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Park Place, Cardiff CF10 3AT, UK

^d Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK

ARTICLE INFO

Article history:

Received 25 September 2014

Received in revised form 3 December 2014

Accepted 4 December 2014

Available online 25 January 2015

Keywords:

Carbon dioxide (CO₂)

Continuous hydrothermal flow synthesis (CHFS) reactor

Heterogeneous catalyst

Graphene oxide (GO)

Ceria, lanthana and zirconia graphene oxide nanocomposite (Ce–La–Zr–GO) catalysts

ABSTRACT

Continuous hydrothermal flow synthesis (CHFS) has been employed as rapid and cleaner route for the synthesis of a novel, highly efficient graphene-inorganic heterogeneous catalyst, denoted as Ce–La–Zr–GO nanocomposite. The catalyst was used for the direct synthesis of propylene carbonate (PC) from the cycloaddition of carbon dioxide (CO₂) and propylene oxide (PO) in the absence of any organic solvents. Ce–Zr–La–GO nanocomposite was synthesized from pre-mixed aqueous solution of cerium, lanthanum, zirconium nitrate and GO (synthesized via conventional Hummers method) under alkaline conditions using the CHFS reactor. The resulting nanocomposite catalyst was heat-treated at various temperatures (773, 973 and 1173 K) and their catalytic properties were assessed. The as-prepared and the corresponding heat-treated catalysts were characterized using transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), X-ray powder diffraction (XRD) and Brunauer–Emmett–Teller (BET) surface area measurements. Effect of various parameters such as heat-treatment temperature, catalyst loading, CO₂ pressure, reaction time and temperature was systematically studied to determine the optimum reaction conditions. The optimum reaction condition for the direct synthesis of PC was found at 443 K, 70 bar and 10% (w/w) catalyst loading. Catalyst reusability study was also conducted to investigate the long life stability for the synthesis of PC and it was found that the catalyst could be reused several times without losing its catalytic activity. These studies revealed that Ce–Zr–La–GO nanocomposite catalyst showed high catalytic activity as compared to other reported heterogeneous catalysts with the conversion of PO, selectivity and yield of PC.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Carbon dioxide, a renewable carbon source has attracted tremendous interest in academia and industry due to its easy

availability, non-flammability, non-toxicity, recyclability and being chemically inert. However, carbon dioxide is a primary greenhouse gas and therefore is considered as the main factor for current environmental issues such as global warming and climate change [1]. Therefore, one of the many attempts aiming to reduce atmospheric concentrations of carbon dioxide is the utilization of CO₂ for the synthesis of valuable products such as cyclic carbonates and polycarbonates including propylene carbonate (PC). Propylene carbonate is a versatile organic carbonate with high commercial value used in several industrial applications e.g. for production of disinfectants, herbicides and pesticides [2], a chemical intermediate used for the production of polycarbonate [3], polyurethanes [4] and dimethyl carbonates [5], a solvents for cleaning and production of lithium rechargeable batteries [6], paint, personal care and personal cosmetics products [7,8]. To date, several routes to organic carbonate synthesis including oxidative carboxylation of alkenes [9], phosgene and oxetanes, oxidative carbonylation of alcohol

Abbreviations: AP, as prepared Ce–La–Zr–GO catalyst; BET, Brunauer–Emmett–Teller; Ce–La–Zr–GO, ceria, lanthana and zirconia graphene oxide; Ce–La–Zr–O, ceria and lanthana doped zirconia catalyst; Ce–Zr–O, ceria doped zirconia; Ce–Zr–O, ceria and zirconia graphene oxide; CO₂, carbon dioxide; DMC, dimethyl carbonate; ECTM-5, Econo-CapTM-5; FID, flame ionization detector; GC, gas chromatograph; GO, graphene oxide; HT-500, Ce–La–Zr–GO catalyst heat-treated at 773 K; HT-700, Ce–La–Zr–GO catalyst heat-treated at 973 K; HT-900, Ce–La–Zr–GO catalyst heat-treated at 1173 K; M–O, metal oxide; PO, propylene oxide; PC, propylene carbonate; *t*, time (h); TEM, transmission electron microscope; scCO₂, supercritical CO₂; SCF, supercritical fluid; XRD, X-ray diffraction; Zr–O, zirconium oxide.

