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Synthesis of glycerol carbonate by transesterification of glycerol with dimethyl carbonate over Mg/Al/Zr catalysts

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ABSTRACT

Glycerol carbonate was synthesized by transesterification of glycerol with dimethyl carbonate using Mg/Al/Zr mixed oxide base catalysts. A series of Mg/Al/Zr catalysts were prepared with different molar ratios by using co-precipitation method and calcining at different temperatures. The catalysts were characterized by FT-infrared spectroscopy, X-ray diffraction and temperature-programmed desorption of CO_2. The transesterification activity depends on the Mg/Al/Zr molar ratio and the catalyst with Mg/Al/Zr molar ratio of 3:1:1 showed excellent activity. The catalyst activity depends on the pretreatment temperature, structure and basicity of the catalysts. The transesterification activity of catalysts was correlated with the structural aspects and the amount of basicity. Various parameters such as reaction temperature, catalyst concentration and molar ratio of dimethyl carbonate to glycerol were studied to optimize the reaction conditions.

1. Introduction

Biodiesel production has received great attention, as it is an alternative to fossil fuels as well as other renewable biofuels including bioethanol, biogas and bio-oil [1–3]. During production of biodiesel, glycerol is formed as an undesired product. For every 1000 kg of biodiesel production by transesterification of oils with methanol around 100 kg of glycerol is produced. The biodiesel production capacity has been increasing annually and results in the accumulation of glycerol content. This glycerol has to be converted into valuable chemicals whereas the majority of glycerol is currently consumed by combustion as a poor heat source [4]. Glycerol can be converted into several important chemicals such as propane diols, acrolein, glyceric acid, esters of glycerol and glycerol carbonate, etc. and the details about the glycerol conversion are discussed in recent reviews [4–6].

One of the important glycerol derivatives is glycerol carbonate (GC) which has been widely used as protic solvent (in resins and plastics), an elastomer, surfactant, adhesive, ink, paint, lubricant and electrolyte [7]. Glycerol carbonate can also be used in the synthesis of valuable intermediates such as glycidol which is employed in textile, plastics, pharmaceutical and cosmetics industries [8]. The general method reported for the synthesis of glycerol carbonate is from glycerol and CO or phosgene in the presence of metallic catalysts [9]. However, in this method of preparation both the starting materials are toxic and the entire process is environmentally hazardous.

Recently another method was proposed to synthesize glycerol carbonate from glycerol and urea in presence of a Lewis acid catalyst [10]. This reaction must be carried at low pressure (40–50 mbar) in order to shift the equilibrium towards glycerol carbonate formation by separating produced ammonia continuously from the gaseous phase [11]. Attempts have been made to produce glycerol carbonate directly from glycerol and CO_2 under supercritical conditions employing zeolites [12] or Sn catalysts [13]. This approach has been unsuccessful because glycerol carbonate yields were very low. Moreover, this method requires drastic reaction conditions.

One of the simplest methods for producing glycerol carbonate is by transesterification of glycerol with dimethyl carbonate [14,15]. Bancquart et al. investigated the transesterification of glycerol with basic solid catalysts in the absence of solvents in order to reduce the waste formation, extraction steps and permit an easier removal of the catalyst [16]. A comparison of several basic solids such as MgO, CeO_2, La_2O_3 and ZnO has shown that when the intrinsic basicity is significant, the catalyst becomes more active. It was found that MgO prepared by hydration followed by calcination of a commercial raw material was the most active catalyst [16].

Other catalytic systems such as Mg/Al hydrotalcite like compound are used for the synthesis of GC from transesterification of glycerol with dimethyl carbonate [17]. These catalysts require 10–54 h to attain maximum glycerol conversion. There is a need to develop suitable catalytic systems for the selective formation of GC in high yields and also to understand the role of different metal ions, their structure and influence of basic character.

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In this paper, a series of Mg/Al/Zr mixed oxide catalysts were prepared and evaluated for the synthesis of glycerol carbonate by transesterification of glycerol with dimethyl carbonate. The variation in structural characteristics and basicity of catalyst with change in molar composition and pretreatment temperature was explored. The relation between the catalyst properties and transesterification activity was evaluated.

