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Upgrading of glycerol from biodiesel synthesis with dimethyl carbonate on reusable Sr–Al mixed oxide catalysts

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ABSTRACT

The high demand for renewable energy has led to the upsurge of methanol-assisted biodiesel synthesis. Therefore, glycerol as a byproduct entered the waste stream given the oversupply of biodiesel to the market. The dimethyl carbonate (DMC)-assisted transesterification of glycerol on a catalyst has been a popular approach for converting glycerol into valuable glycerol carbonate (GLC). The synthesis of GLC from the DMC-assisted transesterification of glycerol on mixed oxide catalysts (Sr_x–Al) with different Sr/Al ratios was examined in this study. A glycerol conversion of 99.4% and a GLC yield of 100% were achieved in a catalyst with Sr/Al = 0.5 ($Sr_{0.5}$–Al). Both values are higher than those in catalysts synthesized with Sr/Al = 0.25 and 0.75. The $Sr_{0.5}$–Al catalyst withstood five transesterification reaction cycles without a serious deactivation induced by the leaching of active SrO. Therefore, the $Sr_{0.5}$–Al catalyst is suitable for consecutive uses in the DMC-assisted transesterification of glycerol with DMC into GLC.

1. Introduction

The world is currently facing various environmental concerns resulting from the excessive use of fossil fuels to satisfy increasing energy demands across the globe. The energy used to sustain increasing global demands can be obtained from biodiesel synthesized from renewable non-edible vegetable oils [1]. Glycerol, which is as an important by-product of the methanol-assisted transesterification of vegetable oils, is produced in excess of the primary product, i.e., biodiesel [2,3]. The rapid growth of biodiesel industries saturates the glycerol market, thereby threatening competitiveness among industries. A huge amount of glycerol enters the waste stream, which then requires environment-friendly processing to avoid environmental issues.

From glycerol, high valued materials, such as fuel additives and chemical intermediates can be produced. Catalytic transesterification with oxidation or carbonylation agents converts glycerol into valuable organic compounds. One example of such compounds is glycerol carbonate, which is obtained from catalyst-aided transesterification reactions with dimethyl carbonate (DMC) [1,4].

Glycerol carbonate (GLC) has attractive properties, including low toxicity, high biodegradability, and high boiling point, for a wide range of applications. Glycerol is a highly functionalized compound that easily reacts with other carbonylation agents; hence, catalysts provide opportunities to obtain value-added GLC. The routes to GLC synthesis require methylating agents, such as phosgene and urea. However, such agents cause dangerous and environmentally unfriendly reactions. Subsequently, catalysts, in the presence of methylating agents (e.g., CO_2), converts glycerol into GLC via transesterification. Although such reaction is attractive, it is seriously affected by prevailing thermodynamic limitations [5,6]. DMC is effective in the transesterification of plant oil and residual glycerol during biodiesel production [7]. It is a better methylating agent in transesterification than methanol and CO_2; DMC is also nontoxic, eco-friendly, and exhibits excellent solvent properties [8].

The catalytic transesterification of glycerol with DMC involves less complex reaction pathways and distributed products, and thus, is a feasible option for direct GLC production [5]. Glycerol had been successfully converted into GLC and biodiesel via metal transesterification [9]. Therefore, focus has shifted to the use of mixed oxide catalysts with carbonylation agents in the synthesis of industrially valuable organic compounds from glycerol. The prospective use of catalysts in the transesterification of glycerol depend on their low corrosiveness, reusability, energy-reducing reaction temperature, simple catalyst/product separation, and decreased chemical waste production [10,11]. During catalytic reaction, metal catalysts frequently behave as a Brønsted base that accepts protons or as a Lewis acid that donates electron pairs. In

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[12,13], the authors explored the capability of catalysts with DMC to produce biodiesel and glycerol-based compounds, such as monoglyceride, glycerol carbonate, and DMC. The DMC and base catalysts tailored the transesterification of glycerol to GLC, unlike in pathways mediated by methylating agents that yield less profitable organic compounds [8,14].

Several catalysts with varying physicochemical and textural properties that influence the upgrade of glycerol to GLC have been presented in the literature [10,15,16]. Base catalysts derived from mixed oxides, such as $MgO–ZrO_2$ [16], Ca–Al hydrocalumite [13], $Mg_{1+x}Ca_{1-x}O_2$ [15], Mg/La [8], and $LiNO_3/Mg_4AlO_{5.5}$ [17], are efficient catalysts with significant glycerol yields and enhanced selectivity. These catalysts can promote complete glycerol conversion with 98% GLC yield at 70–80 °C. Simanjuntak et al. [8] volarized different Ma–La mixed oxide catalysts and demonstrated their reasonable catalytic activities during GLC synthesis with DMC. They reported that Mg/La ratio considerably influenced catalytic activity and surface basic site concentration. The authors of [18,19] explored the potential of Sr-based mixed oxide catalysts in biodiesel and methane production. The performance of Sr-based catalysts is linked to their crystalline phases, which in turn, are associated with Sr/Al ratio. The amount of Sr influenced the catalytic activity of the Sr-based mixed oxide catalyst and its selectivity towards the synthesis of GLC. The overall success of mixed oxide catalysts can encourage their volarization in catalytic reactions for the production of industrially valuable organics.

The current study explored the potential of Sr-Al mixed oxides as catalysts in the DMC-aided transesterification of glycerol to GLC. Also, the study elaborated on the effect of different Sr/Al ratios on the catalyst proficiency during the synthesis of GLC from the DMC-assisted transesterification of glycerol.

