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Title:  $Mg_{1+x}Ca_{1-x}O_2$  as reusable and efficient heterogeneous catalyst for the synthesis of glycerol carbonate via the transesterification of glycerol with dimethyl carbonate



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2	glycerol carbonate via the transesterification of glycerol with dimethyl carbonate
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#### 1 Abstract

2 A reusable and highly active heterogeneous catalyst of the type Mg<sub>1+x</sub>Ca<sub>1-x</sub>O<sub>2</sub> has 3 been developed and thermally treated at 850 °C for 6 h. The catalytic activity was investigated during the transesterification of glycerol with dimethyl carbonate to synthesize 4 5 the valuable glycerol carbonate. A typical Mg<sub>1,2</sub>Ca<sub>0,8</sub>O<sub>2</sub> mixed oxides catalyst was 6 characterized by BET surface area, surface base amount, CO<sub>2</sub>-TPD, XRD and FTIR, and its 7 microstructure was studied by the aid of scanning and transmission electron microscopy. The 8 investigated characteristics gave a clear insight into the catalytic performance of the catalyst. 9 Over 0.30 g of this catalyst, glycerol conversion was almost complete and the yield of 10 glycerol carbonate was 100% under atmospheric pressure. The best reaction conditions are: molar ratio of glycerol/DMC of 1:2, reaction temperature of 70 °C and 90 min of reaction 11 12 time. The transesterification results showed that the synergism interaction between Ca and 13 Mg species in the catalyst structure was the reason for its high activity.

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- 21 *Keywords:* Glycerol; Glycerol carbonate; Mixed oxide catalyst; Fuel additives.

#### 1 1. Introduction

2 Due to the escalating prices of the petroleum crude in international markets and the 3 growing concern to reduce the greenhouse gas emission, biodiesel has gained increased 4 acceptability as an alternative to petrol-diesel fuel [1]. It has several advantages such as the 5 substantial reduction of unburned hydrocarbon emissions, higher cetane number compared to 6 petrol-diesel resulting in better engine performance [2]. Moreover, it is non-toxic and 7 biodegradable fuel which almost completely eliminates life cycle carbon dioxide emission 8 [3]. Today, there are significant demands in energy consumption worldwide leading to an 9 increased production of biodiesel. One of the inevitable technical problems accompanying the 10 biodiesel industry and affecting its economy is the glycerol by-production, which is about 10 11 wt.% of the total product [4]. Consequently, the market is flooded with the oversupplied glycerol due to the expansion in biodiesel industry worldwide resulting in plummeting the 12 13 price of glycerol and subsequently jeopardizing the biodiesel production economy.

Recently, the abundance of glycerol at low prices, together with the quest of new economic synthetic routes for renewable chemicals, have resulted colossal interest in this renewable polyol as a building block molecule, mainly due to the wide realm of its valuable derivatives [5]. In this sense, various technologies have emerged for the valorization of glycerol to valuable chemicals and prominent among these is the synthesis of glycerol carbonate via transesterification with dimethyl carbonate.

Glycerol carbonate (4-hydroxymethyl-1,3-dioxolan-2-one, CAS #931-40-8) is one of the most promising glycerol derivatives that attracts presently, more scientific and industrial concern [6]. It is an important green alternative for petrol-based components like ethylene and propylene carbonates for CO<sub>2</sub> sequestration membranes [7, 8] and also a building block monomer for the synthesis of biodegradable polymers such as polyesters, polycarbonates, polyurethanes and polyamides [9]. In addition to its importance in textile, plastics,

pharmaceutical and cosmetics industries, glycerol carbonate has gained increased attention in
 lithium ion batteries as eco-friendly electrolyte solvent [6].

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3 The traditional synthesis of glycerol carbonate from glycerol has been carried out 4 through different routes: the reaction of glycerol with urea [10], the direct carbonation of 5 glycerol with phosgene [11] or carbon monoxide and oxygen [12]. However, technical and 6 environmental drawbacks accompanying the reaction of glycerol with urea include the toxicity of urea and high reaction temperature (150 °C). The carbonation reaction has been 7 8 categorized as non-environmental process due to the toxicity of phosgene and CO [13]. It was 9 also reported that glycerol carbonate can be obtained by carbonylation with CO<sub>2</sub> at harsh reaction conditions [14]. In this regard, serious limitations associated with this synthetic route 10 11 have been addressed, particularly the low yield of glycerol carbonate and the unfavorable thermodynamic equilibrium limitations [15]. 12

13 In another approach, the synthesis of glycerol carbonate was performed via the transesterification of glycerol with cyclic carbonate, such as dimethyl carbonate (DMC) in 14 15 the presence of catalyst with basic sites (Scheme 1) [16-18]. DMC, which can be obtained 16 from urea and methanol, is widely utilized as a green carbonylation agent due to its 17 environmentally benignant nature [19]. In this context, several homogeneous catalysts were 18 used to facilitate this reaction such as CaO [20] and  $K_2CO_3$  [21] with high yield of glycerol 19 carbonate. However, the possible interactions of such catalysts with the reaction system and 20 the difficulty to separate them from the product are the demerits of using homogeneous 21 catalysts. The heterogeneous catalyst of lipase Novozym 435 immobilized onto molecular 22 sieves also catalyzed the synthesis of glycerol carbonate from glycerol and DMC [22]. 23 Besides the high cost of lipase catalyst and the large amount of molecular sieve used, this 24 catalyst showed poor activity and 25 h of reaction time was needed for completion. Recently, various heterogeneous catalysts such as CaO [6], Mg/Al/Zr [18] and KF/HAP [23] have been 25

used for the synthesis of glycerol carbonate from glycerol and DMC. However, some studies
were carried out at high temperate with a high molar ratio of DMC/glycerol [6] or in the
presence of toxic solvent [13] to achieve a high yield of glycerol carbonate.

Therefore, it is of importance to the research community and the industry to develop a new catalytic process for the synthesis of glycerol carbonate using an economic reaction conditions with the aid of highly active and reliably reusable heterogeneous catalyst. In this work, a series of Mg-Ca mixed oxide catalysts were prepared and evaluated for the synthesis of glycerol carbonate from glycerol and DMC. The variation in the textural and structural characteristics of the prepared catalysts with the change in atomic composition and calcination temperature were investigated.