2. Experimental

2.1. Catalyst preparation

MAZ catalysts were prepared by a co-precipitation method. The catalysts with different Mg/Al/Zr molar ratios (3:1:1, 2:1:1, and 1:1:1 molar ratio) were prepared by co-precipitation at constant pH of 10. The calculated amounts of $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, and $ZrO(NO_3)_2 \cdot H_2O$ were dissolved in distilled water and allowed to precipitate using aqueous solution of KOH and K_2CO_3 at a constant pH of 10. After aging for an adequate time of 18 h at 80 °C the solid was filtered off and washed with excess water to remove alkali ions. Thus obtained solid was dried at 120 °C in an oven overnight. These hydrated samples were calcined in air at 450 °C for 4 h. Some of the catalysts are also calcined at a temperature of 450–750 °C. These catalysts are designated as MAZ-111, 211, 311, where the alphabetical represent the metal ion and the numbers represents their molar ratios respectively.

2.2. Characterization of catalysts

X-ray powder diffraction (XRD) patterns of the catalysts were recorded on a Rigaku Miniflex diffractometer using CuKα radiation (1.5406 Å) at 40 kV and 30 mA. The measurements were obtained in steps of 0.045° with account time of 0.5 s and in the 2θ range of 10–80°. FT-IR spectra were recorded on Biorad Excalibur series spectrometer in the range of 500–4000 cm^{-1} employing the KBr disc method.

Temperature programmed desorption of CO_2 (TPD–CO_2) was carried out for the measurement of basicity of the catalysts. The catalyst sample was pre-treated in He flow at 300 °C for 1 h, and then cooled to 50 °C prior to the adsorption of CO_2 at this temperature. After the adsorption of CO_2 for 30 min the sample was flushed with He for 1 h at 100 °C in order to remove physisorbed CO_2 from catalyst surface. The desorption profile was recorded at a heating rate of 10 °C min^{-1} from 100 °C to 800 °C and the evolved CO_2 was monitored with a thermal conductivity detector.

2.3. Reaction procedure

Glycerol carbonate was synthesized in liquid phase at a reaction temperature of 75 °C at atmospheric pressure. In a typical experiment, 2 g of glycerol and 9.78 g of dimethyl carbonate were taken in 50 ml two necked round bottom flask and 0.217 g of catalyst was added and carried the reaction at desired temperature. In order to monitor the reaction, the samples were withdrawn after every 30 min and analyzed using gas chromatography by separating the products on a 30m × 0.25 mm DB-1 WAX column. The products were identified by GC-MS and FT-IR analysis.

3. Results and discussion

3.1. Catalyst characterization

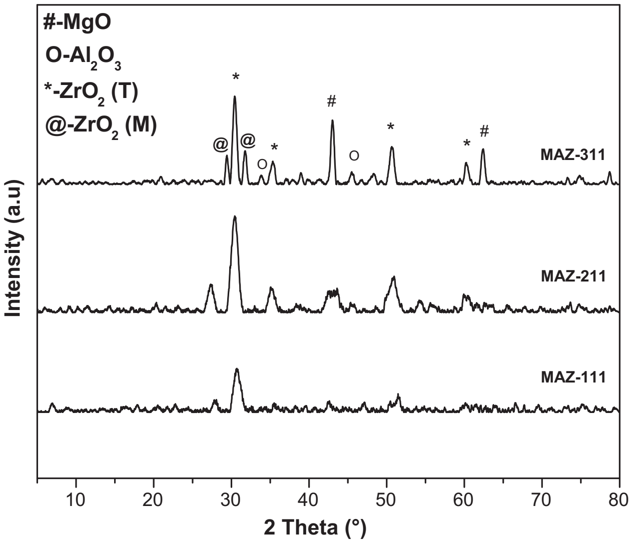

Fig. 1. X-ray diffraction patterns of the MAZ catalysts.