2. Materials and methods reagents

2.1. Materials

The chemicals used for the entire study were reagent grade obtained from suppliers in Malaysia. Acrons, USA supplied the anhydrous glycerol (>99%). High-purity dimethyl carbonate ($\geqslant$99%), glycidol (97%), and aluminum oxide (99%) were obtained from Sigma-Aldrich. Merck, Malaysia supplied the HPLC-grade methanol (99.7%), 25% ammonia solution, aluminum nitrate nonahydrate and strontium nitrate.

2.2. Catalyst preparation

The Sr-Al catalysts were prepared using mixed-solutions of $Sr(NO_3)_2$ and $Al(NO_3)_3·9H_2O$ via coprecipitation. About 6.3 g of $Sr(NO_3)_2$ was dissolved in 30 ml deionized water, afterwards 15 g of $Al(NO_3)_3·9H_2O$ was added to obtained a mixed-nitrate solution. The mixed-nitrate solution was stirred at 800 rpm on a hot plate. A 5M NH_4OH solution was added dropwise to the stirred nitrate solution until pH 11. A mixed hydroxide of Sr–Al was precipitated and were filtered and washed with deionized water until pH 7 to serve as catalyst precursor. Subsequently, the precipitated were oven dried at 70 °C and calcined for 4 h at 900 °C. A series of mixed oxide catalysts with 0.25 to 0.75 Sr/Al atomic ratios and classified according to 70–100 μm mesh sizes was prepared and coded as Sr_x–Al catalysts, where x indicates the Sr/Al atomic ratio. The catalysts were calcined at different temperatures and screened to establish a suitable calcination temperature for high GLC yield. The catalysts were characterized to identify their morphology and surface characteristics prior to use.

Bulk $Sr(NO_3)_2$ was calcined for 4 h in a muffle furnace at 600 °C and yielded SrO to serve as a catalyst in DMC-assisted transesterification of glycerol to GLC. A Sr_x–Al catalyst with Sr/Al = 0.5 was prepared via impregnation technique. A mixture of $Al(NO_3)_3$ and 0.5 M solution $Sr(NO_3)_2$ was stirred for 6 h at 60 °C and 500 rpm. The mixture was dried for 24 h in an oven set at 105 °C, then calcined at 800 °C in a muffle furnace under air to obtain the Sr_x–Al catalyst. The relevant functional groups and chemical bonding finger print on the catalysts were analyzed with Fourier transform infrared spectroscopy (FTIR). The X-ray diffraction (XRD) analyzed the crystal structure of the catalysts. The textural and surface properties of the catalysts were examined through Brunauer–Emmett–Teller (BET), then scanning electron microscopy (SEM) analyzed the catalysts morphology. These catalysts characterization techniques have been important in analyzing the essential features of catalysts for tranesterifiaction reactions [20,21]. The methods showed the inherent properties of Sr–Al mixed oxide catalysts that are relavant to the transesterification of glycerol with DMC.

2.3. Characterization of $Sr_{0.5}$–Al mixed oxide catalyst

The $Sr_{0.5}$–*Al* surface and textural properties were examined through BET using a Micromeritics ASAP™ 2020, surface area and porosity analyzer (Micromeritics Instruments Corporation, USA). The crystallite structure of the catalyst was analyzed on a diffractometer (D8 FOCUS, Bruker, Germany) with Cu Kα radiation (λ = 1.5406°). The functional groups on the catalysts were identified using an FTIR spectrophotometer (PerkinElmer System 2000). The spectra of the catalysts were obtained at 1500–400 cm^{-1} wavelength via the KBr procedure. The morphology of the $Sr_{0.5}$–Al catalyst was investigated via SEM using a scanning electron microscope (Philips XL30S). Energy-dispersive X-ray spectrometer mounted on a microscope was used to analyze the elemental composition of the catalysts. Then, basic strength (H_) of the Sr_x-*Al* catalysts was analyzed with the Hammett indicator technique and neutral red (H_ = 6.8).

2.4. Procedure for DMC-assisted transesterification of on a Sr_x–Al mixed oxide catalyst

The reaction mixture, with 12 mL glycerol, 27 mL DMC, and 1–3 wt.% Sr_x–Al catalyst, was placed in a two-neck glass reactor (50 mL) connected to a condenser. The reactor was heated to 55–75 °C on a heating mantle and transesterification was allowed to proceed for 30 min to 120 min. The reactor was shut down at the end of each reaction time. The catalyst and the product mixture were recovered after cooling to ambient temperature. The catalyst was separated from the products mixture with a centrifuge, and the product mixture was decanted. Samples of the products were collected for gas chromatography (GC). The catalysts were recovered and washed with methanol for reuse in subsequent reaction cycles.

Gas chromatograph (model: GC-2010 Plus, Shimadzu, Japan) using helium as the carrier gas was used to analyzed the compositions of reaction products. The gas chromatograph was fitted with flame ionization detectors (FIDs), a GC capillary column (30 m × 0.25 mm × 0.25 μm) (Zebron, ZB5-HT) and a split/splitless injection unit. The procedures for the samples analysis were described in our previous report [12].

3. Results and discussion

3.1. Effect of atomic ratio on basicity of the Sr_x–Al mixed oxide catalysts

Table 1 presents the effect of Sr/Al metal ratio on the basicity of the Sr_x–Al mixed oxide catalysts. The inherent basicity of the catalysts depends on the Sr/Al ratio. Al_2O_3 has sufficient Lewis acid