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Magnesia-ceria mixed oxide catalysts for the selective transesterification of glycerol to glycerol carbonate

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ABSTRACT

MgO-CeO_2 catalysts were investigated for selective synthesis of glycerol carbonate by glycerol transesterification with dimethyl carbonate as carbonating source. Co-precipitation technique was used to prepare Mg-Ce oxides by with different molar ratios. Samples characteristics were derived by N_2 adsorption, XRD, FE-SEM, TGA-DTA and CO_2 -TPD. The catalysts surface structural properties and basicity were directed by the composition of oxides and treatment temperature. The sample with 3:1 Mg/Ce ratio exhibited highest basicity. The same catalyst treated at a temperature of 650 °C, exhibited highest glycerol carbonate yield of 86%. The reaction conditions were also optimized.

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1. Introduction

Glycerol, a by-product obtained during the production of biodiesel. It was anticipated that about four billion gallons of glycerol could be produced by biodiesel industry. This will encourage to use glycerol as source as the cost of glycerol will substantially decrease in the market [1–3]. This led to find different glycerol applications for the preparation of variety of value added chemical compounds [4]. Among the possible chemicals, glycerol carbonate (GLC) is a useful chemical from glycerol as it has potential applications like gas separation, monomer of poly carbonate, green solvent, co-solvent in Li-ion batteries etc. [5].

Various approaches have been employed to synthesize GLC from glycerol. Different carbonate source such as phosgene, CO, CO_2, urea and alkyl carbonates [5–8] was used for this reaction. The carbonylation of glycerol with phosgene or carbon monoxide is a traditional method, but it has been in practice due to the high toxicity of reactants. Recently urea, alkyl carbonates and CO2 have been used as carbonate sources. Using CO_2 as a carbonate source for the synthesis of GLC is ideal approach. However, this method is limited due to difficulty in activating CO_2 and the overall activity is very limited. In case of urea, the by-product NH_3 needs to be removed continuously during the reaction. The transesterification of glycerol with dialkyl carbonate is important route to prepare GLC as these carbonate source is better than compared to other carbonate sources.

Glycerol transesterification can be conducted by using base catalysts under homogeneous or heterogeneous conditions. Homogeneous bases, such as KOH, NaOH, and K_2CO_3, were active catalysts for glycerol transesterification. However, homogeneous catalysts have certain drawbacks [9]. Lipase Novozym 435, a enzymatic heterogeneous catalyst, reported for GLC synthesis [10]. Unfortunately, as for now this system is suffering from many drawbacks, such as high cost, poor activity and long reaction time.

Heterogeneous catalysts such as, Mg–Al hydrotalcite [11], Mg/La mixed oxide [12], KF modified hydroxyapatite [13], CaO [9], CaO/Al_2O_3 [14], $Mg_{1+x}Ca_{1-x}O_2$ [15], $KF/\gamma\text{-}Al_2O_3$ [16], $NaOH/\gamma\text{-}Al_2O_3$ [17], and K_2CO_3/MgO [18] have been scrutinized for GLC synthesis. Recently, mixed oxides have been broadly applied as solid base catalysts for GLC synthesis as these materials posses strong basicity with large surface area compared to single metal oxides [19].

Among base metal oxides, magnesium oxide received much attention as a basic catalyst and support. Even though MgO is known for high basicity, many drawbacks like low reusability and less stability were associated. To overcome the difficulties associated with MgO, different mixed oxides have been prepared [20–29].

Ceria a wonderful metal oxide with wide applications particularly in catalysis studied extensively in recent years. CeO_2 is an imperative metal oxide due to its distinctive acid-base and redox

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Table 1
Physico-chemical properties of MgO-CeO_2 catalysts.

Catalyst	BET surface area (m^2/g)	Total basicity (mmol/g)		
		Weak (100–250 °C)	Medium (250–400 °C)	Strong (400–800 °C)
Mg1Ce1	60	–	–	0.191
Mg2Ce1	85	0.016	–	0.198
Mg3Ce1	122	0.002	–	0.289
Mg1Ce2	74	0.159	0.035	–
MgO	27	–	0.051	0.030
CeO_2	42	–	–	0.022

properties [30]. It is frequently used as support or catalyst. CeO_2 as solid catalyst, showed exceptional activity in some reactions, such as alkylation [31], reduction of carboxylic acid [32] and alcohols dehydration [33]. Recently, CeO_2 was employed as catalyst to prepare diverse cyclic carbonates from CO_2 and diols [34]. Modification of ceria with other metal/metal oxide by substitution into its lattice to form mixed oxide is a better approach to modify the catalytic properties. The structural- electronic property of metal can be varied by the blend of two metals, subsequently favouring its activity and selectivity. It is anticipated to develop Mgo-CeO_2 based mixed oxides to tune their catalytic properties towards the preparation of glycerol carbonate by glycerol transesterification.