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#### 12 2. Materials and methods

#### 13 2.1 Materials

Anhydrous glycerol of high purity (>99%) and sodium hydroxide (98%) were 14 15 obtained from Sigma, Germany. Anhydrous dimethyl carbonate (DMC) of purity  $\geq 99.8\%$ , HPLC grade methanol of purity  $\geq$ 99.0% and Calcium nitrate tetrahydrate Ca(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O 16 17 (99%) were supplied by Merck, Malaysia. Magnesium nitrate hexahydrate  $Mg(NO_3)_2 \cdot 6H_2O_3$ , 18 synthetic hydrotalcite and 25% Ammonia solution were purchased from Sigma-Aldrich 19 (Malaysia). Hydrochloric acid (HCl 37%) from Mallinckrodt, USA was used. All reagents 20 were used without further treatments. Standard glycerol carbonate of 93-95% purity was 21 freely obtained from Hunstman, USA.

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#### 23 2.2 Synthesis of the mixed oxide catalyst

1 The mixed metal oxide catalysts  $Mg_{1+x}Ca_{1-x}O_2$  (0.1  $\ge x \ge 0.9$ ), were synthesized by the 2 co-precipitation of the metals hydroxides from their nitrates in 5 M NH<sub>4</sub>OH solution as 3 alkaline precipitation media [24]. On the basis of 10 g of the final catalyst, a solution 4 containing the calculated amounts of metal salts,  $Ca(NO_3)_2.4H_2O$  and  $Mg(NO_3)_2.6H_2O$ , was 5 firstly prepared and magnetically stirred at 550 rpm in 250 mL round bottom flask. The mixture was heated over a water bath to 75 °C and thoroughly mixed for 30 min. Then, 5 M 6 7 ammonia solution (29 ml of 25% ammonia in 150 ml of distilled water) was added and stirred 8 for 6 h. Thereafter, a white precipitate was formed signifying the formation of metals 9 hydroxides. The mixture was then filtered off and the solid was removed and subsequently 10 dried at 80 °C for 24 h. Samples were calcined in air at 850 °C with a heating rate of 5 °C/min 11 and dwelling for 6 h. The foregoing method describes the synthesized catalyst and in 12 particular sample Mg<sub>1.2</sub>Ca<sub>0.8</sub>O<sub>2</sub> with Ca: Mg mass ratio of 1: 1.1. Single oxides of MgO and 13 CaO were separately precipitated from their nitrates adopting the above procedure, except CaO which was calcined at 900 °C, and directly employed for the transesterification of 14 15 glycerol with dimethyl carbonate. It is worth mentioning that the number of oxygen atoms (2) 16 in the chemical formula was proposed to achieve the zero-valent charge for the catalyst 17 formula.

#### 18 2.3 Catalyst characterization

The total surface area, pore volume and average pore diameter of the developed catalysts were measured by nitrogen adsorption/desorption isotherms at -197 °C by the Brunauer-Emmet-Teller (BET) method using ASAP 2020 V3.02 H Micromeritics instrument (Micromeritics instruments corporation, USA). The base amount was determined by the neutralization titration method [25]. Catalyst powder 0.10 g was dispersed in 25 mL of 0.02 M HCl solution and the resulting suspension was gently stirred at room temperature for 48 h. Thereafter, the mixture was filtered off and the alkali filtrate solution was titrated against 0.02

M NaOH solution. The following formula was used to calculate the concentration of basic
sites (*C*):

3 4

 $C \text{ (mmol/g)} = \frac{\text{(Initial moles of HCl - Final moles of HCl)}}{\text{Mass of catalyst (g)}} \tag{1}$ 

Also, the base amount of the prepared catalysts was studied with temperature-5 programmed desorption of CO<sub>2</sub> as probe molecule (TPD-CO2) using Micromeritics 6 7 AutoChem 2920 II apparatus equipped with thermal conductivity detector. The analysis was 8 performed by heating 50 mg of the catalyst sample under a He flow from room temperature to 700 °C for 1 h (20 °C min<sup>-1</sup>, 100 mL min<sup>-1</sup>). Then, the temperature was decreased to 100 9  $^{\circ}$ C, and a flow of pure CO<sub>2</sub> (50 mL min<sup>-1</sup>) was subsequently introduced into the reactor 10 11 during 1 h. The TPD of CO<sub>2</sub> was carried out between 100 and 700 °C under a He flow (10 °C  $min^{-1}$ , 30 mL  $min^{-1}$ ), and the detection of the desorbed CO<sub>2</sub> was by an on-line gas 12 13 chromatograph provided with a TCD.

14 The mean metallic amounts of Ca and Mg presented within the structure of the 15 catalyst before and after the transesterification reaction were determined by EDX using Zeiss 16 Supra TM 35 VP scanning electron microscope (Zeiss, Jena, Germany) coupled with FEI as a 17 source of electrons and accelerated at 300 kV. The identification of the surface functional 18 groups was performed by Fourier transform infrared spectroscopy (FTIR). The IR spectra for 19 the as-synthesized catalysts were obtained on Perkin-Elmer System 2000 spectrometer by 20 using the standard KBr disc method. The spectra were recorded in the fingerprint region of 2000–400  $\text{cm}^{-1}$ . The structure and the unit cell parameters of the synthesized catalysts have 21 22 been investigated by wide angle X-ray diffraction patterns over a diffractometer (Bruker D2 23 Phaser Germany, 2011). The Cu K<sub> $\alpha$ </sub> radiation electrons ( $\lambda$ =1.5406 Å) were accelerated at 30 24 kV and 10 mA in an evacuated X-ray tube with Ni filter, and the data were interpreted using 25 the EVA software.

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#### 1 2.4 Catalytic reaction

2 The transesterification reaction of glycerol with dimethyl carbonate (DMC) for the 3 synthesis of glycerol carbonate was investigated using different molar ratios of 4 glycerol/DMC. Glycerol (10 g, 108.6 mmol), DMC (19.5-34.3 g, 217.2-380 mmol) and 0.30 5 g of the catalyst were charged into 50 mL round-bottom glass reactor equipped with a magnetic stirrer. Reactions were carried out at 50-90 °C, being those conducted at 6 temperatures higher than 75 °C were performed in a high pressure autoclave reactor. After the 7 completion of the reaction, the catalyst was removed by centrifugation and repeatedly washed 8 with methanol at 45 °C and subsequently dried in an oven at 80 °C for 12 h. The unreacted 9 10 DMC was separated by evaporation at reduced pressure.

