GREENER SYNTHESIS OF 1,2-BUTYLENE CARBONATE FROM CO_2 USING GRAPHENE-INORGANIC NANOCOMPOSITE CATALYSIS

Victor Onyenkeadi, Suela Kellici and Basu Saha

CORRESPONDENCE ADDRESSES: Victor Onyenkeadi, Ph.D., London Southbank University, School of Engineering, SE1 0AA, United Kingdom, e-mail: onyenkev@lsbu.ac.uk, Suela Kellici, Ph.D., Associate Professor, London Southbank University, School of Engineering, SE1 0AA, United Kingdom, e-mail: kellicis@lsbu.ac.uk, Basu Saha, Ph.D., Professor of Chemical and Process Engineering London Southbank University, School of Engineering, SE1 0AA, United Kingdom, e-mail: b.saha@lsbu.ac.uk,.

Abstract

The synthesis of 1,2 butylene carbonate (BC) from cycloaddition reaction of 1,2 butylene oxide (BO) and carbon dioxide (CO_2) was investigated using several heterogeneous catalysts in the absence of organic solvent.

Several Continuous hydrothermal flow synthesis (CHFS) has been employed as a rapid and cleaner route for the synthesis of highly efficient graphene-inorganic heterogeneous catalyst, represented as Ce–La–Zr/GO nanocomposite. The graphene-inorganic heterogeneous catalyst has been characterised using transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS), while X-ray powder diffraction (XRD) and Brunauer–Emmett–Teller (BET) methods have been used for the surface area measurements.

Ceria, lanthana, zirconia doped graphene nanocomposite catalyst studies have shown high catalytic activity as compared to other reported heterogeneous catalysts in the absence of any organic solvent with a higher selectivity of 76% and 64% yield of 1,2 butylene carbonate at the reaction conditions of 408 K, 75 bar in 20 h.

Keywords: 1,2 butylene carbonate (BC), carbon dioxide (CO_2), continuous hydrothermal flow synthesis (CHFS), ceria-lathana-zirconia and graphene oxide nanocomposite (Ce-La-Zr/GO), heterogeneous catalysis.

1 INTRODUCTION

The global emission of carbon dioxide (CO_2) into the atmosphere has reached an unsustainable level that has resulted in climate change and therefore there is the need to reduce the emission of CO_2 [1]. Recently, there has been a tremendous interest in the use of CO_2 as an environmentally benign building block in the chemical industry due to its chemical and physical properties such as chemical inert, stability, non-flammability, non-toxicity and therefore it can be considered as an attractive green replacement of toxic reactants such as isocyanates and phosgene [2, 3]. CO_2 is regarded as a stable compound due to its carbon covalently bonded to two oxygen atoms, although the thermodynamic stability of CO_2 requires a significant amount of energy to be decomposed [4]. The reactions of CO_2 with epoxides give an exothermic reaction and generate an organic carbonate such as cyclic and polycyclic carbonates [5].

Organic carbonates such as acyclic, cyclic and polycyclic carbonates are widely used chemicals in agriculture, automobile, cosmetic, lithium battery, paint and pharmaceutical industries [1, 5-8].

1,2-butylene carbonate is a valuable chemical of great commercial interest. It is an excellent reactive intermediate material used in industry for the production of plasticisers, surfactant, and polymers and can also be used as a solvent for degreasing, paint remover, wood binder resins, foundry sand binders, lubricants as well as lithium battery because of its high polarity property [5].

The use of continuous hydrothermal flow synthesis (CHFS) reactors was also considered for catalyst preparation in order to improve the catalyst stability and enhance performance.

2 EXPERIMENTAL

2.1 Materials

Natural graphite powder, hydrochloric acid, sulphuric acid, sodium nitrate, potassium hydroxide pellet, hydrogen peroxide, acetone, octane and potassium permanganate were purchased from Fisher Scientific UK Ltd. Methanol, cerium(III) nitrate hexahydrate, Lanthanum (III) nitrate hexahydrate, zirconium (IV) oxynitrate hydrate, 1,2-butylene oxide, 1,2-butylene carbonate were purchased from Sigma–Aldrich Co. LLC, UK. The catalysts used for the experiments were magnesium oxide, titanium silicate, zirconium oxide, cerium oxide, lanthana oxide, lanthana doped zirconia, lithium doped zirconia, zirconium doped hydrotalcite, ceria doped zirconia and ceria, lanthana doped zirconia. The following catalysts were supplied by MEL Chemical Company except for magnesium oxide and titanium silicate which were purchased from Sigma Aldrich. The liquid CO_2 cylinder (99.9%) equipped with a dip tube was purchased from BOC Ltd., UK. All chemicals were used without further pre-treatment or purification.