In the current work, a set of Mg/Ce mixed oxides were synthesized and their catalytic activity was evaluated for glycerol transesterification with DMC. DMC is substitute for conventional toxic and poisonous reagent such as phosgene and carbon monoxide. Moreover, because of its low toxicity, medium volatility, and high polarity. The effects of Mg/Ce ratio and treatment temperature were investigated. The role of surface-structural properties of the catalysts and their influence on transesterification activity is also the aim of the present study.

2. Experimental section

2.1. Catalyst preparation

Co-precipitation method was used to prepare MgO-CeO_2 catalysts. On the basis of 10 g of the final catalyst, required quantities of $Mg(NO_3)_2{\cdot}6H_2O$ and $Ce(NO_3)_3{\cdot}6H_2O$ were dissolved in de-ionised water and allowed to precipitate using 0.1 M Na_2CO_3 and 0.1 M NaOH mixture solution up to pH value reached 10 under constant stirring. The solution temperature was then raised to 80 °C and maintained at same temperature for 2 h with vigorous stirring. The precipitate was further aged at room temperature for 5 h. Then the precipitate was collected after filtration and washed thoroughly. The obtained mass was dried at 110 °C for 12 h and finally calcined in a furnace at 650 °C for 4 h. MgO and CeO_2 single oxides were individually precipitated from their respective nitrates adopting the above procedure. MgO and CeO_2 catalyst with molar ratios of 1:1, 2:1, 1:2 and 3:1 were prepared and labelled as Mg1Ce1, Mg2Ce1, Mg1Ce2, and Mg3Ce1 respectively.

2.2. Catalyst characterization

BET surface area of all the catalysts was calculated using Quantachrome Quadrasorb SI by N_2 adsorption–desorption at liquid N_2 temperature. The catalysts X -ray powder diffraction (XRD) patterns were recorded on a Rigaku Miniflex diffractometer using CuKα radiation (1.5406 A°) at 40 kV and 30 mA. The measurements were captured in the 2θ range of 10–80°. TGA was performed with Q5000IR, TA Instruments. Samples of approximately 3–5 mg were placed on aluminum pan. Data was obtained at a heating rate of 10 °C/min in the temperature range of 100 °C–1200 °C. Morphology of the catalysts was observed by field emission scanning electron microscopy (FE-SEM, JEOL JSM-7610F) equipped with an energy-dispersive X-ray spectroscopy (EDS) facility.

Temperature programmed desorption of CO_2 (TPD of CO_2) was carried on BELCAT II instrument. The pre-treatment of samples was carried in He flow at 300 °C for 1 h, prior to CO_2 adsorption at 70 °C. The CO_2adsorption was continued for 45 min and then the sample was flushed with He for 1 h at 100 °C to remove physically adsorbed 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 desorbed CO_2 was monitored with thermal conductivity detector.

2.3. Reaction procedure: transesterification of glycerol with DMC

The transesterification reaction of glycerol was carried in liquid phase under atmospheric pressure. In a typical experiment, 2 g of glycerol, 9.78 g of DMC and 0.3 g catalyst were taken into a 50 ml capacity two-neck round-bottom flask containing reflux condenser. The reaction mixture was heated to 90 °C while stirring on oil bath. After completion or desired time the reaction mixture was cooled and diluted with methanol. The catalyst was separated by filtration. Reaction mixture was analyzed by gas chromatograph (GC; Shimadzu 2010 plus, Japan) equipped with a flame ionization detector (FID) using Inno wax capillary column (30 m × 0.25 mm × 0.25 μm).

3. Results and discussion

3.1. Characterization of catalysts

Table 1 represents the surface areas of Mg/Ce mixed oxides along with their monoxides. The catalysts surface area increased as the Mg to Ce molar ratio increases. An enhancement in surface area from 60 to 122 m^2 g^{-1} was noticed with enhancement in Mg content. The surface area of the catalysts was increased with increase in Ce content also. When Ce content is more (Mg1Ce2 catalyst) the surface area is also high (74 m^2 g^{-1}) compared to the catalyst with less Ce content (Mg1Ce1).

Fig. 1 represents the catalysts XRD profiles. The patterns of MgO and CeO_2 were also included for comparison. The patterns indicate the crystalline nature of catalysts. The characteristic phases of CeO_2 and MgO were seen for these catalysts and there was no formation of any mixed oxide phase. Diffraction peaks for pure MgO were noticed at 2θ of 37°, 42.7°, 49°, 62°, 75° and 78° which were assigned to cubic and hexagonal crystalline phases [12,15]. While the 2θ values at 28.8°, 33.3°, 47.7°, 56.6° and 70° were assigned to CeO_2 phase [35–37]. In case of Mg/Ce oxide catalysts the crystalline phase of MgO was not observed. This indicates that MgO might be present in amorphous phase. CeO_2 phases were predominant in mixed oxide catalysts.

CO_2 adsorption–desorption approach enables us to find out the base sites strength of catalyst together with total basicity. Fig. 2 shows the CO_2-TPD profiles of the catalyst samples. The distribution of basicity was calculated depending on their strengths from the profiles and the calculated values are depicted in Table 1.

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