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Vapor phase synthesis of glycerol carbonate over honeycomb monolith coated with zirconia based base catalysts

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Abstract

In this article the synthesis, characterization and catalytic activity studies of zirconia based base catalysts such as $Mg(II)/ZrO_2$, $Ca(II)/ZrO_2$ and $Ba(II)/ZrO_2$ coated on honeycomb monoliths is reported. Honeycomb monoliths were coated with $Mg(II)/ZrO_2$, $Ca(II)/ZrO_2$, $Ba(II)/ZrO_2$ and characterized for their physico-chemical properties such as surface basicity, crystallinity and morphology by using relevant techniques. The catalytic activity of these catalytic materials was evaluated in vapor phase synthesis of glycerol carbonate. The reaction conditions were optimized by varying reaction parameters such as nature of catalytic material, molar ratio of the reactants, catalyst bed temperature, feed-rate of the reactants and time-on-stream to obtain highest possible yield of glycerol carbonate with greater selectivity. The catalytic materials were found to be highly efficient in the synthesis of glycerol carbonate with a possible highest yield up to ~98%. These catalytic materials can be easily reactivated and reused in this reaction.

Keywords: Vapor phase; Glycerol carbonate; Honeycomb monolith, $Mg(II)/ZrO_2$; $Ca(II)/ZrO_2$; $Ba(II)ZrO_2$

Introduction

Biodiesel has attracted a reasonable attention as an alternative fuel (Refaat *et al.*, 2011). However, production of biodiesel by methanolysis generates a large amount of glycerol as the addition product. Therefore, transformation of glycerol into value-added products is of great interest. Several methods of glycerol conversion such as etherification, esterification, oxidation, etc., have been reported (Pagliaro *et al.,* 2007). Among various glycerol related products, glycerol carbonate (GC) is an important glycerol derivative which is less toxic, less volatile and biodegradable (Marakatti *et al.,* 2015). GC is being used in cosmetic, detergent, paint and gas separation membrane industries (Zhenmin *et al.,* 2014).

There are several routes for producing GC from glycerol with different reagents such as phosgene, urea, CO, etc (Vidhyaa *et. al.,* 2014). Because of the safety issues related to these reagents, their use in laboratory an industrial scale is limited. One of the important industrially important methods to synthesize GC is the transesterification of glycerol with dimethyl carbonate (DMC) in presence of a suitable catalyst (Bai *et. al.,* 2013). Several catalysts including lipase, NaOH, K_2CO_3, etc have been employed in the synthesis of GC (Zhenmin *et al.,* 2014). However, disadvantages associated with these homogenous catalysts such as difficulty in separation from the reaction mixture, poor reusability and toxicity makes these homogenous catalysts less preferable. Therefore, efforts have been made to replace these catalysts with heterogeneous solid acid or base catalysts. It is reported that the synthesis of GC from glycerol and DMC is more facile over basic catalysts than acid catalysts (Bancquart *et al.,* 2001). Some of the solid base catalysts that have been used in the synthesis of GC are Mg/Al mixed oxide, hydrotalcite, KF/Al_2O_3, etc (Takagaki *et al.,* 2010). Though a reasonable amount of work on the synthesis of GC via liquid phase is done, still there is a need for an efficient and facile catalytic system to produce GC in higher yields at an industrial level.

Metal oxides and their modified forms have been successfully employed as catalysts in many industrially important organic transformations such as isomerization, esterification, transesterification, nitration, etc (Corma *et al.,* 1995). Metal oxide based catalysts could be used over a wide range of temperatures and they have high resistance to thermal extrusions. Especially, zirconia based solid acids and solid bases have gained attention in a variety of organic reactions due their eco-friendly, economical and efficient nature (Yadav *et al.,* 1999).

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Cordierite ($Mg_2Al_4Si_5O_{18}$) honeycomb monoliths play an important role as catalyst carriers in heterogeneous catalysis especially in automotive applications which involve gas phase reactions (Nijhuis *et al.*, 2000). But, honeycomb monoliths (HMs) coated with solid acid/base catalysts have not been explored much in the field of organic fine chemical synthesis. Though, a limited literature could be found on the application of HMs coated with solid acids in liquid phase reactions (Shyamsundar *et al.*, 2015), no literature could be found on the application of such HMs for the synthesis of fine chemicals via vapor phase.

Generally organic fine chemicals are synthesized either in liquid phase or vapor phase conditions. Vapor phase conditions are better suited in many equilibrium driven organic reactions than in liquid phase. In vapor phase reactions, the product molecules of the reaction will not be in contact with the catalyst during the entire reaction period, thereby preventing backward reaction and hence yield of the desired reaction product will also be high (Joyce D'Souza *et al.*, 2004).