2.2 Preparation and characterisation of ceria-lanthana-zirconia/graphene inorganic nanocomposite synthesis via CHFS

CHFS experiments were conducted using a reactor, basic design that has been reported [6-10]. CHFS reactor consists of three high performance pressure pumps used for delivery aqueous solution of reagents. The catalyst was successfully prepared and characterised by (Adeleye et' al 2015). The properties of the prepared ceria-lanthana-zirconia/graphene inorganic nanocomposite catalyst via CHFS are tabulated in Table 1.

Table 1: Physical and chemical properties of graphene oxide (GO) and ceria, lanthana, zirconia/graphene(Ce-La-Zr/GO)

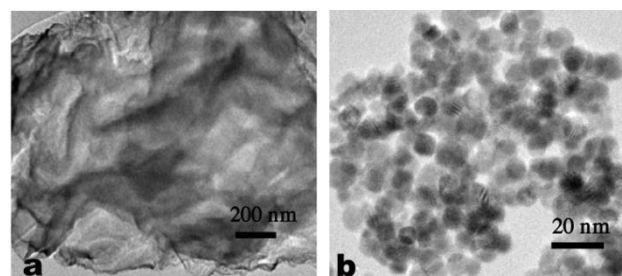| Catalyst properties	Graphene based catalyst of ceria, lanthana and zirconia	
	GO	Ce-la-zr/Go
Physical form	Black powder	Black powder
% Atomic composition(XPS)	O: 24.64	Ce: 2.98
	C:75.36	La:1.19
		O: 34.99
		C: 47.29
		K: 0.8
		Zr: 12.75
Mean particle size (nm)	-	5.78±3.9
BET surface area ($m^2 g^{-1}$)	124	115
Pore volume (cm3 g-1)	0.049	0.047
Average pore diameter (nm)	2.37	2.16

Figure 1. Transmission electron microscopy (TEM) images of graphene oxide and ce-la-zr/GO catalyst assessed for the synthesis of 1,2 butylene carbonate
Key: a (grapheme oxide) and b (ce-la-zr/GO as prepared via CHFS).

2.3 Experimental procedure for the synthesis of 1,2 butylene carbonate

The synthesis of 1,2 butylene carbonate was carried out in a 25 mL stainless steel high pressure equipped with a stirrer, thermocouple and a heating mantle and controller . The reactor was charged with a required amount of BO and catalyst. The reactor was heated to the required temperature and continuously stirred at a known stirring speed. Supercritical fluid pump was used to pump CO_2 at a desired pressure from the cylinder to the reactor and left for a specified time. After the reaction, the reactor was cooled down to room temperature using an ice bath. The reactor was depressurized and the reaction mixture was filtered. The recovered catalyst was washed with acetone and dried in an ovum while the products were analysed using a gas chromatography (GC) equipped with a flame ionization detector (FID) with a capillary column using octane as an internal standard. The effect of various parameters such as catalyst types, catalyst loading, CO_2 pressure, reaction temperature and reaction time was studied for the optimization of the reaction conditions. Catalyst reusability studies were also conducted to assess the stability of the catalyst for synthesis of BC.
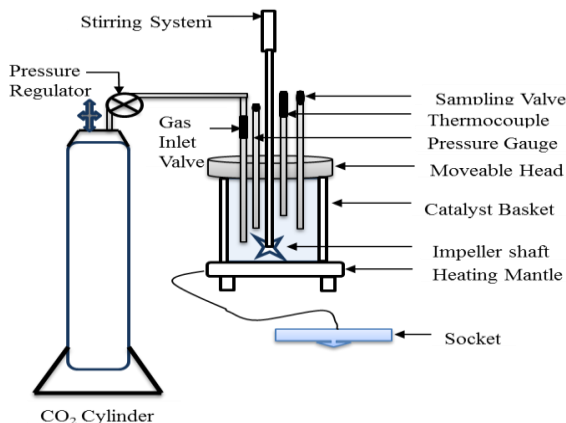
Figure 2. Schematic diagram of a high pressure reactor.