* Corresponding author. Tel.: +44 (0)20 7815 7190; fax: +44 (0)20 7815 7699.

E-mail address: b.saha@lsbu.ac.uk (B. Saha).

and phenol, and reaction of urea and alcohol/phenol [8,10] have been widely reported. These conventional synthetic approaches have major drawbacks include the use of toxic chemicals such as phosgene and isocyanides, production of large amount of waste chlorinated compounds (hydrochloric acids) and low selectivity to the organic carbonates [7]. Therefore, greener routes are highly desirable. As such, cycloaddition of CO₂ and epoxide to produce organic carbonates has attracted much interest due to the high atom efficiency and high environmental benefits of the synthetic reaction [11]. Generally, the reaction between inert CO₂ and high energy starting material epoxides is exothermic [12], and requires a suitable catalyst with high energy substrate to achieve desirable conversion and selectivity of the end product (PC). The existing conventional methods of PC synthesis use homogeneous catalysts including salt and metal halide [13], salen metal complex [14] and ionic liquid [15]. The shortcomings of the homogeneous catalytic processes include expensive method of separation of product from the reaction mixture, high cost of catalyst preparation, multi-step process, potential production of toxic species, use of co-solvent, deactivation and instability of the catalyst [12,16]. As such, solvent free heterogeneous catalytic system is considered as more efficient, economically feasible and greener synthetic route for valuable chemical synthesis. Notably, it offers many advantages over conventional routes including the use of non-hazardous catalysts with increased thermal stability, reusability, elimination of toxic by-products and easy separation of catalyst from reaction mixture [17,18]. However, the efficiency of the method is limited by the use of high amount of catalyst. As such, graphene based inorganic nanocomposite represent a new class of advanced catalysts materials with exciting novel properties [19]. Graphene is a unique 2D single layer of one atom thick sp² carbon in which the atoms have a hexagonal arrangement [20,21]. Graphene's amazing properties are revealed when layers of graphite are reduced to give a single sheet of carbon atoms which is the thinnest material ever made. It is exceptionally strong, transparent to light, yet impermeable to any gas and electronically fascinating [22,23]. However, graphene alone does not possess the properties that are required in a range of technological applications. Therefore, in order to enhance its conducting properties, it is important to blend it at the atomic level to get best performance. By simply decorating graphene with nanocomposite opens up other possibilities for new and unexpected phenomena [24,25]. However, producing sheets of high quality graphene and graphene based nanomaterials in an economical and environmentally benign way is still challenging. The current methods for homogeneously producing graphene nanomaterial composites involve lengthy and time consuming processes that often lack control of synthetic parameters leading to variation in materials properties from batch to batch. Thus, better synthetic approaches are required. In this work, we look at ways to make new advanced graphene based inorganic nanocomposite functional materials in a more unique and exotic manner by using superheated water with unusual properties [26,27]. The continuous hydrothermal flow synthesis (CHFS) route generally is utilized for syntheses of metal oxide(s) involves mixing continuous flows of supercritical water with a flow of aqueous metal salt(s) to give nanocomposite with defined composition and properties [26]. The CHFS also represents a single step synthetic approach which is highly tunable, e.g. with temperature and pressure control to give materials minimal structural and electronic defects. This not only enables control over oxidation state of graphene, but also offers an optimal route for homogeneously producing and depositing highly crystalline nanostructures into graphene oxide.