Reaction samples were analyzed by gas chromatograph (GC; Shimadzu 2010 plus,
Japan) equipped with a flame ionization detector (FID) and using a ZB5-HT capillary column
(30 m × 0.25 mm × 0.25 µm). Samples for analysis were prepared by extending 50 mg of the
DMC-free reaction sample in 1 mL of methanol. The column temperature was initially set at
75 °C (2 min) followed by ramping of 25 °C/min to 225 °C and then heating to 275 °C at 10
°C/min. The FID and injection temperatures were fixed at 250 °C and 220 °C, respectively.
Helium at 1.3 ml/min was used as carrier gas. The injection split ratio was 20.

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#### 19 3. Results and discussion

- 20 3.1 Catalysts Characterization
- 21 *3.1.1 Textural properties and surface basicity (base amount)*

Table 1 presents the textural characteristics (BET surface area, pore volume, and average pore size) of selected  $Mg_{1+x}Ca_{1-x}O_2$  catalyst samples. According to the obtained results, it revealed that the values of BET surface area of Mg-Ca catalyst samples varied from 9.33 to 31.7 m<sup>2</sup> g<sup>-1</sup> and those of pore volumes are close to 0.09 cm<sup>3</sup> g<sup>-1</sup>. It was observed that

the surface area decreases as the amount of Ca in the catalyst increase, which could be
 attributed to the increased crystallite size of the catalyst by increasing the Ca content [26].

Indeed, all the tested catalysts exhibited low values of surface area which could merely be attributed to the high calcination temperature (850 °C) that enhanced the sintering of fine crystals and lead to the agglomeration of them onto the pore walls [27]. These agglomerates could contribute to the partial occlusion of the pores and thereby the reduction of the surface area of the catalyst. Moreover, Taufiq-Yap and coworkers reported that the excessive presence of CaO phases causes the unfavored filling of the surface pores, which logically result in the reduction of the total surface area [26].

On the contrary, the textural properties (BET surface area and pore volume) marginally increased by increasing the Mg content, which can be ascribed to the ameliorated crystal phase of the catalyst. This observation is corroborated with the physical elucidation reported in literature [28]. The catalyst formulation  $Mg_{1.2}Ca_{0.8}O_2$  exhibited BET surface area of 31.7 m<sup>2</sup> g<sup>-1</sup> and pore volume of 0.091 cm<sup>3</sup> g<sup>-1</sup>, that are better than those obtained with the former catalyst formulation  $(Mg_{1-x}Ca_{1+x}O_2)$ .

16 Fig.1a & b are the obtained Nitrogen physisorption isotherms of two different catalyst 17 samples (Mg<sub>1</sub>  $_{2}Ca_{0,8}O_{2}$  and Mg<sub>0.8</sub>Ca<sub>1.2</sub>O<sub>2</sub>) investigated in this work. It is evidently clear that 18 all the obtained isotherms of type IV with type H2 hysteresis loops, which are the 19 characteristics of mesoporous materials [29]. This type of hysteresis loops represents the pore 20 structure, size and shape of materials which have disordered distributions. At a relative 21 pressure range from 0.45 to 1.0, the isotherms for both catalysts exhibited the typical 22 hysteresis loops of highly mesoporous materials. A distinguished feature is observed in the isotherm of the Mg<sub>1.2</sub>Ca<sub>0.8</sub>O<sub>2</sub> sample, which is the total volume of N<sub>2</sub> adsorbed. That is 23 24 apparently shown by the corresponding values of Y-axis in each plot, and explains the higher 25 N<sub>2</sub> adsorption in larger pore volume than smaller one.

1 The base amount of the prepared catalysts was evaluated and the results are also 2 presented in Table 1. It revealed that the base amount increases with increasing the MgO content in the catalyst, i.e., it increased in the trend of  $Mg_{0.8}Ca_{1.2}O_2 < Mg_{1.2}Ca_{0.8}O_2$  < 3  $Mg_{1,8}Ca_{0,2}O_{2}$ . For all the Ca-Mg combinations, the base amount was found to be higher than that of 4 5 bulk MgO and CaO. The improved base amount might be ascribed to the synergistic effect between 6 MgO and CaO [30]. The decrease in base amount with increasing CaO content could partly be 7 attributed to the structural changes caused by the high amount of calcium, which led to partial damage 8 of the binary oxide structure [26]. These results strongly suggest that the combination of both oxides 9 has resulted in materials with higher alkalinity, which could be of higher catalytic activity than pure 10 oxides. Despite the fact that the catalyst formulation Mg<sub>1.8</sub>Ca<sub>0.2</sub>O<sub>2</sub> has possessed higher base amount than Mg<sub>1.2</sub>Ca<sub>0.8</sub>O<sub>2</sub> catalyst, but their catalytic activity during the transesterification reaction has 11 12 increased in reverse trend. This suggest that the base amount is not the only factor controlling the 13 catalytic activity of these materials. These results are corroborating with several scientists [26, 31, 14 32], as they observed that stronger base amount of Ca–Mg binary system than pure oxides and the catalytic activity mainly depends on the nature of the active sites rather than the base amount. 15

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#### 17 *3.1.2 CO*<sub>2</sub>*-TPD*

Fig.2 shows the TPD-CO<sub>2</sub> profiles of CaO, MgO and the mixed metal oxide catalyst 18 samples (Mg<sub>0.8</sub>Ca<sub>1.2</sub>O<sub>2</sub> and Mg<sub>1.2</sub>Ca<sub>0.8</sub>O<sub>2</sub>), and the desorbed amounts CO<sub>2</sub> of are listed in 19 Table 1. Pure magnesium oxide shows weak desorption band between 450 and 600 °C, 20 21 whereas pure calcium oxide present a very broad desorption band extending from 480 to 660 22 °C. The mixed oxide catalysts present a broad desorption band between 450 to 700 °C, which 23 was noticed to enlarge as the amount of MgO in the catalyst increased, and another smaller 24 desorption peak at about 735 °C. According to the literature [32], the very broad desorption 25 band located between 450 and 700 °C might be ascribed to the interaction of CO<sub>2</sub> with basic

sites of weak and medium strength, mainly associated with  $Mg^{2+}-O^{2-}$  pairs, for which the basic strength is very high. Whereas the well-resolved desorption peak at about 735 °C can be associated to  $Ca^{2+}-O^{2-}$  pairs. It is observed that the base amount increases with increasing MgO content in the mixture. The findings of Taufiq and co-workers were considered to interpret the obtained desorption profiles [26].