3   RESULTS AND DISCUSSION

3.1 Proposed reaction mechanism

The synthesis of 1,2 butylene carbonate through the reaction of cycloaddition of carbon dioxide to 1,2 butylene oxide in the present of ce-la-zr/GO inorganic nanocomposite catalyst can be seen in figure 3a and 3b.
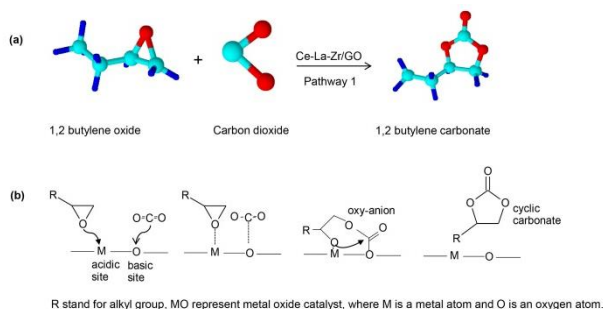

Figure 3. Reaction scheme and pathway for synthesis of 1,2 butylene carbonate.

3.2 Effect of different heterogeneous catalysts

The study of various heterogeneous catalysts such as catalytic activity, conversion, yield and selectivity were conducted in order to ascertain the best performing metal oxide or mixed metal oxide catalyst for the synthesis of 1,2 butylene carbonate through the reaction of cycloaddition of carbon dioxide to 1,2 butylene oxide using a high pressure reactor (Figure 2). Figure 4, show the results of different heterogeneous catalysts and also the corresponding improvement of Ce-La-ZrO through using graphene oxide as a base catalyst decorated with Ce-La-Zr in 1:1 ratio via CHFS route on the conversion of 1,2 butylene oxide, the yield and selectivity of 1,2 butylene carbonate using the optimum reaction

conditions. Ce-La-Zr/GO catalyst gave an improved conversion of BO (84%) and highest BC yield (64%) and selectivity (76%) at optimum reaction conditions of reaction temperature 408 K, CO_2 pressure 75 bar, reaction time 20 h, stirring speed 300 rpm and catalyst loading of 10% (w/w).
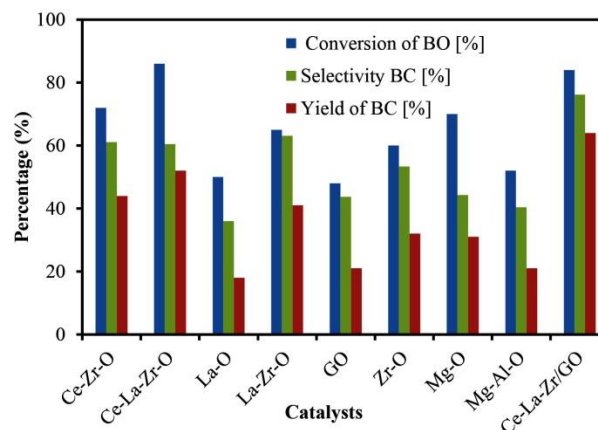

Figure 4. Effect of different heterogeneous catalysts

3.3 Effect of Reaction Temperature

The catalytic heterogeneous reaction of 1,2 butylene oxide and CO_2 were carried out at different reaction temperature from 368 K to 443 K in order to study its effect on 1,2 butylene oxide conversion, 1,2 butylene carbonate on yield and selectivity. The reaction conditions for this study were set at 10% catalyst loading, 75 bar CO_2 pressure and duration for 20 h. As it was expected, the higher the temperature, the more the conversion of 1,2 butylene oxide into carbonates isomers and oligomers. Figure 5, shows the temperature dependence on the yield and selectivity of 1,2 butylene carbonate.

It was observed from Figure 5, that there was a corresponding increase in conversion of 1,2 butylene oxide, 1,2 butylene carbonate yield and selectivity as temperature increases from 368 K to 408 K but further increase of temperature 408 K to 443 K, there was less significant drop of 1,2 butylene carbonate yield from 64% to 60% whilst its respectively 1,2 butylene oxide conversion increases from 84% to 90%.
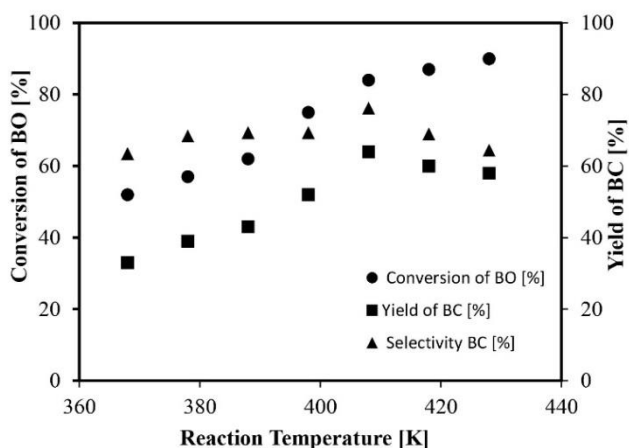
Figure 5. Effect of reaction temperature

