Tuning the basicity of Cu-based mixed oxide catalysts towards the efficient conversion of glycerol to glycerol carbonate

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ABSTRACT

A series of efficient and robust Cu based mixed oxides were synthesized by a simple co-precipitation method and utilized for the production of glycerol carbonate (GC) via transesterification of glycerol with dimethyl carbonate (DMC). The synthesized materials were characterized using XRD, UV–vis spectroscopy, SEM, TEM, N_2 sorption, CO_2-TPD, and XPS. The addition of Cu on Mg/Al mixed oxides exhibits significant changes in its physicochemical properties and catalytic activity. The obtained mixed oxides showed remarkably high transesterification activity towards the efficient conversion of glycerol to GC under economical reaction conditions without using any solvent. Among all the catalysts employed, highest catalytic activity was observed over MAC-0.6 catalyst with glycerol conversion of 96.4% and GC yield of 91.2%. The improved catalytic performance was observed mainly due to the optimized catalyst molar ratio and strong surface basicity. The strong surface basic sites were greatly attributed to the incorporation of Cu^{2+} cations in the MgAl (O) periclase that efficiently catalyzed the transesterification of glycerol with DMC. Furthermore, the reported catalyst was robust and could be recycled for more than five times without any significant loss in its catalytic activity.

1. Introduction

The utilization of renewable sources for the fine chemical synthesis became revolutionary research area in the perspective of both industry and academia [1]. Owing to the increasing day-by-day demand for renewable biofuels, biodiesel production has received significant attention, as it is a viable alternative to non-renewable fossil fuels as well as other sustainable biofuels [2]. Glycerol, a globally traded commodity chemical which is generated as an undesired side product during the production of biodiesel. Also, the available literatures conferred, 10% of waste glycerol is assigned during every ton of biodiesel production by transesterification of oils with methanol [2]. The utilization of surplus waste glycerol as a low-cost platform molecule stands for a promising substrate to procure value-added chemicals from renewable raw materials [3–5]. Recent research has been mainly centered on the development of modern chemical pathways for the efficient conversion of glycerol to value-added chemicals. Glycerol carbonate (GC) is one of the crucial glycerol derivatives that attract major scientific and industrial interest owing to its distinct physical, chemical properties and uses [6]. Moreover, GC has diverse applications such as a solvent,

chemical intermediate, polycarbonates synthesis, glycidol-based polymers, and surfactants etc., [6,7].

Diverse synthesis methodologies have been developed to upgrade a large amount of waste glycerol into GC over the past few decades. Traditionally, GC has been synthesized via the carbonylation of glycerol with carbon monoxide or phosgene [7], but this route has been deserted due to their toxicity and unsafe reactants. Besides, the GC production from glycerol with CO and CO_2 also demonstrated, however, these routes suffer from low GC yield and exorbitant operation cost [8–10]. Additionally, the carbonylation synthesis route has severe environmental concerns due to the use of CO, CO_2 and the intrinsic crisis to handle it securely both at the laboratory and industrial scale. The production of GC from glycerol and urea also another method for the synthesis of GC, however, the high GC yield can be achieved only the continuous removal of the produced ammonia gas while the reaction progress [11]. Importantly, the transcarbonation with various carbonates process provides a facile approach for GC synthesis owing to the ease of operation and mild reaction conditions [12–16]. Climent et al. reported basic oxides and mixed oxides catalyzed transesterification of ethylene carbonate with glycerol and achieved 98% of GC yield [17].

Among the employed catalytic pathways, the transesterification of glycerol with dimethyl carbonate (DMC) is the most promising route for the production of GC as it is much safer and greener over other methods [15]. Despite various catalyst systems have been explored towards GC synthesis, the requirement for an efficient, single step, economic and environmentally benign catalyst for sustainable GC production still remains. The extensive literature studies proved that the strong surface basic sites rather than the moderate and weak basic sites can efficiently catalyze the transesterification of glycerol with DMC [12]. In recent years, several reports on the synthesis of GC from glycerol using various heterogeneous base catalysts, such as KF-hydroxyapatite composites [13], CaO [18], CaO-La$_2$O$_3$ [19], ZnO/La$_2$O$_3$ [20] and K$_2$CO$_3$-MgO [21], have been accounted. However, in the future perspective of sustainable heterogeneous catalysts, there are still some issues required to be addressed, such as poor GC yield, solvent-free conditions, low reaction temperature and economical operating cost. Hence, the immense attention to a modern approach needs to be developed with the aim of achieving excellent GC production with robust catalyst stability at mild reaction conditions.