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#### 7 3.1.3 X-ray diffraction (XRD)

8 Fig.3a depicts the powder X-ray diffraction patterns of Mg-Ca catalyst samples after 9 calcination at 850 °C. The patterns were recorded for tow reversed catalyst samples with 10 varied metallic content, Mg<sub>1,2</sub>Ca<sub>0,8</sub>O<sub>2</sub> and Mg<sub>0,8</sub>Ca<sub>1,2</sub>O<sub>2</sub>, to estimate the effect of metallic content on the crystallographic phases. The typical peaks of the separate metal oxide 11 12 crystalline phases and that of mixed metal oxides were obviously detected in the obtained 13 patterns [33]. The presence of both oxides has been proven by the characteristic peaks of cubic CaO ( $2\theta = 32.3^{\circ}$ ,  $37.2^{\circ}$  and  $78.9^{\circ}$ ) and hexagonal MgO ( $2\theta = 42.7^{\circ}$  and  $63.0^{\circ}$ ). The 14 catalyst formulation Mg<sub>0.8</sub>Ca<sub>1.2</sub>O<sub>2</sub> showed a higher degree of crystallinity of CaO as it 15 contained higher Ca<sup>+2</sup> amount than the catalyst formulation Mg<sub>1.2</sub>Ca<sub>0.8</sub>O<sub>2</sub>, indicated by the 16 17 increased intensity of the corresponding peaks. As such, the typical MgO peaks were decreased as the Ca<sup>+2</sup> content increased. It is worthy to mention that the presence of calcium 18 19 carbonate as calcite in the  $Mg_{0.8}Ca_{1.2}O_2$  sample was detected by the low intensity peak 20 located at  $2\theta = 29.4^{\circ}$ . It is well established that the formation of CaCO<sub>3</sub> is possible as the CO<sub>2</sub> 21 easily to absorb by CaO and form CaCO3, as indicated by the following equation [34];

22 
$$\operatorname{CaO} + \operatorname{CO}_2 \longrightarrow \operatorname{CaCO}_3 \Delta H = -178.3 \text{ kJ mol}^{-1}$$
 (2)

Fig.3b shows the typical XRD patterns of MgO, CaO and that of Mg<sub>1.8</sub>Ca<sub>0.2</sub>O<sub>2</sub> catalyst sample. It can be clearly seen that pure MgO exhibit two typical XRD peaks at  $2\theta =$ 

1	$42.7^{\circ}$ and $62.3^{\circ}$ , assigned to the cubic and hexagonal crystalline phases [26], respectively.
2	Whereas the XRD pattern of the CaO showed four main peaks located at $2\theta = 17.8^{\circ}$ , $29.2^{\circ}$ ,
3	33.8°, and at 46.9°, assigned to different CaO crystalline phases [26, 34]. Other smaller peaks
4	and shoulders were also observed in the pattern of CaO, possibly ascribed to the presence of
5	CaCO <sub>3</sub> . The XRD pattern of the Mg <sub>1.8</sub> Ca <sub>0.2</sub> O <sub>2</sub> catalyst formulation showed combination of
6	MgO and CaO peaks as follows:
7	1. A sturdy peak at $2\theta = 42.8^{\circ}$ assigned to the cubic MgO phase.
8	2. A lesser intensity peak at $2\theta = 62.1^{\circ}$ assigned mainly to hexagonal MgO.
9	3. A sharp peak at $2\theta = 31.2^{\circ}$ and a shoulder at $2\theta = 31.2^{\circ}$ assigned to cubic CaO.
10	Based on the above argument, the presence of MgO and CaO in the Mg-Ca catalyst
11	samples was observed in the obtained patterns in the form of pure oxides, with no
12	distinguished crystalline phase attributable to the formation of the mixed MgCa oxide was
13	observed, mainly due to the different ionic radii of the $Ca^{2+}$ and $Mg^{2+}$ ions [28]. Therefore,
14	further characterization by FTIR could provide more information and evidences on the
15	formation of mixed metal oxides.
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#### 17 *3.1.4 Fourier transform infrared analysis (FTIR)*

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In order to verify the presence of surface species that were not detected by other techniques, FTIR spectroscopy was used to characterize the as-synthesized Mg-Ca catalyst samples. The spectra were recorded for MgO, CaO,  $Mg_{1.2}Ca_{0.8}O_2$ , and  $Mg_{1.5}Ca_{0.5}O_2$  materials in the range of 4000–400 cm<sup>-1</sup>. Since there was no distinct peaks observed in the range of 3000-2000 cm<sup>-1</sup> for all the characterized materials, the spectra are presented separately in two regions.

1 Fig.4a presents the obtained IR spectra of the prepared catalyst in the range of 2000– 400  $\text{cm}^{-1}$ , while those in the range of 4000–3000  $\text{cm}^{-1}$  are shown in Fig.4b. The spectra of all 2 the tested materials revealed the presence of mono and bidentate carbonates at 1600  $\text{cm}^{-1}$ , 3 which could be ascribed to the absorption of CO<sub>2</sub> by CaO and MgO to form CaCO<sub>3</sub> and 4 MgCO<sub>3</sub>, respectively, as also verified by XRD. The spectrum of MgO shows a distinct peak 5 at 1380 cm<sup>-1</sup>, which was not observed in the CaO spectrum. Therefore, this peak was 6 believed to represent the typical IR response of pure MgO. As such, the pure CaO was 7 identified by the sharp peak at 880  $\text{cm}^{-1}$  in its spectrum. The intensity of those sharp peaks 8 (1380 and 880 cm<sup>-1</sup>) was observed to reduce as the metallic content varied in the catalyst 9 10 formulation Mg<sub>1+x</sub>Ca<sub>1-x</sub>O<sub>2</sub> for both X=0.2 and X=0.5. Thus, the presence of MgCa combined oxides could be assigned by the broad band in the  $1400-1600 \text{ cm}^{-1}$  region and by the 11 appearance of the sharp peaks at 1380 and at 880 cm<sup>-1</sup> with reduced intensities. In addition, 12 the spectrum of the mixed oxide catalysts shows two distinct peaks at 3610 and 3640  $\text{cm}^{-1}$ , 13 14 that can be ascribed to the  $v_{OH}$  of surface hydroxyl groups (Mg–OH) and (Ca–OH), 15 respectively. In the spectra of all catalysts, the presence of the physisorbed water molecules is noticed by the wide bands at 3450 and 1583 cm<sup>-1</sup>. The interpretation of the obtained FTIR 16 17 peaks was correlated with the confirmed arguments in the literature [26, 28].