In this work, a novel approach has been employed for synthesizing advanced ceria, lanthana and zirconia graphene oxide labelled as Ce–La–Zr–GO nanocomposite catalysts using CHFS. The catalytic activities of the Ce–La–Zr–GO catalysts have been evaluated using

a new, greener and sustainable process for the direct synthesis PC in the absence of organic solvent. Effects of numerous factors such as catalyst heat-treatment, catalyst loading, CO₂ pressure, reaction temperature and reaction time have been studied systematically to optimize the reaction condition. Catalyst reusability studies have been conducted to investigate reusability and stability of the catalyst for the synthesis of PC.

2. Experimental methods

2.1. Chemicals and materials

Acetone (99%), *iso*-octane (99.8%), propylene oxide (99.5%), propylene carbonate (98%), hydrochloric acid (~37%), sulfuric acid (95+%), graphite powder, sodium nitrate (98+%), cerium (III) nitrate hexahydrate (99.5%), potassium hydroxide (86+%), hydrogen peroxide (>30%) and potassium permanganate (99%) were purchased from Fisher Scientific UK Ltd. Lanthanum (III) nitrate hexahydrate (99.99%), zirconium (IV) oxynitrate hydrate (99.99%), 2-ethyl-4-methyl-1,3-dioxolane (99%) and *n*-pentane (99.8%) were procured from Sigma–Aldrich Co. LLC, UK. The liquid CO₂ cylinder equipped with a dip tube was purchased from BOC Ltd., UK. All chemicals were used without further purification or pre-treatment. The experiments were conducted using deionized water (>10 MΩ).

2.2. Preparation of graphene oxide (GO)

The improved method by Hummer and Offeman [28] was adopted for the synthesis of graphene oxide from natural graphite powder (NGP) using potassium permanganate as oxidizing agent. In the typical reaction, 2.5 g of NGP and 2.5 g of sodium nitrate (NaNO₃) was added to 115 mL of sulphuric acid (H₂SO₄). The black slurry was stirred with a magnetic stirrer for about 15 min in an ice bath. 20 g of potassium permanganate (KMnO₄) was added slowly (for about 5 min) to the reaction mixture. The resulting dark green mixture was left for another 15 min with continuous stirring and the mixture was transferred to an oil bath at 40 °C and stirred at 600 rpm for 90 min. 200 mL of deionised water was added gradually (for about 15 min) to the mixture, followed by addition of 30 mL of hydrogen peroxide (H₂O₂) gradually for about 5 min and 200 mL of deionised water added dropwise for another 15 min. The resulting light brown mixture was stirred at 600 rpm for 15 min at 90 °C. The mixture was cooled to 15 °C and the product was separated using a centrifuge (5000 rpm, 5 min per cycle). GO was washed 4 times with dilute hydrochloric acid (HCl) (*i.e.* 10 mL of HCl in 80 mL of deionised water) and 3 times with deionised water to remove any impurities, dried for 24 h using a freeze-drier.

2.3. Preparation of Ce–La–Zr–GO nanocomposite catalysts

Continuous hydrothermal flow synthesis (CHFS) experiments were conducted using a reactor, basic design of which has been reported previously [29–31]. Briefly, the CHFS reactor consists of three high pressure pumps used for the delivery of water and aqueous solution of precursors as shown in Fig. 1. The tubing and fittings consisted of 1/8 in. 316 SS Swagelok, except the heater, counter-current reactor and the cooler, which were constructed using 1/4 in. fittings. Pump 1 (Gilson 307 fitted with 25 mL pump head) was utilized for delivering deionized water through a custom made 2.5 kW electrically powered pre-heater at a flow rate of 20 mL min⁻¹. Pumps 2 and 3 (Varian Pro Star 210 fitted with 5 mL pump head) were used for pumping pre-sonicated aqueous GO solution premixed with corresponding cerium, lanthanum and zirconium salts at the desired Ce:Zr:La atomic ratios (15:80:5) and the base solution, KOH, respectively, at a flow rate of 5 mL min⁻¹. In a typical experiment, each pre-mixed aqueous

Download English Version:

<https://daneshyari.com/en/article/53665>

Download Persian Version:

<https://daneshyari.com/article/53665>

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