In the present article, a attempt has been made to synthesize glycerol carbonate via vapor phase transesterification of glycerol with dimethyl carbonate over honeycomb monoliths coated with base catalyst such as modified forms of zirconia ($Mg(II)/ZrO_2$, $Ca(II)/ZrO_2$ and $Ba(II) ZrO_2$). The basic catalysts such as $Mg(II)/ZrO_2$, $Ca(II)/ZrO_2$, $Ba(II) ZrO_2$ were coated on honeycomb monoliths and these catalysts were characterized for their properties such as surface basicity, crystallinity and morphology by using suitable techniques. Honeycomb catalysts were then evaluated in vapor phase transesterification of glycerol with dimethyl carbonate to synthesize glycerol carbonate. Reaction conditions were optimized to obtain highest possible yield of glycerol carbonate with greater selectivity. Reactivation and reusability of honeycomb catalysts was also taken up.

Materials and methods

Cordierite honeycomb monoliths (height = 1.20 cm, diameter = 2.50 cm and hole = 0.2 cm) were obtained from Shreya ceramics, Vadodara, India. Zirconyl nitrate, barium nitrate, calcium nitrate, magnesium nitrate, glycerol and dimethyl carbonate were ultra pure with 99.9% purity and were supplied by Rolex and Sd. Fine Chem India (P) Ltd.

Preparation of HM catalytic material

Honeycomb monoliths (HMs) were coated with ZrO_2, 5% $Mg(II)/ZrO_2$, 5% $Ca(II)/ZrO_2$ and 5% $Ba(II)/ZrO_2$ by using 'dip and dry' method (Shyamsundar *et al.*, 2015).

Coating of ZrO_2 on a HM

A dilute solution of zirconyl nitrate (3.0 g) with 50 ml of deionized water was prepared in a beaker. The resulting solution was coated on a HM by 'dip & dry' method (Shyamsundar *et al.*, 2015) in a furnace preheated to 400 °C. Dip and dry steps were repeated for 6-8 times till ~0.15 g of ZrO_2 is coated on the HM.

Coating of 5% $Mg(II)/ZrO_2$, 5% $Ca(II)/ZrO_2$ and 5% $Ba(II)/ZrO_2$ on HMs

Dilute solutions consisting of known amounts of zirconyl nitrate (5.8 g) and barium nitrate/calcium nitrate/magnesium nitrate (4.4 g/4.65 g/4.6 g) was made. These solutions were coated on different HMs by 'dip & dry' method in a furnace preheated for 1 h at 400 °C. The 'dip & dry' steps were repeated 6-8 times till ~0.15 g of 5% $Mg(II)/ZrO_2$ or 5% $Ca(II)/ZrO_2$ or 5% $Ba(II)/ZrO_2$ were coated on the HMs. The HMs coated with catalysts was calcined at 550 °C for 2 h before using them as catalytic materials. These catalytic materials were abbreviated as ZrO_2 (Z), 5%$Mg(II)/ZrO_2$ (MZ), 5% $Ca(II)/ZrO_2$ (CZ) and 5%$Ba(II)/ZrO_2$ (BZ).

Characterization of HM catalytic material

The HM catalytic material (Z, MZ, CZ, BZ) were characterized for their physico-chemical properties such as surface basicity by CO_2-TPD (Mayura TPD unit), crystalinity by Powder X-ray diffraction (Philips X'Pert X-ray diffractometer using $CuK\alpha$) and morphology by SEM (JEOL-2010) techniques. Elemental analysis was carried out using ICP-OES technique (Thermo-iCAP 6000).

Catalytic activity studies of HM catalytic material (in the vapor phase synthesis of glycerol carbonate)

Vapor phase synthesis of glycerol carbonate (GC) was carried out over HMs catalytic material (Z or MZ or CZ or BZ) using glycerol and dimethyl carbonate (Scheme 1). The vapor phase reactions were carried out in a specially designed (to accommodate honeycomb catalysts) fixed bed downstream vapor phase glass reactor maintained at 200 °C. The reaction mixture consisting of known amounts of glycerol and dimethyl carbonate (DMC) was fed into the pre-heater at a flow rate of 10 mL/h maintained at 230 °C by means of an infusion pump before passing over the catalytic material.