Figure 6. Effect of CO_2 pressure

3.4 Effect of CO_2 Pressure

The application of CO_2 pressure is very significant in the synthetic of 1,2 butylene carbonate through the reaction of 1,2 butylene oxide and CO_2. The use of supercritical state of CO_2 reaction system can cause an increase in mass transfer efficiency of the reactants and lead to a shift in the reaction equilibrium to open up the thermodynamic limitation of this reaction [8, 11]. The effect of CO_2 pressure on 1,2 butylene conversion and 1,2 butylene carbonate yield were studied in order to ascertain the optimum CO_2 pressure for the reaction of cycloaddition of CO_2 to 1,2 butylene oxide. The experiments were carried out in a high pressure reactor at 408 K with CO_2 pressure ranging from 55 bar to 105 bar for 20 h and the results are shown in Figure 6. It can be seen in Figure 6, that an increase in CO_2 pressure from 55 bar to 75 bar increases the 1,2 butylene oxide conversion and the yield of 1,2 butylene carbonate but beyond 75 bar there were further increase in 1,2 butylene oxide conversion but no significant increment in the yield of 1,2 butylene carbonate rather a slight drop in the yield.

The CO_2 pressure at 75 bar, 1,2 butylene oxide conversion and 1,2 butylene carbonate yield was of 84% and 64% respectively. Beyond 75 bar, there was a slight drop in 1,2 butylene carbonate yield and that might be as a result of decomposition of 1,2 butylene carbonate to form oligomers. Therefore, it can be concluded that the optimum CO_2 pressure for this reaction is 75 bar. This study shows an improvement in polarity and solubility of 1,2 butylene oxide conversion at supercritical condition of CO_2 as the reaction pressure increases.
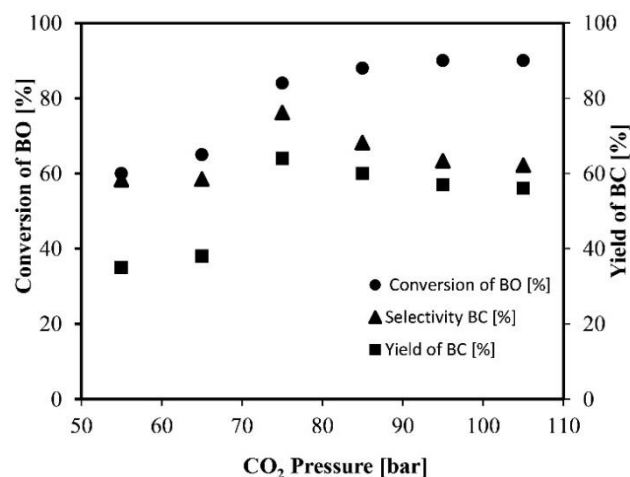
3.5 Catalyst reusability studies

The heterogeneous catalyst reusability experiments were conducted to investigate the catalytic activity of the best performed heterogeneous catalyst. Ceria, lanthana, zirconia with graphene inorganic nanocomposite reusability test was investigated in order to obtain its performance in different runs. The experiments were carried out in a high pressure reactor at optimum reaction conditions of temperature 408 K, pressure 75 bar, fresh 10%(w/w) catalyst loading of Ce-La-Zr/GO for 20 h. The catalyst was used for 6 runs and as it can be seen in Figure 7, the conversion and yield were approximately the same results. Therefore, it can be concluded that Ce-La-Zr/GO catalysts can be reused several times and still maintain its catalytic activity.
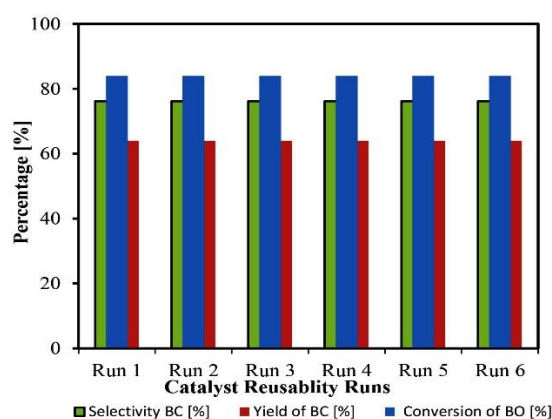

