

Biodiesel byproduct glycerol upgrading to glycerol carbonate over lithium–oil palm ash zeolite



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ABSTRACT

Mesoporous oil palm ash zeolite (OPAZ) was synthesized and impregnated with various lithium ion loadings (5–15 wt%). The synthesized Li–OPAZ catalyst was used to upgrade biodiesel byproduct glycerol to glycerol carbonate (GC) via transesterification pathway. Results indicated that Li–OPAZ sustained the transesterification reaction to appreciably high glycerol conversion (100%) and GC yield (98.1%) under the optimal reaction conditions of 343 K, 90 min, DMC/glycerol molar ratio of 2, and 2 wt% catalyst loading. The crystallinity and framework of zeolite was preserved after lithium incorporation with a slight decrease in pore volume and surface area. However, basicity increased with increased lithium impregnation, explaining the observed high catalytic activity of the theoretical 10 wt% Li loaded OPAZ. Hence, 10 wt% Li–OPAZ was reused in five successive cycles of experiment with sustained appreciable catalytic activity toward glycerol conversion and GC yield.

1. Introduction

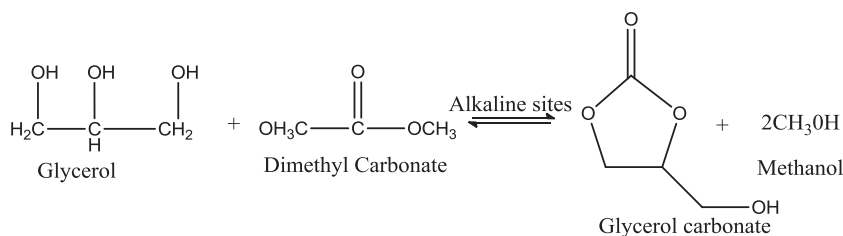
Alternative sources of energy that are environmentally benign have been the subject of global discussion to minimize CO₂ emission from fossil fuels. This awareness has led to vast research effort to replace fossil fuels with clean and renewable energy sources that impact the environment. Among the inventions in this research area, biodiesel (BD) has been commercialized in numerous countries [1]. The demand for BD is on the increase, with a global production capacity of 3.1×10^{10} L in the year 2015 [2]. During the industrial production of BD via transesterification with methanol, glycerol is obtained as a major by-product. The quantity of co-produced glycerol during BD synthesis is approximately 10 wt% of the total BD weight [3]. Thus, the high consumption of BD, which is occasioned by increasing BD demand, has created a glycerol surplus that affects the cost of BD. The United States Department of Energy reported that the average cost per gallon of 100% BD in clean cities is approximately USD 0.89 higher than that of fossil diesel fuel [4]. Hence, the price difference between BD and fossil diesel must be bridged to make BD production attractive. Therefore, researchers should explore methods to convert glycerol into valuable commodity to reduce the net energy requirement for BD production and to compensate for the cost difference between BD and fossil diesel, and to increase the market viability of BD.

Reaction pathways, such as etherification, esterification, dehydration, selective oxidation, transesterification, hydrogenolysis, acetylation,

co-liquefaction and dehydrogenation, have been applied for use over supplied glycerol [5–11]. These pathways upgrade glycerol to a valuable commodity, which can boost the BD industry from an energy and economic perspective. Low-cost and low-energy intensive route to upgrading glycerol into fine chemicals is required for faster commercialization. The transesterification of glycerol using dialkyl sources, such as dimethyl carbonate (DMC), under mild reaction conditions would be ideal for synthesizing fine chemical(s) from abundant glycerol. DMC is ideal because it is a green solvent that can be tailored during glycerol transesterification reaction into valuable glycerol carbonate (GC) (Scheme 1) [12]. A three-step reaction mechanism has been identified in the transesterification reaction. First, the alkaline sites on the catalysts activate the glycerol molecule via deprotonation to form glyceroxide anion. Then, the anion reacts with carbonyl group of DMC to form a complex intermediate, hydroxyl alkyl carbonate and a methoxide anion. Thereafter, further intermolecular reactions in the presence of the alkaline sites generates a five ring cyclic carbonate (glycerol carbonate) and methanol [13]. Apart from application of the GC as solvents, carriers in lithium batteries, surfactants, cement composite aggregates, and others, GC exhibits potential as fuel additives or methanol substitute to prevent the co-production of glycerol by-product during BD synthesis [14]. Therefore, readily available glycerol can be utilized in a transesterification reaction to synthesize GC. Catalysts with alkaline active sites are required to minimize energy consumption and improve efficiency during GC synthesis. Heterogeneous catalysts are more favorable for preventing

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Scheme 1. Synthesis of GC via glycerol transesterification with DMC.

challenges in separation and reusability that are commonly encountered in homogeneous catalysts. Moreover, the yield of GC and conversion of glycerol are largely functions of the utilized active catalyst and optimized reaction conditions.

