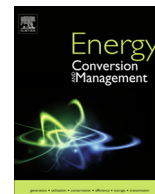




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Stabilized ladle furnace steel slag for glycerol carbonate synthesis via glycerol transesterification reaction with dimethyl carbonate

P.U. Okoye, A.Z. Abdullah, B.H. Hameed *

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia

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ABSTRACT

Abundant waste from ladle furnace (LF) steel slag industry was utilized to catalyze the glycerol transesterification reaction with dimethyl carbonate (DMC) to synthesize valuable glycerol carbonate (GC). LF slag was modified using various sodium hydroxide (NaOH) loadings (1–15 wt.%), and the catalyst samples were characterized using XRD, FTIR, TPD-CO₂, and EDS techniques. Modifying the LF using different NaOH loadings enhanced the stability, basicity, and basic strength of LF. Favorable reaction conditions at the best glycerol conversion and GC yield were investigated via reaction influencing parameter screening. Thus, the 10 wt.% NaOH incorporated in LF under the reaction conditions of 75 °C, DMC-to-glycerol molar ratio of 2, and 3 wt.% catalyst dosage achieved 99% glycerol conversion and 97% GC yield. The catalyst exhibited sufficient heterogeneity and was utilized in five successive cycles of the experiment without serious deactivation.

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1. Introduction

Glycerol, a major biodiesel production by-product, constitutes 10% w/w of the total global biodiesel [1]. The oversupply and physicochemical properties of glycerol make it a valuable material that requires defunctionalization [2]. Pathways to synthesize fine chemicals from glycerol were discussed in detail in Refs. [3–8]. The base-catalyzed transesterification reaction of glycerol using dialkyl carbonate sources is a popular pathway to upgrade abundant glycerol into fine chemicals [9–11]. Dialkyl carbonate sources, such as dimethyl carbonate (DMC), is a popular choice because these sources are environment-friendly and nontoxic [12]. Under mild reaction conditions, basic catalysts were employed to modify the glycerol transesterification reaction with DMC to synthesize valuable glycerol carbonate (GC). The base catalytic materials are synthesized mainly from alkaline earth metals and alkali metal oxides. Their outstanding activity in transesterification reaction is attributed to their strong basic sites and high basic density [13]. Too high a basic strength above $H_- > 18.4$ can propagate GC decomposition or dehydration to glycidol [14]. Methanol is coproduced in the reversible equilibrium reaction, and it can be positively shifted to produce appreciably high GC, utilizing DMC in excess of glycerol. GC has various applications, such as cement composite aggregate, solvent, surfactant, plant bolster, carrier in

lithium ion battery, methanol replacement to avoid glycerol coproduction in biodiesel synthesis, and fuel additive [15].

Reported studies based on CaO, MgO, double-layered hydrotalcite of Ca or Mg, Na-zeolite, K-zeolite, and sodium hydroxide (NaOH)/ γ -Al₂O₃ alkaline materials describe the considerable high activity performance toward a high GC yield [16–20]. Research in the recent decade focused on the beneficial utilization of abundant wastes generated from many processing industries. Waste utilization decreases handling problems and averts environmental hazards caused by improper disposal. Millions of tons of waste are generated in many steel industries around the world. Available information on steelmaking processes indicates that approximately 135 million tons of steel were produced in April 2016 from 66 countries [21]. The volume of generated slag increases with the consumption of steel products, which affects utilization methods. Slag waste is categorized as electric arc furnace (EAF) steel slag, ladle furnace (LF) basic slag, blast furnace (BF) iron slag, and basic oxygen furnace (BOF) slag based on the source furnace [22]. Iron and steel slag are mostly utilized in structural and civil construction. Slag is applied in various areas, such as soil stabilization in erosion-prone areas, soil acidity correction, fertilizers, and adsorbents in CO₂ sequestration.

The varying mineralogy in different proportions provides steel slag wastes with properties that could be further explored from the economic and technical standpoints. The slag mineral compositions for each slag category provide specific characteristics for specific applications [22]. For instance, BOF and EAF slag are often

* Corresponding author.

