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Greener synthesis of dimethyl carbonate using a novel tin-zirconia/graphene nanocomposite catalyst

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ABSTRACT

A green, rapid and continuous hydrothermal flow synthesis (CHFS) route has been employed to synthesise highly efficient and active novel heterogeneous catalysts. Tin doped zirconia (Zr–Sn–O) and tin doped zirconia/graphene nanocomposite (Zr–Sn/GO) have been assessed as suitable heterogeneous catalysts for the synthesis of dimethyl carbonate (DMC). The catalysts have been extensively characterized using powder X-ray diffraction (XRD), transmission electron microscopy (TEM), Brunauer-Emmett-Teller (BET) surface area measurement and X-ray photoelectron spectroscopy (XPS) analysis. Extensive batch studies for the synthesis of DMC *via* the transesterification of propylene carbonate (PC) and methanol (MeOH) using Zr–Sn/GO catalyst in a solvent free process were also conducted. The effect of various reaction conditions such as reactant molar ratio, catalyst loading, reaction temperature and reaction time has been extensively evaluated. Response surface methodology based on Box-Behneken Design (BBD) was employed to derive optimum conditions for maximising PC conversion and DMC yield. The correlations and interactions between various variables such as MeOH:PC ratio, catalyst loading, reaction temperature, reaction time and stirring speed were extensively studied. A quadratic model by multiple regression analysis for the PC conversion and DMC yield was developed and verified by several methods BBD revealed that optimum conditions for high yield values of DMC are 12.33:1 MeOH:PC molar ratio, 446.7 K, 4.08 h and 300 rpm using 2.9% (w/w) Zr–Sn/GO nanocomposite. The maximum predicted responses at the optimum conditions are 85.1% and 81% for PC conversion and yield of DMC respectively. Experimental results at optimum model predicted reaction conditions agree very well with the model predicted response, where 82.4% PC conversion and 78.2% yield of DMC were obtained. Catalyst reusability and stability studies have been conducted at optimum reaction condition to investigate the long term stability of Zr–Sn/GO and it has been found that the catalyst could be reused more than six times (about 42 h) without losing its catalytic activity. These experimental and model predicted values showed an excellent agreement for tin doped zirconia/graphene nanocomposite as a heterogeneous catalyst for the synthesis of DMC from PC and MeOH.

1. Introduction

Dimethyl carbonate (DMC) is a promising environmentally benign compound that has gained considerable interests due to its versatile and excellent chemical properties. DMC's low toxicity and high biodegradability makes it a green reagent and a safer alternative to poisonous phosgene. Its high oxygen content (53%) makes it an excellent oxygenate additive to gasoline to improve its performance and reducing

Abbreviations: CHFS, continuous hydrothermal flow synthesis; Zr–Sn–O, tin doped zirconium oxide; Zr–Sn/GO, tin doped zirconia/graphene nanocomposite; DMC, dimethyl carbonate; XRD, X-ray powder diffraction; TEM, transmission electron microscopy; BET, Brunauer Emmett-Teller; XPS, X-ray photoelectron spectroscopy; PC, propylene carbonate; MeOH, methanol; BBD, Box-Behneken design; CO, carbon monoxide; O_2, oxygen; CO_2, carbon dioxide; RSM, Response Surface Methodology; IPA, isopropyl alcohol; $ZrO(NO_3)_2{\cdot}6H_2O$, zirconium(IV) oxynitrate; SnC_2O_4, tin (II) oxalate; HCl, hydrochloric acid (HCl); H_2SO_4, sulfuric acid; NGP, natural graphite powder; $NaNO_3$, sodium nitrate; H_2O_2, hydrogen peroxide; KOH, potassium hydroxide pellets; $KMnO_4$, potassium permanganate; GO, graphene oxide; HPLC, high performance liquid chromatography; GC, gas chromatography; FID, flame ionisation detector; ANOVA, analysis of variance; OFAT, ,one-factor at a time analysis

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exhaust emissions [1]. DMC can be used as a good precursor material for the production of polycarbonates [2,3]. It can also be used as an intermediate in the synthesis of various pharmaceuticals and agricultural chemicals. Therefore, DMC is considered as an environmentally benign building block.

The conventional method for DMC synthesis involves the utilization of phosgene, a toxic feedstock. Thus, greener, safer and efficient processes for the synthesis of DMC are required. Recently, non-toxic synthetic routes have been explored; these include, oxidative carbonylation of carbon monoxide (CO), oxygen (O_2) and MeOH, direct synthesis from MeOH and CO_2 and the transesterification of cyclic carbonates and MeOH [4,5]. The oxidative carbonylation route suffers from the use of expensive raw materials and corrosive reagents as well as being potentially hazardous due to the explosive potential of CO. The direct production of DMC from MeOH and CO_2 offers an attractive and green synthetic route for DMC synthesis. However, this approach suffers from low DMC yields due to the equilibrium nature of the reaction and the un-reactivity of the stable CO_2 molecule. The synthesis of DMC *via* the transesterification of cyclic carbonates and MeOH has gained substantial interest recently, where cyclic carbonates can be synthesized from their corresponding epoxides and CO_2, thus making the synthesis of DMC *via* transesterification route more environmentally friendly and desirable in terms of green chemistry and sustainable development.

Much effort has been dedicated for the design of new greener catalytic processes for the synthesis of DMC. Several reports have been published describing the efficiency of various catalysts including alkali metal hydroxide [6], metal oxide [7], double metal cyanide [8], anion exchange resin [9], hydrotalcite [10,11], smectite [12], mesoporous carbon nitride [13], mesoporous ceria oxide [14], tungstate-based catalysts [15], ionic liquids [16] and gold nanoparticles [17].