Typically, utilized catalysts in tailoring glycerol transesterification reaction with DMC are mainly inorganic base that comprise alkaline earth metals and alkali metals in mixed oxide form. Different catalysts, such as KNO_3/CaO , $\text{LiNO}_3/\text{MgAl}$, MgAl , CaO , MgO , Ca-La , Ca-Al , Zn-La , Na-zeolite , and others, have been utilized for the synthesis of GC in glycerol transesterification reaction with DMC [15–19]. The stability of these catalysts is a primary issue that affects the application of catalysts that thus far demonstrated outstanding performance. Pure calcium oxide, for instance, favors appreciably higher yield of GC > 90%, but deactivates over a short period because it readily absorbs water, which changes the form of calcium oxide to the inactive lime [20]. Thus, the material cannot be reused in successive experiments and is not economically viable. The alkaline site strength contributes to the catalytic activity and high yield of GC, and alkali metals of Group I elements have been utilized to enhance the catalytic activity of hydrotalcite and zeolites with relatively weak alkaline sites [21]. In particular, Na and K functionalized zeolites have displayed remarkable performance in tailoring glycerol transesterification with DMC to an appreciable yield of GC [22,23]. The notable catalytic performance was attributed to high alkalinity ($15 < \text{pH} < 18.4$) and the mesoporous structure of the synthesized catalyst. Apart from Na and K precursors of alkali metals, LiNO_3 can create strong alkaline sites because of its strong ion size effects. Previously conducted studies [21] indicate that the catalytic activity of hydrotalcite can be markedly enhanced by doping with LiNO_3 . The Li^+ bonds easily with Al and forms a new strong alkaline site of LiAlO_2 that accounts for the outstanding performance in glycerol carbonate synthesis.

Recently, emphasis has been focused on the utilization of industrial and municipal wastes as heterogeneous catalysts to tailor chemical reactions to products. These wastes (such as municipal waste, biomass, and coal fly ash, among others) contain active mineral elements that confer catalytic properties on catalysts. In addition, these materials can be used directly in experiments with or without further processing. In the glycerol carboxylation pathway, studies conducted using these wastes are scarce. For instance, coal fly ash has been modified and utilized to achieve 90% GC yield [22]. Oil palm ash is a waste that is disposed of in tons from palm oil mills in Malaysia. Oil palm ash waste that consists of empty fruit bunches, oil palm fronds, and palm oil shells as burn materials are used to produce steam for electricity generation in oil palm mills [24]. The rich silicate-alumina constituents of oil palm ash waste renders it a durable geopolymer material that can be used as fire retardants, hazardous wastes encapsulation, and toxic chemical resistant [25]. This ash contains approximately 40% SiO_2 and 6% Al_2O_3 [26], which are essential constituents for zeolite formation.

The aim of the study was to successfully convert a waste oil palm ash into a mesoporous and highly reusable zeolite catalyst with basic functional sites so as to catalyze the glycerol transesterification reaction with DMC to give high GC yield and glycerol conversion under mild reaction conditions.

2. Experimental

2.1. Materials

Oil palm ash was obtained from a local palm oil mill in Penang,

Malaysia, and used without purification. Anhydrous glycerol (> 99% purity), anhydrous DMC (> 99.8% high purity), NaOH pellets (> 99% assay), kaolin (> 70 wt%), high-performance liquid chromatography-grade methanol (> 99.0% purity), and LiNO_3 (> 98% assay), were purchased from Merck. Huntsman (USA) supplied the gas chromatography–flame ionization detector (FID) standards (93–95% purity). All reagents and chemicals used in the experiment were of analytical grade.

2.2. Synthesis of lithium-impregnated oil palm ash zeolite (Li-OPAZ) catalyst

A 10 g portion of oil palm ash was mixed with 2 g kaolin as an aluminum oxide source. Then, the resulting mixture was suspended in 2 M NaOH under stirring and aging overnight. The mixture was then transferred to a Teflon-lined autoclave and heated for 8 h at 373 K. After hydrothermal treatment, the product was filtered and washed with double deionized water to lower the pH to 7. The resulting palm ash zeolite was doped with an appropriate amount of lithium nitrate salt (typically 5–15 wt%), dried in an oven at 373 K for 6 h, followed by calcination in air for 4 h at 723 K. The samples were ground into fine powder (< 30 nm) to increase surface area and contact with the reacting species. The lithium-impregnated palm ash zeolite was used to synthesize GC in the glycerol transesterification reaction with DMC.

2.3. Catalyst characterization

An X-ray diffraction (XRD) SIEMENS XRD D5000 equipment was used to detect the crystallinity of the synthesized catalyst. Samples were placed in an Al sample holder after sieving through a 0.074 mm sieve. The details of the operational technique were as follows: $\text{K}\alpha$ Cu radiation at 30 mA/40 kV, goniometer scanning rate of $2^\circ/\text{min}$, and 2θ range of 5° to 50° . The XRD results of 10 wt% Li-OPAZ (palm ash zeolite) were obtained before use and after 5th reuse.

The surface functional groups of 10 wt% Li-OPAZ were characterized by using Perkin Elmer Spectrum GX Infrared Spectrometer within wavenumber range of $4000\text{--}400\text{ cm}^{-1}$ and a resolution of 4 cm^{-1} . Functional group analysis was carried out in accordance with the KBr method, in which 0.007 g of 10 wt% Li-OPAZ was mixed with 0.1 g of KBr, and then ground and pressed to form a transparent pellet.

Nitrogen adsorption by Autosorb I (Quantachrome Corporation, USA) was used for surface physical property measurements at 77 K using the multipoint Brunauer–Emmett–Teller (BET) method. Mesopore volume, external surface area, and mesopore surface area were obtained from surface area analysis technique by *t*-plot method. Barrett–Joyner–Halenda (BJH) method was employed to determine pore size distribution and average pore width.

Surface micrographs of unused and used 10 wt% Li-OPAZ catalyst were obtained by field emission scanning electron microscopy (FE-SEM LEO SUPRA 35VP) EDAX-SEM instrument. Scanning electron micrographs of these samples were taken at $10,000\times$ magnification to understand the surface morphologies. The chemical compositions of unused and used 10 wt% Li-OPAZ catalyst were obtained quantitatively from energy dispersive X-ray spectroscopy (EDX) with the same instrument.

CO_2 -temperature programmed desorption (TPD) was carried out on a Micromeritics AutoChem 2920 II apparatus equipped with a thermal

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