The XRD patterns of the catalysts are shown in Fig. 1. The XRD patterns show major reflections at 2θ of 30.3°, 50.4° and 60.2° which are attributed to tetragonal phase of ZrO_2 [18,19]. Another prominent pattern related to cubic form of MgO [20] was also observed at 43.03° and 62.3°. One cannot rule out the formation of mixed oxide structure ($Mg_5Al_{2.4}Zr_{1.7}O_{12}$) as small patterns at 2θ of 21.153°, 31.9° are noticed [21]. Reflection at 35.1° particularly in the case of MAZ-211 catalyst is related to γ-Al_2O_3 phase [22]. The XRD patterns suggest that with increase in the ratio of Mg to Al and Zr leads to increase in crystallite sizes of Mg and Zr oxides.

The FT-IR spectra of the catalysts are shown in Fig. 2. The broad absorption band around 3500 cm^{-1} is attributed to O–H vibration mode of hydroxyl group and water molecules in interlayer region [20]. Two absorption bands observed around 1400 cm^{-1} and 2500 cm^{-1} are related to carbonate ion in interlayer region [23].

The TPD of CO_2 measurements are carried out for Mg/Al/Zr catalysts to know the total basicity and basic strength distribution of the catalysts. The CO_2 desorption profiles of the catalysts are presented in Fig. 3. The MAZ-111 and MAZ-211 catalysts showed a broad low temperature desorption peak in the range of 200–300 °C. These desorption peaks are related to the moderate basic sites present in the catalyst. The desorption peak that appears at 250–400 °C, related to desorption of CO_2 from the sites having medium basic strength [24]. MAZ-311 catalyst showed a strong desorption peak centered

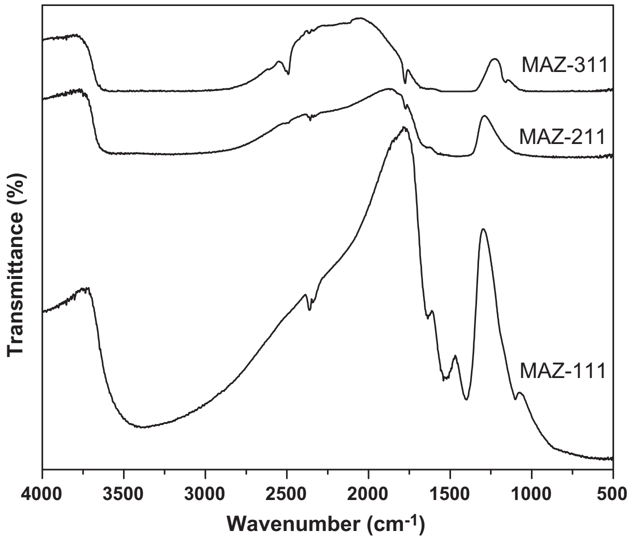

Fig. 2. FT-infra red spectra of the MAZ catalysts.

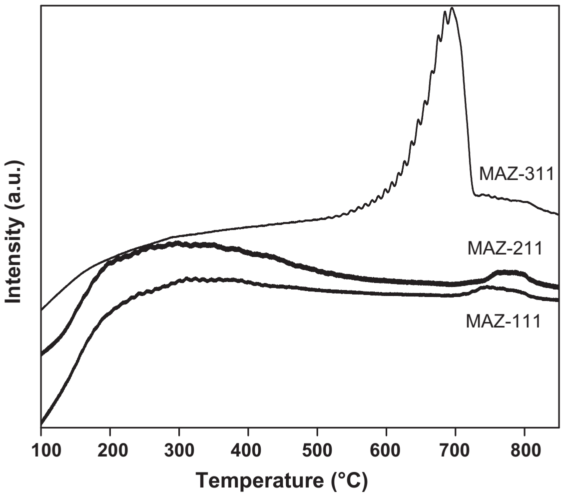

Fig. 3. Temperature programmed desorption of CO_2 patterns of the MAZ catalysts.

at 650 °C, which can be attributed to CO_2 desorbed from sites with strong basic strength. The basicity of the catalyst varied with the variation of Mg content in MAZ catalysts. The CO_2–TPD results suggest that MAZ-311 catalyst has large number of strong basic sites where as MAZ-211 and MAZ-111 contains moderate basic sites.