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#### 19 3.1.5 Surface morphology

Fig.5a shows the SEM micrograph of the  $Mg_{1,2}Ca_{0,8}O_2$  catalyst sample calcined at 850 °C, whereas Fig.5b for the same sample calcined at 700 °C. The micrographs show the textural structure of the catalyst with cuboids clusters, which belong to the metallic oxides. It can be observed that the size of these cuboids reduced as the calcination temperature increased, which can be explained due to the destruction of bigger crystals into agglomerated fine crystals and thereby the formation of smaller cuboids. In addition, the obtained images

revealed the porous nature of the catalyst, which is believed to be one the reasons behind its
high performance during the transesterification of glycerol with DMC. The conclusions made
from SEM images are corroborating with the results of BET analysis and are in good
agreement with those for nano-sized MgO and CaO reported in the literature [12].

5 On the other hand, the porous structure of the catalyst was evidenced by means of 6 TEM analysis. The obtained TEM images are shown in Fig.6a & b for the same catalyst 7 samples calcined at 700 °C and 850 °C, respectively. It is evidently clear that the porosity of 8 the catalysts increases with increasing the calcination temperature. This might be explained 9 by the changes of the crystallite phases accompanied by the modification of the surface pores 10 due to the thermal treatment.

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#### 12 3.1.6 Elemental composition of the synthesized catalyst

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14 The elemental composition of Mg<sub>1.2</sub>Ca<sub>0.8</sub>O<sub>2</sub> catalyst was determined by using an 15 energy dispersive X-ray detection technique (EDX) conducted in conjunction with SEM 16 analysis. The knowledge of actual metallic content in the catalyst can provide additional verification to the role of  $Mg^{+2}$  and  $Ca^{+2}$  in enhancing the catalytic performance. The results 17 18 obtained from EDX analysis unveiled that the catalyst formulation Mg<sub>1.2</sub>Ca<sub>0.8</sub>O<sub>2</sub> contained 19 33.25 at.% Mg, 24.64 at.% Ca and 42.1 at.% O. The theoretical values for the atomic 20 percentage (at.%) were 30 at.% Mg, 20.24 at.% Ca and 48.76 at.% O, as calculated using the 21 atomic ratio formula.

The difference between the theoretical and actual values for the metallic content is logical and could be attributed to the precipitation conditions of the metal oxides from their nitrates, as the preparation used ammonia solution to maintain the pH value close to 10. The

values obtained from this analysis depend mainly on the proportions by weight of each
 contributing component.

3

#### **3.2** *Catalytic activity*: *Transesterification of glycerol with DMC*

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6 In this work, the catalytic activity of the synthesized pure and mixed oxide catalysts 7 was defined by means of glycerol conversion and glycerol carbonate (GC) yield. Different 8 Mg-Ca catalysts were prepared based on the various chemical formulae of the possible metals 9 combinations. The results presented in Table 2 are the conversion of glycerol and the GC10 yield obtained after 90 min of reaction for the prepared Mg-Ca catalysts. It is obvious that 11 MgO has presented higher value of glycerol conversion and lower GC yield than CaO. The 12 formation of byproducts (methanol and high boiling point diols) was observed and could be 13 attributable to the selective behavior of CaO species in the tested catalysts. Thus, the 14 continuous removal of the by-produced methanol resulted in high yield of GC with low molar 15 ratio of DMC/glycerol, as also observed by Li and Wang [13]. Therefore, two catalyst 16 formulae were proposed in this study; the first suggests the increase of Ca content; and the 17 second with increased Mg content. As the Ca content increases in the first catalyst formula, 18  $Mg_{1-x}Ca_{1+x}O_2$ , the GC yield was found to decrease. This behavior suggests that Ca is 19 responsible on the selective formation of GC, whereas Mg enhances the conversion of glycerol. 20

On the contrary, in the second formula,  $Mg_{1+x}Ca_{1-x}O_2$ , catalyst samples with decreased Ca content presented high values of glycerol conversion and *GC* yield. This was not true for the case of  $Mg_{1.8}Ca_{0.2}O_2$  and  $Mg_{1.9}Ca_{0.1}O_2$  catalysts, as they showed decreased values of *GC* yield as the Ca amount decreased. This might be explained by encapsulation of the Ca by Mg species due to the higher amount of the latter. The obtained results using the

1 binary oxide catalysts (for both formulae) are stratifying with those obtained using each of 2 the oxides separately as heterogeneous catalyst. It was also figured out that GC yield 3 increases with surface area and pore volume increase in the trend of Mg<sub>0.8</sub>Ca<sub>1.2</sub>O<sub>2</sub> < 4  $Mg_{1.8}Ca_{0.2}O_2 < Mg_{1.2}Ca_{0.8}O_2$  (as shown in Table 2 and earlier shown in Table 1). This 5 observation is not correlating with the increase in base amount, as one can see that 6 Mg<sub>1.8</sub>Ca<sub>0.2</sub>O<sub>2</sub> possessed the highest base amount of 1519 µmol/g but showed lower value of 7 GC yield than Mg<sub>1.2</sub>Ca<sub>0.8</sub>O<sub>2</sub> catalyst. Therefore, it seems logical not to attribute the catalytic 8 activity to the catalyst base amount only, but to other characteristics as well. Out of all the 9 formulae tested, the catalyst formulation  $Mg_{1,2}Ca_{0,8}O_2$  presented complete conversion of 10 glycerol with almost 100% yield of GC. To this end, this catalyst was selected for further 11 investigations of its catalytic performance.

12 On the other hand, the catalytic activity of the prepared catalysts was compared with 13 that of conventional hydrotalcite (HT) under the same reaction conditions. It was found that 14 HT possesses lower catalytic activity than most of the tested Mg<sub>1+x</sub>Ca<sub>1-x</sub>O<sub>2</sub> catalyst series. 15 Over 0.30 g of HT, glycerol conversion was about 48% and the GC yield was 46.7% after 90 16 min. As the reaction time was prolonged to 2 h, GC yield has reached to 68%. This could be 17 explained by the role of Mg-Al interactions in the HT structure. Takagaki *et al.* have studied 18 the relationship between the GC yield and the Mg/Al ratio [35]. They observed that synthetic 19 HT with Mg/Al ratio of 5 (close to that of conventional hydromagnesite) has higher catalytic 20 activity than other samples with Mg/Al ratio of less than 5. They attributed the catalytic 21 activity to the HT structure and correlated the activity with the base amount of the catalysts.