Transition metal incorporated Mg/Al mixed oxides in the form of layered double hydroxide (LDH) type materials has attracted growing attention in the area of heterogeneous catalysis. The layered Mg/Al-based mixed oxides has many applications in various research fields owing to their atomic level distribution of transition metal cations in the brucite layered structure and the capability to intercalate various interlayer anions [22–25]. Furthermore, LDH derived mixed oxides displays a great potential as a precursor and support to develop a promising catalytic material as it assists high dispersion and firm thermal stability to afford eminent catalytic performance and reusability [24]. One of the most pertinent properties of layered mixed oxides is that they behave as an excellent solid base material. Due to its distinct basic nature, Mg/Al mixed oxide type materials have been extensively explored as heterogeneous solid base catalysts for different organic transformations, such as hydrogenation, transesterification, alkylation and Aldol condensation [25–29]. Salomão et al. reported that the origin of the basic properties of these materials is directly associated with their chemical composition, nature of intercalated ions, structure and thermal activation conditions [30]. The basic sites can be mainly attributed due to the presence of interlayer OH$^-$ groups and surface O^{2-} species, which can be assigned as Brønsted and Lewis type basic sites, respectively [17,31]. Additionally, presence of the surface hydroxyl groups favors as charge compensation anions and strongly improve the accessibility of the Brønsted-type basic sites [17,31], whereas, the presence of surface O^{2-} species upon calcination leads to the formation of surface Lewis basic sites [17,23]. Being basic in nature, mixed oxide based materials has been extensively utilized for the GC synthesis in recent years. Malyaadri et al. achieved an appreciable yield of GC over Mg/Al/Zr oxides [2]. Parameswaram et al. showed the Mg/Zr/Sr based mixed oxides are highly active for the production of GC through the transesterification of glycerol with DMC [14]. Takagaki et al. accomplished tunable basic site density of calcined LDHs by altering the Mg/Al ratio and calcination temperature and found that the transesterification activity primarily correlated with surface basic site density [32]. Recently, Liu et al. demonstrated the basicity of Mg/Al mixed oxides can be tuned by the addition of transition metal ions and emphasized that the strong surface basicity has high influence on GC yield [23]. However, an extensive study on the influence of individual metal incorporation on Mg/Al based mixed oxides in favour of glycerol conversion is seldom reported and we considered it is worth investigating.

Based on the exhaustive analysis of the reported literature and patents, efforts were made towards achieving a single step conversion of glycerol to GC employing a room temperature synthesized Cu-based mixed oxides as an efficient heterogeneous base catalyst. Herein, the synergistic influence of combining Cu loading on the physicochemical properties and catalytic performance of Mg/Al mixed oxide has been

systematically investigated. Moreover, the diverse reaction parameters were optimized and correlated to the GC yield. The appreciable GC yield for more than 91% can be achieved through the fine-tuned surface basicity and optimized reaction conditions. The obtained results clearly indicate the basicity optimized Cu-based mixed oxides have been found to be a promising catalyst towards the highly efficient conversion of glycerol to GC under affordable reaction conditions with robust performance.

2. Experimental section

2.1. Synthesis of Cu-based mixed oxide catalysts

The Cu-based mixed oxide catalysts were synthesized by conventional co-precipitation method at room temperature. All chemicals purchased from S D Fine-Chem Limited were directly used without further purification. In a typical synthesis, a 0.25 M of metal precursor solution A was prepared by dissolving Mg (NO$_3$)$_2$. 6H$_2$O, Al (NO$_3$)$_3$. 9H$_2$O and Cu (NO$_3$)$_2$. 3H$_2$O in 100 ml of double distilled water. Precipitating base solution B was prepared by dissolving a 0.5 M of NaOH and 0.25 M of Na$_2$CO$_3$ in 100 ml of double distilled water. The co-precipitation has been done by dropwise addition of metal precursor solution A and base solution B simultaneously into a beaker with gentle stirring. The pH was maintained at 9.5 ± 0.2 and the solution was further stirred for an hour, subsequently, the slurry was allowed for aging at room temperature for 12 h. The obtained precipitate was washed thoroughly with double distilled water to remove the surplus base. Then, the sample was dried in a hot air oven for 12 h at 110 °C. Finally, the obtained sample was calcined at 450 °C for 6 h with a heating rate of 2 °C min^{-1}. For the systematic study, a series of Cu-based mixed oxides Mg$_{3-x}$Al$_1$Cu$_x$ (with the ratio of Mg^{2+}:Al^{3+} cations is 3:1) was prepared with a various molar ratio of Cu (x = 0.2, 0.4, 0.6, 0.8) and denoted as MAC-0.2, MAC-0.4, MAC-0.6 and MAC-0.8, where MAC stands for magnesium, aluminium and copper, respectively. A Cu-free catalyst was synthesized by using the same procedure without adding copper precursor and the obtained sample is denoted as MgAl (O). In addition, 5–20 wt% of Cu loaded on MgAl (O) were synthesized by impregnation method and the calcined sample denoted as x-wt% Cu/MgAl(O), where x stands for the Cu loading in wt%.

2.2. Characterization techniques

X-ray diffraction (XRD) data of synthesized powder samples were collected from D8 advance BRUKER (Germany) in the 2θ range between 05°-90°. The Bragg equation is applied to determine the interlayer distance (d) nλ = 2d sin θ, where λ = 0.154 nm. UV–vis spectra of the samples were recorded using JASCO-V670 spectrophotometer. The morphology of the sample was observed using Scanning electron microscopy (SEM) with energy dispersive x-ray analyzer (SEM-EDX) from FEI Nova Nano SEM 450 FE-SEM. Transmission electron microscope (TEM) micrographs of all the materials were recorded by a FEI TECNAI F20 electron microscope operating at 200 kV. The TEM sample was prepared using 2-propanol as a solvent with standard procedure. The copper wt% present in the calcined samples was quantified by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES, Spectro Arcos, FHS-12) analysis. CO$_2$-Temperature Programmed Desorption (CO$_2$-TPD) studies were carried out in Micrometrics 2920 instrument. Nearly 50 mg of powder sample was loaded in "U" shaped quartz tube for CO$_2$-TPD analysis. The sample was pre-treated from room temperature to 450 °C (5 °C/min ramping) using Helium as a carrier gas. For analysis, 10% CO$_2$ in Helium gas mixture was allowed to adsorb on the sample surface and allowed to desorb in a temperature range from room temperature to 900 °C (10 °C /min ramping). The surface area and pore characteristics of the calcined materials were determined by N$_2$ sorption analysis at −196 °C using Quantachrome Instruments version 5.0. The Brunauer–Emmett–Teller (BET) equation