3.2. *Catalyst evaluation for glycerol carbonate synthesis*

The MAZ catalysts were evaluated for the transesterification of glycerol with dimethyl carbonate to yield glycerol carbonate and the results are shown in Fig. 4. The catalytic activity of Mg/Al and Mg/Zr oxides are also showed in the figure for the sake of comparison. All the three MAZ catalysts showed good activity towards transesterification of glycerol with dimethyl carbonate compared to their bimetal oxide catalysts. The Mg/Al and Mg/Zr catalyst showed relatively less yield compared to MAZ catalysts. The formation of glycerol carbonate from glycerol transesterification without using any catalyst is negligible. The formation of glycerol carbonate increased with increase in Mg to Al or Zr ratio. Among these catalysts the catalyst with high Mg to Al or Zr ratio (MAZ-311 catalyst) showed highest transesterification activity. These results suggest that the activity of the base catalyzed reaction can be enhanced with using more number of mixed oxides.

The transesterification activity observed for the MAZ catalysts can be speculated from the observed catalyst characteristics. The MAZ-311 catalyst showed the presence of strong basic sites. This catalysts exhibited well define crystalline sites of constituent metal oxides. The presence of strong basicity is responsible for high transesterification activity as this reaction is facilitated by the presence of basic sites. Other catalysts also showed reasonable activity due to the presence of moderate basic sites. These results support that the basicity of the catalyst is the main factor in obtaining high glycerol carbonate yield.

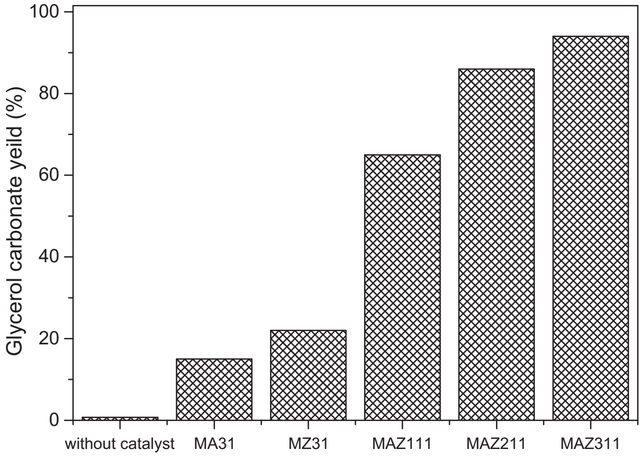

Fig. 4. Transesterification of glycerol activity over MAZ catalysts.

Table 1
Effect of catalyst pretreatment temperature on glycerol transesterification activity.

S. No	Catalyst	Calcination temperature °C	Glycerol carbonate yield (%)
1	MAZ-311-UC	Uncalcined	8
2	MAZ-311-450	450	86
3	MAZ-311-550	550	91
4	MAZ-311-650	650	94
5	MAZ-311-750	750	68

Reaction conditions: Glycerol: 2 g (0.0217 mol); Dimethyl carbonate: 9.783 g (0.1085 mol); Catalyst: 0.00217 mol; Reaction time: 90 min and Reaction temperature: 75 °C.

3.3. *Effect pretreatment temperature of the catalysts*

As the MAZ-311 catalyst showed highest glycerol carbonate yield and this catalyst is further studied to know more about the surface-structural properties and their relation with transesterification activity. The MAZ-311 catalyst was subjected to different calcination temperatures in the range of 450–750 °C. It is known that the mixed metal oxide acidic and basic properties will vary with the change in pretreatment temperature apart from its composition [25]. The MAZ-311 catalyst calcined at different temperatures is studied for the transesterification of glycerol and the results are presented in Table 1.