The metallic interaction is evidently responsible for the high *GC* yield (100%) obtained over the mixed oxide catalyst (Mg<sub>1.2</sub>Ca<sub>0.8</sub>O<sub>2</sub>). On the contrary, the pure metallic oxides showed a poor *GC* yield, as earlier presented in Table 2. This could also be confirmed by the varied values of glycerol conversion and *GC* yield obtained over a series of catalysts

with varied Mg and Ca content. As the Mg/Ca ratio was changed, their synergistic interaction led to catalysts with varied porous structure as would be noticed by the results of BET analysis. The porous structure is thought to be enhanced by the Mg<sup>+2</sup> that form MgO clusters masking the backbone of the catalyst structure. In fact, this could physically be explained by the fact that the ionic radius of Mg atom (150 pm) is slightly bigger than that of Ca atom (114 pm) and thereby the crystallite sizes of their oxides will be accordingly ordered.

After the preliminary evaluation of the catalytic performance, further investigations
were performed to study the effect of different reaction parameters on the conversion of
glycerol and the corresponding *GC* yield.

10 *3.3 Effect of reaction parameters* 

#### 11 *3.3.1 Effect of calcination temperature*

12 The investigations on the catalytic performance of the Mg<sub>1.2</sub>Ca<sub>0.8</sub>O<sub>2</sub> catalyst were 13 moved to examine the effect of calcination temperature on the conversion of glycerol and GC 14 yield. In this context, series of  $Mg_{12}Ca_{0.8}O_2$  catalyst samples were calcined at different 15 temperatures (700-900 °C). Fig.7 shows the results of glycerol conversion and GC yield 16 obtained using these catalysts calcined at varying temperatures and dwelling time (4 and 6 h). 17 The results showed that calcination temperature is a key factor affecting the performance of 18 the catalyst. The conversion of glycerol increased from 41% to 77% as the calcination 19 temperature changed from 700 °C to 850 °C for catalyst sample calcined for 4 h dwelling. 20 Increasing calcination dwelling time to 6 h resulted in a catalyst sample with improved 21 performance, as evidenced by the results of catalytic performance for catalyst samples 22 calcined at different temperatures but dwelled for 6 h. An increase in GC yield was observed 23 with further increase in the calcination temperature and time, indicating the role that these 24 parameters played in GC production. Further increasing the calcination temperature to 900 °C 25 resulted in a catalyst sample with decreased catalytic activity, which can be explained due to

the probable constriction of surface pores occurred by the effect of the gaseous diffusion out of the pores during the thermal treatment. Another possible reason for the reduced activity is the partial removal of the binding water molecules from the catalyst structure, that could possibly lead to the destruction of the binary oxide system and thereby the formation of unknown species of those metals (Mg and Ca).

6 It was also found that the calcination time and temperature applied during the 7 preparation of the  $Mg_{1,2}Ca_{0,8}O_2$  catalyst have affected the catalytic activity dramatically, as 8 this catalyst was shown to be more efficient when calcined at 850 °C for 6 h. In the following 9 catalytic studies, the influence of different reaction parameters such as catalyst amount, the 10 molar ratio of glycerol/DMC, reaction temperature, and reaction time was also studied in 11 response to the conversion of glycerol and *GC* yield.

12

#### 13 3.3.2 Effect of catalyst amount

14 In this study, the effect of catalyst amount on the transesterification profile (glycerol 15 conversion and GC yield) was investigated. The catalyst amount varied between 0.1–0.50 g 16 (0-5 wt.% with respect to glycerol amount), whereas the other reaction were fixed, i.e. molar ratio of 1:2, reaction temperature of 70 °C, and reaction time of 90 min. According to Fig.8, it 17 18 is clear that the addition of catalyst enhanced the conversion of glycerol and ameliorated the 19 yield of GC. A linear increase in glycerol conversion and the GC yield was observed by the 20 effect of the incremental amounts of catalyst added, due to the increase in the number of 21 accessible active sites over the catalyst surface that participate in the catalysis process. Over 22 0.40 g of Mg<sub>1.2</sub>Ca<sub>0.8</sub>O<sub>2</sub> catalyst, glycerol was completely converted and the yield of GC was 23 100%. It was noticed that further increase in the catalyst amount beyond 0.40 g did not 24 influence the conversion of glycerol and GC yield, which explain the stability of this catalyst 25 against the possible emulsification of the solid-liquid mixture. The obtained results are in 26 good agreement with those reported in literature [20]. The observed stability of  $Mg_{1,2}Ca_{0,8}O_2$ 

catalyst structure against the emulsification by the co-produced methanol is not surprising,
 since it has found by XRD analysis that this catalyst has a highly crystalline cohered
 structure.

4 5

3.3.3 Effect of reaction temperature and the molar ratio of glycerol/DMC

6 The effect of temperature on the transesterification of glycerol with DMC was 7 investigated by carrying out the reaction at varying temperatures (50 to 80 °C). Whereas the 8 effect of molar ratios of glycerol/DMC was studied in conjunction with that of temperature 9 by using two molar ratios; 1:1 and 1:2. Fig.9 shows the obtained results of glycerol 10 conversion and GC yield at different temperatures and molar ratios. Since the 11 transesterification of glycerol with DMC is a reversible reaction, excess DMC was required 12 to shift the equilibrium towards the GC formation. It can be seen that the obtained values of 13 conversion and GC yield using 1:1 molar ratio were less than those obtained using a molar 14 ratio of 1:2 at the same reaction temperatures, which explain the role of the excess DMC in 15 shifting the forward reaction.

Generally, the conversion was observed to steadily increase as the temperature increases at both of the tested molar ratios. This behavior could be explained by the dependence of the reaction rate on temperature. In such a case, the reaction can perform faster as the temperature increased and this situation not only increases the contacting properties but also the *GC* yield as well. In the case of using a molar ratio of 1:2, the conversion of glycerol attained its maximum value of 100% at 70  $^{\circ}$ C, which can be considered as the least among the reported studies [16-18, 23, 35, 36].

23

#### 24 3.3.3 Effect of reaction time

In accordance with the investigations made and discussed earlier, the transesterification of glycerol with DMC over  $Mg_{1.2}Ca_{0.8}O_2$  catalyst was studied at varying

1 reaction duration and the obtained results and shown in Fig.10. The figure revealed the effect 2 of time when it is increased to achieve higher glycerol conversion and GC yield. It was 3 observed that the conversion of glycerol substantially increased from 37% to 81% as the 4 reaction time elongated from 30 to 60 min. The highest conversion close to 100% was 5 achieved after 90 min, a time at which the reaction was shifted to completion as the obtained 6 GC yield was 100%. Further increasing the reaction time beyond 90 min did not influence 7 glycerol conversion, but resulted in a slight decrease of GC yield which is attributed to the 8 solubility effect of the co-produced methanol.