Figure 7. Catalyst reusability studies

4 CONCLUSIONS

The synthesis of 1,2 butylene carbonate (BC) through cycloaddition reaction of carbon dioxide (CO_2) and 1,2 butylene oxide (BO) was successfully carried out using a high pressure reactor in the presence of various heterogeneous

catalysts without any organic solvent. Transmission electron microscopy (TEM) and x-ray diffraction (XRD) was used to investigate catalyst characterization. The effect of various parameters such as the reaction time, reaction temperature, CO_2 pressure, catalyst loading and stirring speed were carried out. Among the used heterogeneous catalysts ceria, lanthana, zirconia/graphene inorganic nanocomposite catalyst (Ce-La-Zr/GO) was found to be the best performed catalyst and the optimum reaction condition was found at 408 K, 75 bar CO_2 pressure, 10% (w/w) catalyst loading and 20 h reaction. Ce-La-Zr/GO catalyst was easily recycled and reused several times without any reduction in its catalytic performance.

ACKNOWLEDGEMENTS

5   REFERENCES

[1] M. Aresta and A. Dibenedetto, "14 - Industrial utilization of carbon dioxide (CO_2)", vol. 2, no. 14, MAY 10, pp. 377-410.

[2] M. Aresta, A. Dibenedetto and A. Angelini, "Catalysis for the Valorization of Exhaust Carbon: from CO_2 to Chemicals, Materials, and Fuels. Technological Use of CO2," *Chem.Rev.*, vol. 114, no. 3, FEB 12, pp. 1709-1742.

[3] W. Dai, S. Luo, S. Yin and C. Au, "'The direct transformation of carbon dioxide to organic carbonates over heterogeneous catalysts," *Applied Catalysis A-General*, vol. 366, no. 1, SEP 15, pp. 2-12.

[4] W. Wang, Y. Himeda, J.T. Muckerman, G.F. Manbeck and E. Fujita, "'CO_2 Hydrogenation to Formate and Methanol as an Alternative to Photo- and Electrochemical CO_2 Reduction," *Chem.Rev.*, vol. 115, no. 23, DEC 9, pp. 12936-12973.

[5] A. Shaikh and S. Sivaram, "'Organic carbonates," *Chem.Rev.*, vol. 96, no. 3, MAY, pp. 951-976.

[6] A.I. Adeleye, D. Patel, D. Niyogi and B. Saha, "'Efficient and Greener Synthesis of Propylene Carbonate from Carbon Dioxide and Propylene Oxide," *Ind Eng Chem Res*, vol. 53, no. 49, DEC 10, pp. 18647-18657.

[7] A.I. Adeleyea, S. Kellici, T. Heil, D. Morgan, M. Vickers and B. Saha, "'Greener synthesis of propylene carbonate using graphene-inorganic nanocomposite catalysts," *Catalysis Today*, vol. 256, NOV 1, pp. 347-357.

[8] R. Saada, S. Kellici, T. Heil, D. Morgan and B. Saha, "'Greener synthesis of dimethyl carbonate using a novel ceria-zirconia oxide/graphene nanocomposite catalyst," *Applied Catalysis B-Environmental*, vol. 168, JUN, pp. 353-362.

[9] Lin, T., Kellici, S., Gong, K., Thompson, K., & Darr, J. A., "'The Rapid Automated Materials Synthesis Instrument (RAMSI): A High Throughput Combinatorial Robot for Nanoceramics Discovery.", no. Advances in Science and Technology, 62, pp. 215-220.

[10] V. Middelkoop, C.J. Tighe, S. Kellici, R.I. Gruar, J.M. Perkins, S.D.M. Jacques, P. Barnes and J.A. Darr, "'Imaging the continuous hydrothermal flow synthesis of nanoparticulate CeO_2 at different supercritical water temperatures using in situ angle-dispersive diffraction," *The Journal of Supercritical Fluids*, vol. 87, 3, pp. 118-128.

[11] E.J. Beckman, "'Supercritical and near-critical CO_2 in green chemical synthesis and processing," *The Journal of Supercritical Fluids*, vol. 28, no. 2–3, 3, pp. 121-191.