The uncalcined MAZ-311 catalyst showed very low glycerol carbonate yield of about 8%. The activity of the catalyst is increased with increase in calcination temperature up to 650 °C and further increase in temperature resulted in low activity. The catalyst calcined at 650 °C showed highest activity among all catalysts. In order to understand the variation in activity with change in calcination temperature these catalysts are further characterized in detail.

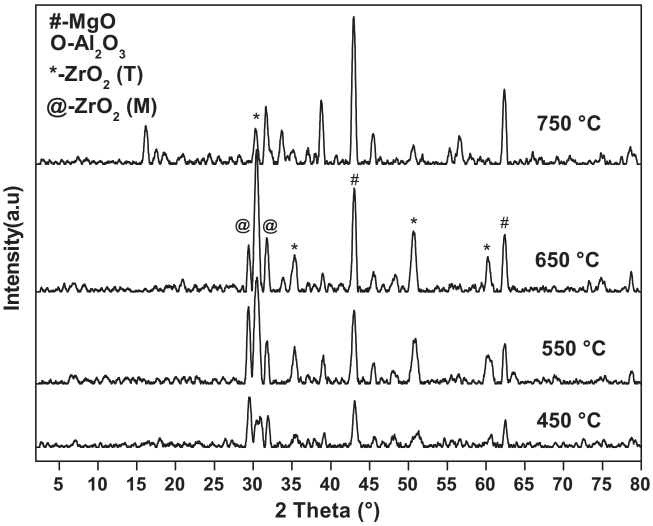

Fig. 5. X-ray diffraction patterns of the MAZ-311 catalyst calcined at different temperatures.

Table 2
Comparison of the catalytic activity of Mg/Al/Zr with other reported catalysts for the synthesis of glycerol carbonate.

Catalyst	Catalyst calcination temp. (°C)	Reaction time (min.)	Reaction temperature (°C)	Glycerol carbonate yield (%)	Ref.
Mg/Al/Zr	650	90	75	94	Present work
Mg/Al HT	RT	60	100	75	[14]
Mg/Al	450	60	130	65	[14]
CaO	–	60	100	43	[14]
CaO	900	90	75	91.1	[15]
MgO	–	60	100	10	[14]
MgO	900	90	75	12.1	[15]
Amberlyst A620H	–	90	60	5.9	[15]

The XRD patterns of the MAZ-311 catalyst calcined at different temperatures are shown in Fig. 5. The XRD patterns suggest well crystalline nature of the catalysts. The patterns mainly showed the presence of MgO, Al_2O_3 and ZrO_2 crystallite phases. The tetragonal phase of zirconia is increased with increase in calcination temperature up to 650 °C. The catalyst calcined at 750 °C showed the presence of new patterns at 2θ values in the range of 15–20°. The intensity of the tetragonal phase of zirconia is low for the catalyst calcined at 750 °C. The intensity related to MgO phase increased with increase in temperature up to 750 °C.

The activation of hydrotalcite like materials is by the controlled thermal decomposition, which leads to the formation of mixed oxides with good dispersion of metals, high surface area and Lewis basic properties [17]. In the present case the decomposition of the Mg/Al/Zr at high temperature of 650 °C resulted in a highly active catalyst. This is might be due to the formation of well dispersed mixed oxides with stabilized tetragonal phase of zirconia up to a calcination temperature of 650 °C.

The TPD of CO_2 patterns of the MAZ-311 catalyst calcined at different temperatures are shown in Fig. 6. The patterns suggest that the catalysts calcined at 450 °C, 550 °C and 650 °C showed the presence of a desorption peak at 650 °C related to strong basic sites. The amount of basicity is more for the catalyst calcined at 650 °C. The catalyst calcined at 750 °C showed different TPD pattern as it exhibited a small desorption peak at 350 °C. This peak can be attributed to the moderate basic sites present in the catalyst. The decrease in basicity for the catalyst calcined at 750 °C might be due variation in the structural properties. The XRD patterns suggest the absence of tetragonal zirconia and presence of new peaks around 2θ of 15–20°.