9 The activity of the synthesized catalyst was compared to other heterogeneous 10 catalysts reported in previous studies (pure MgO and CaO) and it was found that the 11 synergistic interactions of the metal anions Mg and Ca played a key role in the observed 12 activity of the mixed oxides formulation Mg<sub>1,2</sub>Ca<sub>0,8</sub>O<sub>2</sub>. Ochoa-Gomez and coworkers 13 reported transesterification of glycerol with DMC over a heterogeneous CaO catalyst [6]. 14 They obtained complete glycerol conversion with a corresponding GC yield of 95% by using a molar ratio of glycerol/DMC of 1:3.5 and performing the reaction at 95 °C for 1.5 h. Thus, 15 the present work emphasized on improving the leaching of the  $Ca^{+2}$  species from the CaO 16 17 catalyst by masking it with MgO crystals and thereby economizing the operational conditions. In this work, glycerol was completely converted to GC by using a molar ratio of 18 glycerol/DMC of 1:2 and running the reaction at 70 °C for 90 min. 19

20

21 3.4 Catalyst stability tests

22

The stability of the catalytic activity of  $Mg_{1.2}Ca_{0.8}O_2$  catalyst was examined by testing the leaching and the reusability. In order to justify the use of mixed metallic oxides as a catalyst rather than using either of them, the leaching test was performed for CaO and  $Mg_{1.2}Ca_{0.8}O_2$  catalysts to show the improved leaching properties. The leaching of the metallic

1 species was tested according to the hot filtration method, where a mixture of the solid catalyst 2 (0.30 g) and DMC (18.2 mL) was heated to the reaction temperature of 70 °C under constant 3 stirring for 90 min. Afterwards, the catalyst was removed and 8 mL of glycerol was added to 4 the residual DMC. The liquid mixture was then subjected to same reaction conditions 5 described above and the values of glycerol conversion and GC yield were accordingly 6 determined and compared to those obtained from uncatalyzed experiment. It was found that 7 CaO catalyst suffered of leaching to about 21.8%, whereas Mg<sub>1,2</sub>Ca<sub>0,8</sub>O<sub>2</sub> catalyst suffered of 8 7.4% leaching of its active metallic species. It is therefore clear that the combination of MgO 9 with CaO resulted not only in increasing the base amount of the latter but also improved the stability of the Ca<sup>+2</sup> species. 10

11 On the other hand, the recyclability of the Mg<sub>1.2</sub>Ca<sub>0.8</sub>O<sub>2</sub> catalyst was examined by utilizing it in four consecutive batch runs. The catalyst was removed after each catalytic 12 13 experiment and regenerated by washing it thoroughly with methanol and drying it in an oven at 75 °C for 4 h. Fig.11 presents the results of glycerol conversion and GC yield obtained 14 15 from four successive transesterification experiments using the regenerated Mg<sub>1.2</sub>Ca<sub>0.8</sub>O<sub>2</sub> 16 catalyst. The results revealed that this catalyst is reliably reusable with no appreciable 17 decrease in its activity. The stability of the catalytic activity of this catalyst during the 18 transesterification of glycerol is attributed to the well organized crystallite structure of its phases which resulted in stabilizing the metallic species of Mg<sup>+2</sup> and Ca<sup>+2</sup>, as also confirmed 19 20 by leaching test. Therefore, it is highly recommended to commercialize this catalyst for 21 industrial scale production of the valuable glycerol carbonate.

The spent  $Mg_{1,2}Ca_{0,8}O_2$  catalyst was also characterized to inspect the changes in its textural and structural properties after the fourth recycle. The BET surface area was found to decrease by 4%, the pore volume by 2% and the base amount by 1.3% (Table 1). This change is associated with the change of catalyst color from white to beige and might be ascribed to

the presence of some of the unreacted glycerol molecules that were not removed by methanol washing. In general, the decrease in surface properties is marginal and lead to the conclusion that this catalyst is stable under the transesterification conditions. Also, FTIR characterization of the spent catalyst unveiled the preservation of the intrinsic chemical bonding within the structure. Moreover, XRD analysis confirmed the stability of the crystalline structure of the spent Mg<sub>1.2</sub>Ca<sub>0.8</sub>O<sub>2</sub> catalyst. Thus, the reusable behavior of this catalyst (Fig.11) could be mainly attributed to its structural stability under the reaction conditions.

8

#### 9 4. Conclusions

It can be concluded that Mg<sub>1+x</sub>Ca<sub>1-x</sub>O<sub>2</sub> mixed oxides are an efficient catalyst for the 10 11 transesterification of glycerol with dimethyl carbonate (DMC) to synthesize glycerol 12 carbonate. The catalytic textural properties and the synergistic interaction between Calcium 13 and Magnesium were observed to influence the catalytic performance. The investigations 14 unveiled that the activities of bulk CaO and MgO were lower than that of bimetallic mixed 15 oxide catalysts, as they gave lower yields of glycerol carbonate when subjected to the 16 transesterification process under the same conditions. The characterization results of FTIR 17 XRD, and EDX indicated the presence of combined metallic oxides at the preferred loading. 18 The Mg-Ca catalysts' activity depends mainly on the mass ratio of the metals and the 19 calcination temperature, being the catalyst Mg<sub>1.2</sub>Ca<sub>0.8</sub>O<sub>2</sub> with Mg:Ca mass ratio of 1:1.1 and 20 calcined at 850 °C was the most active due to the presence of strong basic sites. Over 0.30 g 21 of this catalyst, the complete conversion of glycerol with corresponding 100% yield of 22 glycerol carbonate were achieved using a molar ratio of glycerol/DMC of 1:2 at 70 °C and 23 after 90 min. The yield of glycerol carbonate also depends upon the metallic content within 24 the catalyst structure and the reaction conditions.