Scheme 1. Transesterification of glycerol with DMC

The reaction products obtained after the reaction were analyzed by gas chromatograph (Mayura) fitted with a column (10% SE-30 chromosorb w-AW, 3 m x 1/800) coupled with a FID detector using N_2 as the carrier gas and preheating time of 90 min (Shyamsundar et al, 2015). The reaction products were also analyzed qualitatively by GC–MS (Varian).
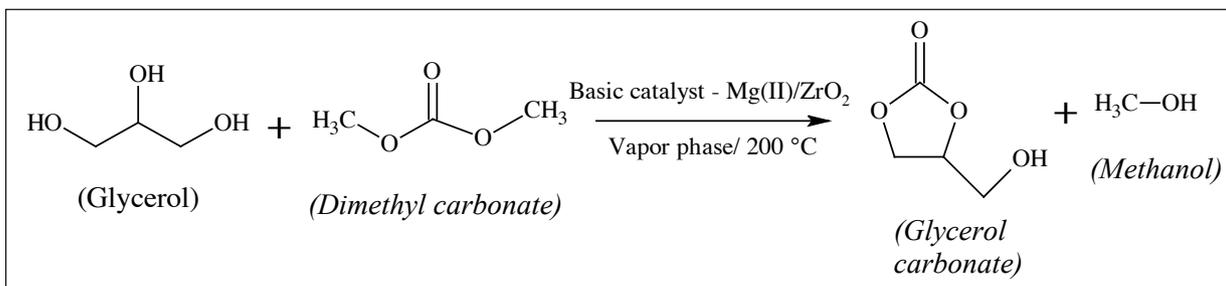
Scheme 1. Transesterification of glycerol with DMC.

The reaction conditions such as nature of catalytic material, molar ratio of the reactants, catalyst bed temperature and feed-rate of the reactants were optimized to obtain highest possible yield of glycerol carbonate with high selective.

Results and discussion

Characterization of HM catalytic materials
Surface basicity studies

The values of basic site distribution and total surface basicity of the catalytic material used for the present work are given in Table I. CO_2-TPD is a powerful tool used to determine number of basic sites (total basicity) and the strength of basic sites on the catalyst surface. The latter is temperature dependent. The catalyst is adsorbed with CO_2 at 300 ºC for 2 h and cooled to room temperature. The catalyst adsorbed with CO_2 is heated slowly in the temperature range of 50-700 ºC. The amount of CO_2 desorbed is calculated from the peak area of the TCD signal. The molecules which desorb at lower temperature are weakly held on the catalyst surface than the molecules desorbed at higher temperatures. Based on the temperature of desorption, the strength of the basic sites are differentiated into 'weak', 'moderate', 'strong' and 'very strong' basic sites.

Table I. Total surface basicity (TSB) and basic site distribution of catalytic material

Catalytic material	Basic site distribution (mmol/g)				
	Weak	Moderate	Strong	Very strong	TSB
Z	0.06	0.21	-	-	0.27
MZ	-	0.17	0.94	-	1.11
CZ	-	0.20	1.00	0.19	1.39
BZ		0.15	0.96	0.31	1.42

Among the catalytic material, HC coated with pure zirconia (Z) was found to be least basic with 'weak and moderate' basic sites. BZ and CZ were highly basic with the presence

of 'moderate, strong as well as very strong' basic sites. Whereas, MZ consisted of 'moderate and strong' basic sites.

PXRD studies

The powder XRD patterns of Z, MZ, CZ, BZ as well as bare honeycomb are shown in Fig. 1. Pure ZrO_2 showed reflections pertaining to monoclinic (2θ = 24.5, 33.1, 45.3) and tetragonal (2θ = 30.2, 35.3, 49.8) phases.
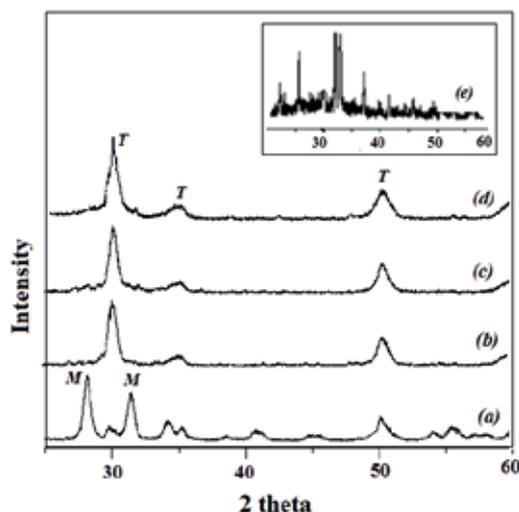

Fig. 1. PXRD patterns of (a) Z, (b) MZ, (c) CZ, (d) BZ and (e) Bare HM (*inset*). [*M – monoclinic; T – tetragonal*]

However, when pure Z was modified with either Mg(II) or Ca(II) or Ba(II) ions, transition from monoclinic phase to tetragonal phase was found to occur. i.e., the PXRD patterns of modified forms of zirconia (MZ, CZ, BZ) were found to consist of only catalytically active and metastable tetragonal phase (T) and no reflections pertaining to monoclinic phase (M) were observed. Interestingly, no reflections related to bare honeycomb were observed in the PXRD patterns of Z, MZ, CZ and BZ indicating that the active catalysts are effectively coated on the bare HM. Similar observations have been made by Shyamsundar *et al*. (2015).