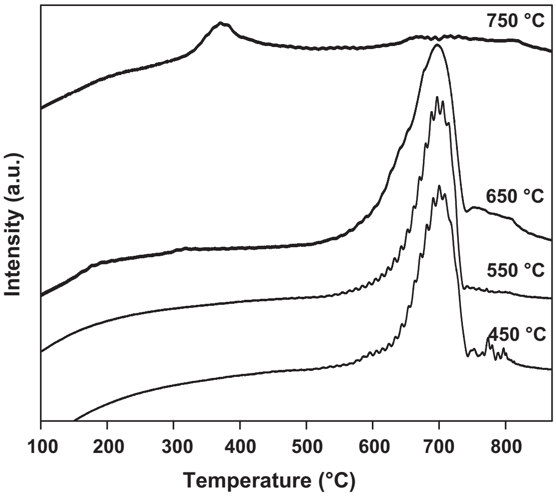

Fig. 6. Temperature programmed desorption of CO_2 patterns of the MAZ-311 catalyst calcined at different temperatures.

3.4. Influence of reaction temperature on transesterification of glycerol

As the MAZ-311 calcined at 650 °C showed highest activity among all the studied catalysts, it is selected as system catalyst for the evaluation of reaction parameters to obtain best reaction condition for the high yield of glycerol carbonate. Various parameters such as reaction temperature, glycerol to dimethyl carbonate molar ratio, and effect of catalyst amount are studied.

The effect of reaction temperature was studied and the results are shown in Fig. 7. The reaction temperature was varied from 50 to 100 °C. The glycerol carbonate yield was increased with increase in temperature up to 75 °C and thereafter there was no much increase in yield with further increase in temperature. The catalyst showed maximum activity at a reaction temperature of 75 °C. The high activity of the present catalyst even at low temperature suggests that the MAZ catalysts are highly basic and their activities can be compared with homogenous base catalysts.

3.5. Effect of the molar ratio of glycerol to dimethyl carbonate

Molar ratios of glycerol to dimethyl carbonate also effect the conversion of glycerol to glycerol carbonate by transesterification reaction with dimethyl carbonate. The effect of the molar ratios of glycerol to dimethyl carbonate was tested using the MAZ-311 catalyst and the results are drawn in Fig. 8. These results suggest that, at high molar ratios of glycerol to dimethyl carbonate, the conversion of glycerol is less and increased with decreasing molar ratio. The glycerol carbonate yield was reached maximum at molar ratio of 1:5. Further decrease in molar ratio of glycerol/dimethyl carbonate decreased the conversion of glycerol and resulted in less glycerol carbonate yield.

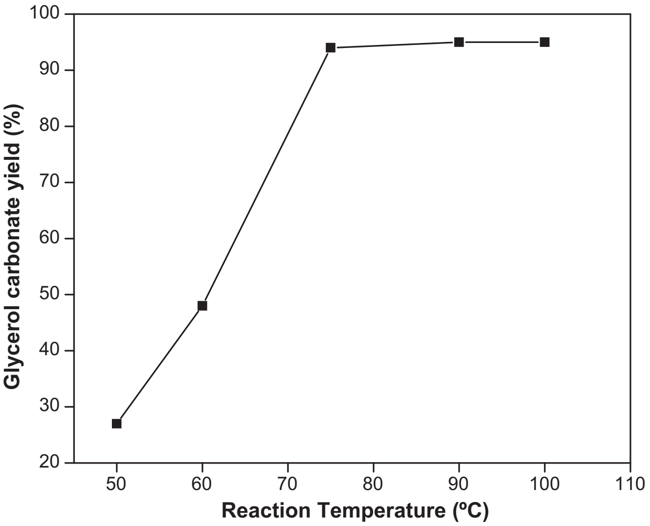

Fig. 7. Effect of reaction temperature on glycerol transesterification activity.