Until now, ionic liquids have been reported to be the most efficient catalysts for transesterification of PC and MeOH [16,18,19]. However, the homogeneous nature of ionic liquids posed a number of drawbacks including high cost of separation of products/catalysts from the reaction mixture and challenges in terms of catalyst stability and reusability [20,21]. Therefore, the development of solvent-less heterogeneous catalytic process for the synthesis of DMC is highly desired and a key aspect for the design of greener chemical synthesis. Heterogeneous catalysts offer numerous advantages including the ease of catalyst separation from the reaction mixture, which is more economically viable due to the elimination of complex separation processes. Heterogeneous catalysts have higher stability, longer shelf life and easier and safer to handle, reuse and dispose compared to the homogenous counterpart [22]. However, advanced, low cost catalysts that perform efficiently are needed.

The (re)discovery of graphene [23,24], a single sheet of hexagonally arrayed sp^2-bonded carbon atoms, by Geim and Novoselov introduced a new era in materials science, the epoch of the 2D materials with applications in transformative technologies including catalysis [20,21,25]. Graphene success revealed that it is possible to obtain a stable, one-atom thick 2D material from layered van der Waals solids with fascinating unique physical, chemical and mechanical properties [24,26–28]. The exciting properties of graphene, such as very high surface area, chemical stability, excellent electrical and thermal conductivity, make graphene a very interesting material for a broad range of potential applications [29] including energy storage and generation (e.g. electrodes for lithium ion batteries, super capacitors, solar and fuel cells) [30–33], optical devices and high speed electronics [29,34,35], as well as CO_2 conversion technologies (e.g. catalysts and absorbers) [25] and biomedical field (sensors, antibacterial) [36,37]. However, the 2D material alone does not possess the properties that are required in a range of technological applications. Owning to the flexible yet robust 2D membranes, it is possible to design and construct novel 2D based functional materials with superior or different properties from parent 2D material. This can be efficiently achieved *via* bottom–up approaches and structural functionalization incorporating 2D materials with nanoparticles or forming nanocomposites [27,30,38,39]. However, making sheets of high quality 2D and strongly coupled homogeneous nanocomposites in an economical and environmentally benign way is still challenging. The current methods for making 2D nanomaterial composites (e.g. homogenization by mixing of inorganic nanoparticles and grinding) can be difficult in order to obtain very well dispersed nanoparticles in good electrical contact with the 2D nanosheets. Thus, the preparation of high quality graphene related materials with desirable functional properties through green synthetic routes is a highly desirable step, since the presence of defects will influence the properties and consequently its applications.

Building from our recent work [20,21,37], the approach for making 2D based nanocomposites uses a clean, rapid technology. It utilises a green, rapid and Continuous Hydrothermal Flow Synthesis (CHFS) route [40–43] for the synthesis of 2D-inorganic nanocomposites with superior properties to those currently available. This will afford advanced functional materials with minimal structural and electronic defects. CHFS reactors offer significant advantages over traditional synthetic methods such as independent control over reaction parameters (e.g. temperature and pressure) and hence particle properties. The CHFS process involves mixing a continuous stream of superheated or supercritical water with a continuous flow of aqueous metal salt(s) to give rapid precipitation and controlled growth of nanoparticles at a defined mixing region [44–46]. A key feature of this process is the way of which the properties of water (such as density, diffusivity and dielectric constant) change dramatically around the critical temperature and pressure (647 K, 22.1 MPa) leading to its use as an exotic, highly controllable reaction solvent/medium. The composition and particle properties can thus be modulated by independently controlling the process parameters such as the ratios and concentrations of any metal salt feeds, flow rates of feeds, pressure, and temperature of mixing and the presence of pH/redox modifiers or surfactants [47]. The 2D plate like structure of the materials of interest offers an attractive substrate for deposition of inorganic nanoparticles for highly dispersed composites with novel properties. Thus, by feeding water dispersions of 2D material into a CHFS process before nucleation it will be possible to fully integrate these two materials into true nanocomposites.

In recent years, Response Surface Methodology (RSM) has been employed to evaluate the relationship between multiple process variables in order to optimise a specified response (i.e. output variable) [48,49]. Applying RSM at experimental stage reduces the number of experimental trials and hence the overall cost of the experiments. RSM is a collection of mathematical and mathematical techniques based on multivariate statistics, which includes experimental design, statistical model and process optimization [50]. RSM has a track record in helping researchers in modelling and optimization of the experimental design for various applications in food industry, catalysis and chemical reaction optimisation [51]. It helps to conclude the most important factors and their direct and interacted effects on the response. A further advantage of using RSM is that it does not require theoretical knowledge or human experience and still could accurately mimic the trends using the design experimental results satisfactorily.

In this study, an innovative approach has been employed for synthesizing advanced heterogeneous catalysts such as mixed metal oxides and graphene-inorganic nanocomposite catalyst *via* utilization of a continuous hydrothermal flow synthesis (CHFS) reactor. The catalytic performance of the synthesized catalysts has been extensively studied for a greener and sustainable route for the synthesis of DMC. RSM using BBD has been conducted for process modelling and optimization, with an aim to better understand the relationships between five operating variables (MeOH:PC molar ratio, catalyst loading (w/w), reaction temperature, reaction time and stirring speed) and their impact on PC conversion and yield of DMC. Furthermore, regression analysis has been applied to establish the validated model used to derive the optimum operating conditions for DMC synthesis.