SEM studies

The SEM images of HM catalytic material (Z, MZ, CZ, BZ and bare HC) are shown in Figure 2A, 2B. The images revealed strong and uniform coating of the active catalysts on the HMs. These images also indicate that the method used to coat the active catalyst on the bare HM is suitable and efficient.

Catalytic activity studies of HM catalytic material (in the vapor phase synthesis of glycerol carbonate)

Vapor phase transesterification of glycerol with dimethyl carbonate (molar ratio of glycerol: DMC = 1:3) was carried out over HM catalytic materials such Z, MZ, CZ and BZ. The reactions were carried out at a pre-heater temperature of
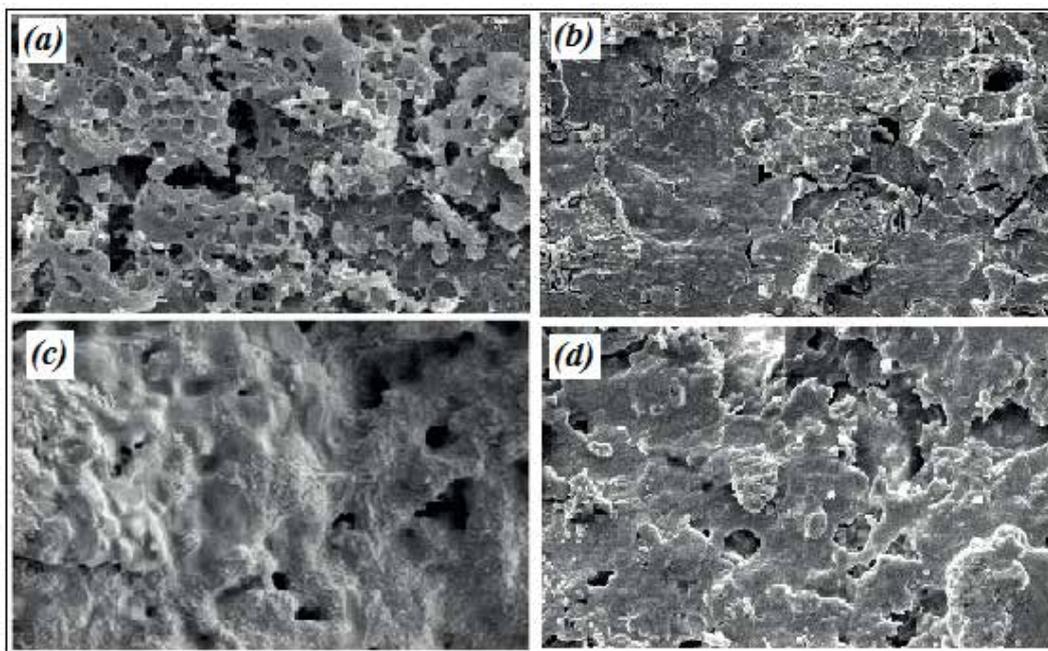

Fig. 2A. SEM images of (a) Z, (b) MZ, (c) CZ and (d) BZ. (Magnification = 2000x; 10 μm)

Fig. 2B. SEM image of bare HC. (Magnification = 2000x; 10 μm)

230 °C, catalyst bed temperature of 200 °C and at a flow rate of 10 mL/h.

Effect of nature of catalytic material

In order to the effect of the catalytic material, the vapor phase transesterification reactions were carried out over all the

Table II. Effect of nature of the catalytic materials on the yield (%) of glycerol carbonate

Catalytic material	Yield of GC (%)
Z	26
MZ	98
CZ	72
BZ	76
No catalyst	14

ICP-OES studies

The elemental analysis carried out via ICP-OES indicated the presence of 4.95%, 4.97% and 5.01% of Mg(II), Ca(II) and Ba(II) in MZ, CZ and BZ samples respectively.

[Reaction Conditions: Molar ratio of glycerol: DMC = 1: 3, flow-rate of reactants = 10 mL/h, amount of the catalyst = 0.15 g, pre-heater temperature = 230 °C, catalyst bed temperature = 200 °C].

catalysts used for the present work i.e., Z, MZ, CZ, BZ and the results are given in Table II.