25

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9	Schem	e caption
10	Scheme	e1: Transesterification of glycerol with dimethyl carbonate.
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12	Figure	e captions
13	Fig.1	Nitrogen physisorption isotherms for mixed Mg-Ca oxide catalysts.
14		
15	Fig.2	TPD-CO <sub>2</sub> of pure and mixed metal oxides catalysts (CaO, MgO, Mg <sub>0.8</sub> Ca <sub>1.2</sub> O <sub>2</sub> and $M_{2.2}$ CaO, MgO, MgO, MgO, MgO, MgO, MgO, MgO, Mg
16		$Mg_{1,2}Ca_{0,8}O_2).$
17	Fig.3	a) XRD patterns of Mg-Ca catalyst samples; (a) $Mg_{1.2}Ca_{0.8}O_2$ ; (b) $Mg_{0.8}Ca_{1.2}O_2$ ; (c)
18		spent $Mg_{1,2}Ca_{0,8}O_2$ .
19		<b>b)</b> XRD patterns of MgO, CaO, Mg <sub>1.8</sub> Ca <sub>0.2</sub> O <sub>2</sub> .
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21	Fig.5	Scanning electron micrograph images of $Mg_{1,2}Ca_{0,8}O_2$ catalyst calcined at; (a) 850
22		°C; (b) 700 °C.
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25		different temperatures (700–900 °C) and times (4–6 h).
26	Fig.8	Effect of catalyst amount on glycerol transesterification with DMC. Reaction
27		conditions: catalyst amount: 0.30 g; molar ratio of glycerol/DMC: 1:2; reaction
28		temperature: 70 °C; reaction time : 90 min.

Fig.9 Effect of reaction temperature on glycerol transesterification with DMC studied at
 two molar ratios of glycerol/DMC (1:1 and 1:2). Reaction conditions: catalyst
 amount: 0.30 g; reaction time: 90 min.

- 4 Fig.10 Effect of reaction time on the transesterification of glycerol with DMC. Reaction
  5 conditions: catalyst weight: 0.30 g; molar ratio of glycerol/DMC: 1:2; reaction
  6 temperature: 70 °C.
- Fig.11 Reusability test of Mg<sub>1.2</sub>Ca<sub>0.8</sub>O<sub>2</sub> catalyst during the transesterification of glycerol
  with DMC. Reaction conditions: catalyst amount: 0.30 g; molar ratio of
  glycerol/DMC: 1:2; reaction temperature: 70 °C; reaction time: 90 min.

#### 10 List of Tables:

- **Table 1.** BET surface area, total pore volume, average pore diameter and base amount
  of the synthesized Mg-Ca catalysts.
- 13
- Table 2. Catalytic activity of different heterogeneous catalysts employed in glycerol
   transesterification with DMC. Reaction conditions: Catalyst weight: 0.3 g;
   molar ratio of glycerol/DMC:1:2; reaction temperature: 70 °C; reaction time: 90
   min.
- 18













Fig. 4

4



2







![](_page_36_Figure_1.jpeg)

![](_page_37_Figure_1.jpeg)

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## Table 1

1	
2	

Catalyst formulation	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Total pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Average pore diameter (nm)	Base amount (µmol/g)
CaO	2.7	0.002	15.7	595
MgO	24.7	0.081	11.2	739
$Mg_{0.2}Ca_{1.8}O_2$	13.5	0.053	10.6	844
Mg <sub>0.5</sub> Ca <sub>1.5</sub> O <sub>2</sub>	8.6	0.062	9.8	968
$Mg_{0.8}Ca_{1.2}O_2$	9.3	0.086	13.7	1032
$Mg_{1.2}Ca_{0.8}O_2$	31.7	0.091	9.4	1486
Mg <sub>1.2</sub> Ca <sub>0.8</sub> O <sub>2</sub> R*	30.4	0.089	9.1	1467
$Mg_{1.8}Ca_{0.2}O_2$	23.8	0.075	10.3	1519

-

### 1 Table 2

Catalyst	X	Chemical	Glycerol	% <i>GC</i>
		formula	conversion (%)	yield
		MgO	94	23
		CaO	79	68
	0.1	Mg <sub>0.9</sub> Ca <sub>1.1</sub> O <sub>2</sub>	76	75.4
	0.2	Mg <sub>0.8</sub> Ca <sub>1.2</sub> O <sub>2</sub>	71	70.3
	0.3	Mg <sub>0.7</sub> Ca <sub>1.3</sub> O <sub>2</sub>	70	70
	0.4	Mg <sub>0.6</sub> Ca <sub>1.4</sub> O <sub>2</sub>	54	54
	0.5	Mg <sub>0.5</sub> Ca <sub>1.5</sub> O <sub>2</sub>	50	48.5
$Mg_{1-x}Ca_{1+x}O_2$ Series	0.6	Mg <sub>0.4</sub> Ca <sub>1.6</sub> O <sub>2</sub>	41	40
	0.7	Mg <sub>0.3</sub> Ca <sub>1.7</sub> O <sub>2</sub>	35	33.8
	0.8	Mg <sub>0.2</sub> Ca <sub>1.8</sub> O <sub>2</sub>	25	23.9
	0.9	Mg <sub>0.1</sub> Ca <sub>1.9</sub> O <sub>2</sub>	19	18.3
	0.1	Mg <sub>1.1</sub> Ca <sub>0.9</sub> O <sub>2</sub>	91	87.5
	0.2	Mg <sub>1.2</sub> Ca <sub>0.8</sub> O <sub>2</sub>	100	100
	0.3	Mg <sub>1.3</sub> Ca <sub>0.7</sub> O <sub>2</sub>	93	89.4
	0.4	Mg <sub>1.4</sub> Ca <sub>0.6</sub> O <sub>2</sub>	94	93.7
Mg <sub>1+x</sub> Ca <sub>1-x</sub> O <sub>2</sub> Series	0.5	Mg <sub>1.5</sub> Ca <sub>0.5</sub> O <sub>2</sub>	92	91.3
	0.6	Mg <sub>1.6</sub> Ca <sub>0.4</sub> O <sub>2</sub>	85	84.5
	0.7	Mg <sub>1.7</sub> Ca <sub>0.3</sub> O <sub>2</sub>	83	82.6
	0.8	Mg <sub>1.8</sub> Ca <sub>0.2</sub> O <sub>2</sub>	72	71.4
	0.9	Mg <sub>1.9</sub> Ca <sub>0.1</sub> O <sub>2</sub>	63	62.3

2

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1	!! Mg <sub>1.2</sub> Ca <sub>0.8</sub> O <sub>2</sub> mixed oxides is an efficient catalyst for glycerol transesterification.
2	!! Complete glycerol conversion with 100% yield of glycerol carbonate were achieved.
3	!! The glycerol carbonate yield depends on the metals content and reaction conditions.
4	!! Catalyst surface basicity plays a key role in promoting the catalytic activity.
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6	5
7	