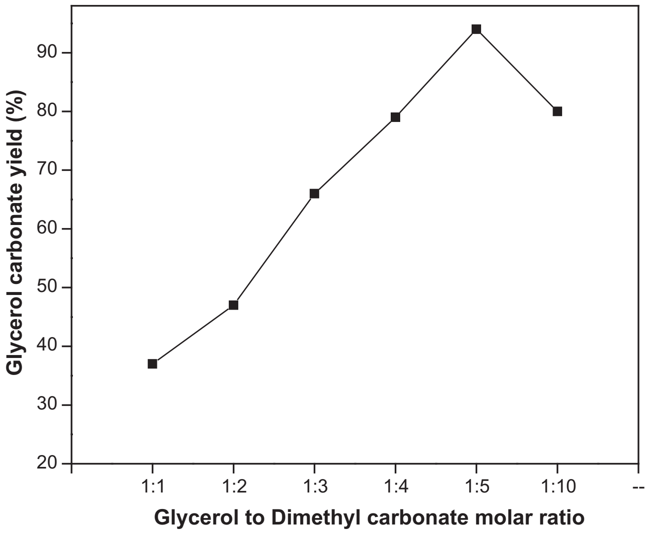

Fig. 8. Effect of glycerol to dimethyl carbonate molar ratio on synthesis of glycerol carbonate.

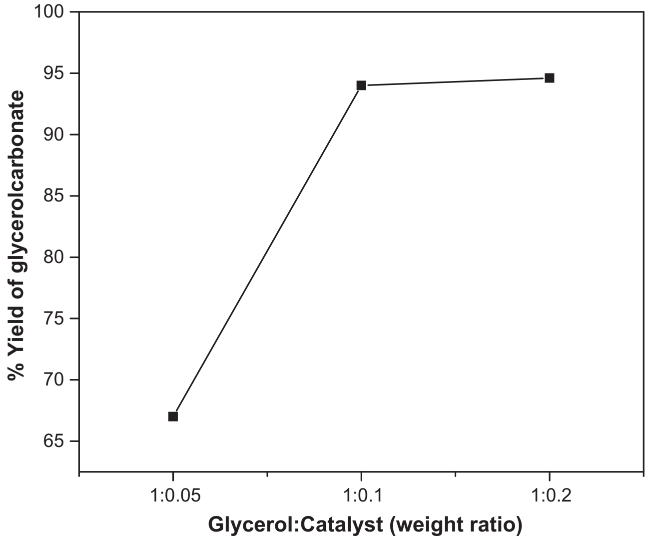

Fig. 9. Effect of catalyst weight on glycerol transesterification activity.

3.6. *Effect of catalyst amount*

Fig. 9 shows the influence of catalyst amount on transesterification reaction of glycerol with dimethyl carbonate. These results suggest that the conversion of glycerol increased with increase in catalyst to glycerol ratio. This is expected as the increase in catalyst amount results in the availability of more number of active sites for reaction. The highest yield of glycerol carbonate was achieved at a catalyst to glycerol ratio of 0.1.

3.7. *Comparison of the catalytic activity of Mg/Al/Zr with other reported catalysts*

The yield of glycerol carbonate during the transesterification of glycerol with dimethyl carbonate was compared with other reported catalysts and the results are presented in Table 2. The commercially available solid bases such as CaO and MgO were showed reasonable glycerol carbonate yield when they are subjected pretreatment at high temperatures [14,15]. The present catalyst showed better activity than the reported Mg/Al HT and commercially available Amberlyst catalysts. These results reiterate the high activity of Mg/Al/Zr catalyst for transesterification of glycerol with dimethyl carbonate to yield glycerol carbonate.

4. Conclusions

In conclusion, Mg/Al/Zr mixed oxides are efficient catalysts for the synthesis of glycerol carbonate by the transesterification of glycerol with dimethyl carbonate. The Mg/Al/Zr catalysts activity depends upon the mole ratio of the oxides and the pretreatment temperature. Tri metallic mixed oxide catalysts are more active than their corresponding bimetallic mixed oxide catalytic systems. The catalysts with Mg/Al/Zr mole ratio of 3:1:1 and calcined at 650 °C showed maximum activity due the presence of strong basic sites. The glycerol carbonate yield also depends upon the reaction temperature, glycerol to dimethyl carbonate ratio and catalyst amount.

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