A correlation between the surface basicity of the catalytic material and the yield (%) of GC was observed. Pure Z being least basic was found to be less active in the synthesis of GC. However, among modified forms of zirconia such as MZ or CZ or BZ, the catalytic material produced highest amount of GC i.e., 98% with 100% selectivity. Even though CZ and BZ are more basic than MZ, the former ones produced less GC compared to MZ catalytic material. It was observed from the gas chromatographic data that CZ and BZ produced by-products in addition to glycerol carbonate. Therefore, the catalytic material CZ and BZ can be inferred as less selective for the formation of GC than MZ. The formation of by-products could be attributed to the presence of 'very strong' basic sites in CZ and BZ. It is also possible that one of the reactant i.e., glycerol may undergo decarboxylation in presence of very strong basic sites leading to the formation of by-products. This also indicates that the formation of GC require 'moderate and strong' basic sites for 100% selectivity. Further, when the reaction was carried out in the absence of any catalytic material the yield of GC was found to be very low (14%) which can be due to the effect of high reaction temperature. For further studies MZ was chosen as the catalytic material.

Effect of molar ratio of the reactants

The effect of molar ratio of the reactants i.e., glycerol and dimethyl carbonate was studied by varying the molar ratio
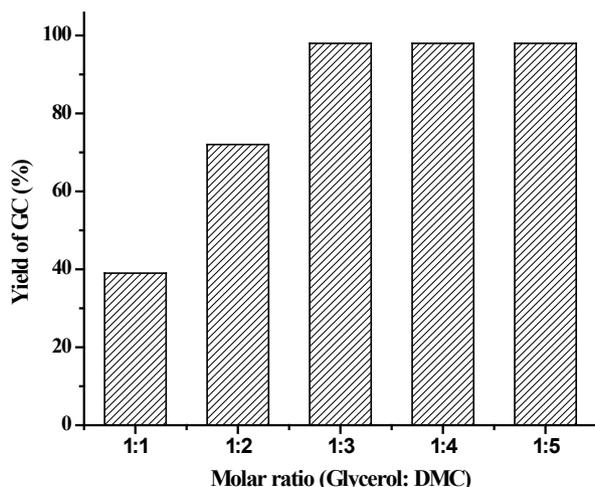
from 1:1 to 1:5 over MZ catalytic material and the results are presented in the form of a graph (Fig. 3).

The yield of GC increased with an increase in the molar ratio of glycerol: DMC till 1:3, beyond which no change in the yield of GC was observed. Since the transesterification of glycerol with DMC is an equilibrium driven reaction, it can be inferred that the reaction attains equilibrium at a molar ratio of 1:3. Further, no by-product formation was observed irrespective of the molar ratio. Hence for further optimization studies a molar ratio of 1:3 was selected.

Effect of catalyst bed temperature

The catalyst bed temperature was varied from 180 °C to 220 °C. It was observed that the yield of glycerol increased when the catalyst bed temperature was increased. The yield increased till the temperature reached 200 °C (Fig. 4).

Interestingly, when the catalyst bed temperature was increased beyond 200 °C, the yield of GC decreased. It was observed that by-products were formed at higher temperatures beyond 200 °C indicating that higher reaction temperature facilitates the formation of by-products. This also indicates that not only the 'very strong' acid sites in the catalytic material but also elevated reaction temperatures are also not suitable for the selective synthesis of GC. Formation of by-products may either be due to side reactions or due to the decomposition of either the reactant or product molecules. From this study it could be inferred that an optimum catalyst bed temperature for the selective synthesis of GC is 200 °C.
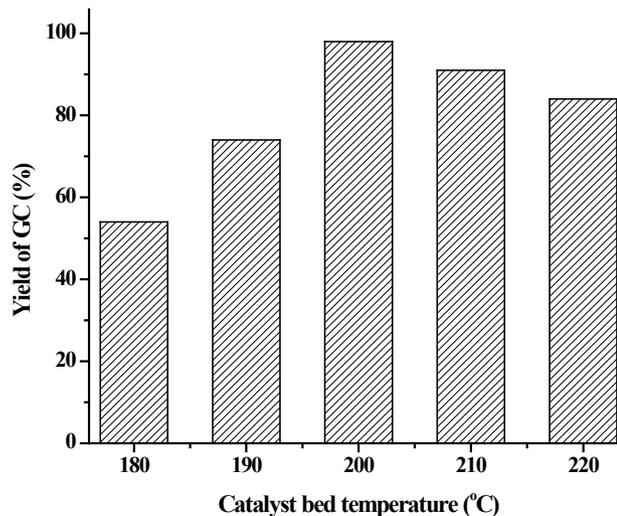

Fig. 3. Effect of molar ratio of the reactants on the yield (%) of GC

[Reaction Conditions: Feed-rate of reactants = 10 mL/h, amount of the catalyst = 0.15 g of MZ, pre-heater temperature = 230 °C, catalyst bed temperature = 200 °C].

Fig. 4. Effect of catalyst bed temperature on the yield (%) of GC

[Reaction Conditions: Feed-rate of reactants = 10 mL/h, amount of the catalyst = 0.15 g of MZ, pre-heater temperature = 230 °C, molar-ratio of glycerol: DMC = 1:3].

Effect of feed-rate of the reactants

The effect of feed-rate (flow-rate) of the reactants on the yield of GC was studied by varying the feed-rate from 7.5 mL/h to 12.5 mL/h (Figure 5).
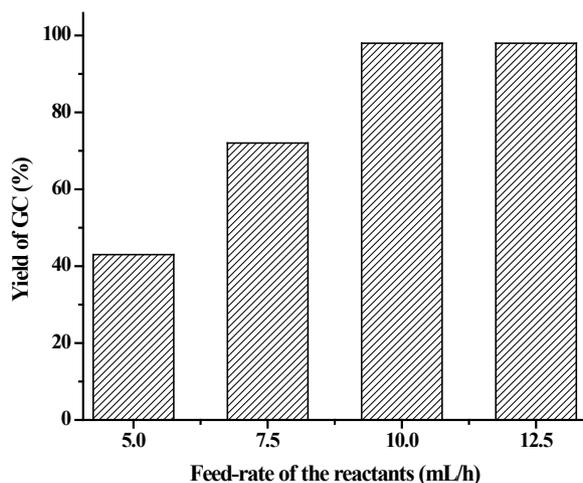

Fig. 5. Effect of feed-rate of the reactants on the yield (%) of GC

[Reaction Conditions: Amount of the catalyst = 0.15 g of MZ, pre-heater temperature = 230 ^{O}C, catalyst bed temperature = 200 ^{O}C, molar ratio of glycerol: DMC = 1:3].

From the figure it is clear that the feed-rate has an impact on the yield of GC. It could be seen that the yield of GC increased with an increase in the feed-rate of the reactants (glycerol + DMC). However, the increase in the yield of GC was observed when the feed-rate was increased till 10 mL/h, beyond which not much increase in the yield was observed. Interestingly at lower flow rates the yield of GC was low and by-product formation was also observed. The formation of by-products can be attributed to the higher contact time between the reaction mixture and the catalyst at lower feed-rate (5 mL/h, 7.5 mL/h). i.e., for the selective synthesis of GC, the feed-rate of the reactants must be atleast 10 mL/h.

Effect of time-on-stream

The effect of time-on-stream on the yield of GC was studied from 0 min to 300 min and the results are presented in the form of a graph (Figure 6).

It could be seen that the yield of GC was stable till 320 min and tends to decrease gradually beyond 320 min. The gradual decrease in the yield of GC beyond time-on-stream of 320 min can be due to the deactivation of the catalytic material with time. Further, time-on-stream had no affect on the selectivity of GC.

Effect of reusability of the catalytic material

The used catalytic material (Z, MZ, CZ, BZ) were reactivated by washing with acetone and drying at 120 ^{o}C for 2 h in an air oven. Thus reactivated catalytic materials were reused in the
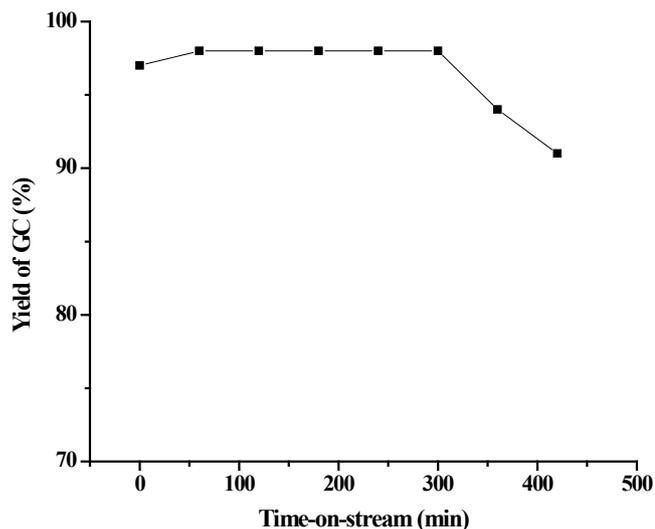

Fig. 6. Effect of feed-rate of the reactants on the yield (%) of GC

[Reaction Conditions: Amount of the catalyst = 0.15 g of MZ, pre-heater temperature = 230 ^{O}C, catalyst bed temperature = 200 ^{O}C, molar ratio of glycerol: DMC = 1:3, feed-rate = 10 mL/h].
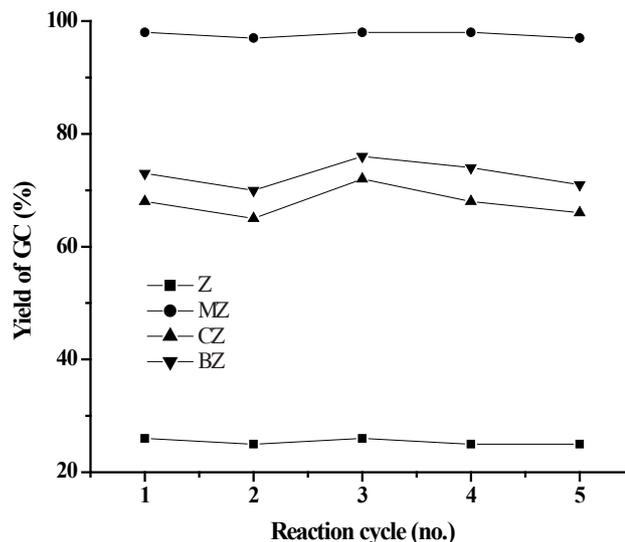

Fig. 7. Effect of reactivation and reusability of catalytic material on the yield (%) of GC

[Reaction Conditions: Amount of the catalyst = 0.15 g of Z or MZ or CZ or BZ, pre-heater temperature = 230 oC, catalyst bed temperature = 200 oC, molar ratio of glycerol: DMC = 1:3, feed-rate = 10 mL/h].

2nd cycle synthesis of GC. The process of reactivation and reusability were repeated for 6 cycles and the results are shown in Figure 7. The figure clearly indicates that Z and MZ catalytic material are more reusable when compared to CZ and MZ catalytic material. However, when the catalytic material were reactivated by calcining at 550 °C for 1 h, interestingly all the catalytic material were found to regain their activity.

found to be less selective towards the formation of glycerol carbonate as they produced by-products. Strength of the basic sites on the catalyst, catalyst bed temperature and feed-rate were found to play a role in selective synthesis of glycerol carbonate. The honeycomb catalytic materials could be easily reactivated and reused atleast for 6 reaction cycles.
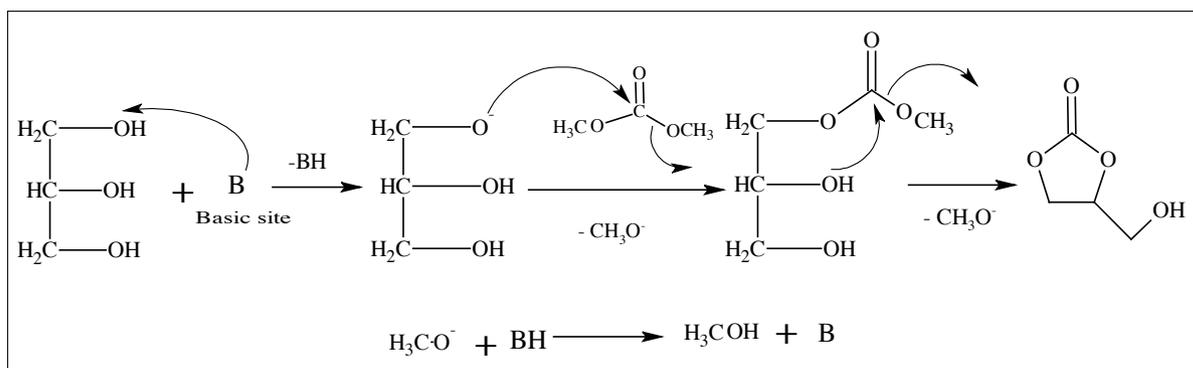
Scheme 2. Mechanism of transesterification of glycerol with DMC over a basic site.

PXRD pattern as well as the elemental composition of the reused catalytic material was measured. Interestingly, no change in the PXRD patterns as well as the elemental composition was observed. This indicates that the physico-chemical properties of the catalyst used for the present work are intact.

Mechanism of formation of glycerol carbonate via transesterification over a basic site

A possible base-catalyzed reaction mechanism of transesterification of glycerol with dimethyl carbonate towards the formation of glycerol carbonate is shown in Scheme 2 (Jose *et al.,* 2009). The basic site (B) of the catalyst attacks a glycerol molecule resulting in the deprotonation leading to the formation of a glyceroxide anion (CH$_3$O-). Glyceroxide anion further attacks the carbonyl group of dimethyl carbonate leading to the formation of glycerol carbonate with the elimination of methanol.

Conclusion

Selective synthesis of glycerol carbonate was achieved by vapor phase transesterification of glycerol and dimethyl carbonate over honeycomb coated with zirconia based basic catalysts. Up to 98% of glycerol carbonate was obtained with 100% selectivity over Mg(II)/ZrO$_2$ under optimized reaction conditions. However, Ca(II)/ZrO$_2$ and Ba(II)/ZrO$_2$ were

References

Bai R, Wang Y, Wang S, Mei F, Li T and Li G (2013), Synthesis of glycerol carbonate from glycerol and dimethyl carbonate catalyzed by NaOH/γ-Al$_2$O$_3$, *Fuel Proc Technol*. **106**: 209-214.

Bancquart S, Vanhove C, Pouilloux Y and Barrault J (2001), Glycerol transesterification with methyl stearate over solid basic catalysts: I. Relationship between activity and basicity, *Appl Catal* A **218**: 1-11.

Corma A (1995), Inorganic Solid Acids and Their Use in Acid-Catalyzed Hydrocarbon Reactions, *Chem Rev* **95**: 559-614.

Jose R, Gomez C, Go O, Aberasturi MJN, Madurga BM, Rodrıguez AP, Lopez CR, Ibarreta L L, Soria J T and Velasco M V (2009), Synthesis of glycerol carbonate from glycerol and dimethyl carbonate by transesterification: Catalyst screening and reaction optimization, *Appl Catal* A **366**: 315-320.

Joyce D'Souza and Nagaraju N (2004), Vapour phase transesterification over solid acids for the synthesis of isoamyl salicylate, *Indian J Chem Technol* **11**: 401-409.

Marakatti SV and Halgeri AB (2015), Metal ion-exchanged zeolites as highly active solid acid catalysts for the green synthesis of glycerol carbonate from glycerol, *RSC Adv*. **5**: 14286-14293.

Mohamed Shamshuddin SZ and Nagaraju N (2010), Vapour phase synthesis of salol over solid acids via transesterification, *J Chem Sci* **122**: 193-201.

Nijhuis TA, Kreutzer MT, Romijn ACJ, Kapteijn F and Moulijn J A (2000), Monolithic Catalysts as More Efficient Three-Phase Reactors, *Chem Engg Sci*, **56**: 823-829.

Pagliaro M, Ciriminna, Kimura H, Rossi M and Della Pina C (2007), From glycerol to value-added products, *Angew Chem Int Ed* **46**: 4434-4440.

Parameswaram G, Srinivas M, Hari Babu B, Sai Prasad PS and Lingaiah N (2013), Transesterification of glycerol with dimethyl carbonate for the synthesis of glycerol carbonate over Mg/Zr/Sr mixed oxide base catalysts, *Catal Sci Technol*. **3**: 3242-3249.

Refaat A A (2011), Biodiesel production using solid metal oxide catalysts, *Int J Environ Sci Technol* **8**: 203-221.

Shyamsundar M, Mohamed Shamshuddin SZ and Aniz CU (2015), Cordierite honeycomb monoliths coated with zirconia and its modified forms for biodiesel synthesis from *Pongamia glabra, J Amer Oil Chem Soc* **92**: 335-344.

Takagaki A, Iwatani K, Nishimura S and Ebitani K (2010), Synthesis of glycerol carbonate from glycerol and dialkyl carbonates using hydrotalcite as a reusable heterogeneous base catalyst, *Green Chem* **12**: 578-581.

Vidhyaa Paroo Indran, Nor Ain Syuhara Z, Mohd Asyarak D, Gaanty Pragas M, Mashitah Mohd Y, Taufiq-Yap Yun Hin and Mohd Hasbi Ab Rahim (2014), An accelerated route of glycerol carbonate formation from glycerol using waste boiler ash as catalyst, *RSC Advances* **4**: 25257-25267.

Yadav GD and Nair JJ (1999), Sulphated zirconia and its modified versions as promising catalysts for industrial processes, *Micropor Mesopor Mater* **33** : 1-48.

Zhenmin Liu, Junwei Wang, Maoqing Kang, Ning Yin, Sinkui Wang, Yisheng Tan and Yulei Zhu (2014), Synthesis of Glycerol Carbonate by Transesterification of Glycerol and Dimethyl Carbonate over KF/γ-Al$_2$O$_3$ Catalyst, *J Braz Chem Soc* **25** : 152-160.