E-mail address: chbassim@usm.my (B.H. Hameed).

used as low-cost materials in road construction and asphalt aggregate mixes. BF slag from iron industry can be used in Portland cement manufacturing. LF slag application differs because of its specific mineral constituents and characteristics. Notably, LF slag is largely composed of lime ($\text{Ca}(\text{OH})_2$) with primary applications in soil acidity correction and is a recycle material to formulate Portland clinker [22]. The slag is generated during the desulfurization of steel at the final stage of the steelmaking process, known as secondary metallurgy process. LF slag is also known as basic slag because of its high calcium content. Thus, LF slag is a suitable material for base-catalyzed reactions. Calcium in LF can be extracted or used directly to synthesize hydroxyapatite, which is highly beneficial in bone treatment.

Calcium-based materials have exhibited potential in modifying the glycerol transesterification reaction [17]. However, these materials are highly unstable because of their solubility in glycerol at glycerol/DMC equimolar ratio and high reactivity in the presence of moisture and CO_2 . Calcium leaches into the reaction mixture and forms an undesired homogeneous catalysis, which results in an evident decline in catalytic activity at less than three cycles of reuse. CaO formed active homogeneous species $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)(\text{OCO}_2\text{-CH}_3)$ at a glycerol/DMC equimolar ratio but exhibited heterogeneity when DMC is in excess of glycerol [18]. However, leaching cannot be avoided because a sharp decline in GC yield was recorded after the third cycle of reuse. Magnesium and potassium sources were employed to improve the stability of calcium [17,23]. The incorporation of magnesium provided a strong bond interaction, resulting in the minimal leaching (7.4%) of metallic species after four cycles of reuse [24]. Incorporating potassium nitrate salt in CaO provided outstanding leaching resistance, which was attributed to surface masking of the catalyst by in situ generated amorphous calcium carbonate [23]. Thus, the rapid leaching of Ca species was minimized and the recovered catalyst can be reused for five cycles with negligible loss in CaO. NaOH exhibited good dispersion force similar to potassium hydroxide, and they can reduce the solubility of portlandite ($\text{Ca}(\text{OH})_2$) [25,26]. Moreover, NaOH is more cost-effective than potassium hydroxide.

This study aims to synthesize GC using highly active and robust heterogeneous waste under mild reaction conditions. Abundant LF steel slag waste is reported for the first time to catalyze glycerol transesterification reaction with DMC. NaOH was loaded on LF slag via impregnation method. The synthesized NaOH-LF catalyst was characterized and utilized in the synthesis of GC. The stability and catalytic activities of NaOH-LF were investigated.

2. Materials and methods

2.1. Materials

LF steel slag was obtained from a local company in Malaysia. NaOH pellets (approximately 99% assay), anhydrous DMC (>99%), HCl (37 wt.% fuming), and methanol (>99%) were supplied by R & M Chemicals. The standards (93–95% purity) used in gas chromatography–flame ionization detector (GC-FID) were obtained from Huntsman, USA. All the chemicals were used without further processing or treatment.

2.2. NaOH-LF synthesis

LF slag was screened with a standard sieve of 100–125 μm mesh to remove large-sized particles and impurities (e.g., marble, stones, and metal debris). The obtained LF was dried for 4 h at 100 °C to remove absorbed water, followed by NaOH (typically 1–15 wt.% loading) impregnation under stirring (500 rpm) for 24 h. Thereafter, the solution was heated at 80 °C for 4 h to evapo-

rate water and dried in static air at 100 °C overnight. The samples were calcined at different temperature ranges of 100–900 °C for 4 h to investigate the effect of calcination. Fresh LF slag was calcined at 800 °C for 4 h and used directly in the transesterification reaction. NaOH-LF was also used in the glycerol transesterification reaction as a catalytic material to synthesize GC.

2.3. NaOH-LF characterization

The mineral compositions of the calcined LF, NaOH impregnated LF and leaching of the constituent minerals for reused catalyst were characterized using energy-dispersive spectroscopy (EDS; FE-SEM LEO SUPRA 35VP).

Nitrogen adsorption–desorption isotherms were obtained using Autosorb I (Quantachrome Corporation, USA) at 77 K. Multipoint Brunauer–Emmet–Teller (BET) method was utilized to calculate the surface area of the samples. Average pore diameter and pore size distribution were calculated using the Barrett–Joyner–Halenda method.

The base amount of the samples was investigated using the acid–base titration method [23]. A total of 100 mg of the samples were dispersed in 10 mL of 0.5 M HCl solution, and the suspension was stirred for 24 h. Thereafter, the solution was filtered using filter paper, and the acid remaining in the liquid phase was titrated against 0.1 M NaOH solution using phenolphthalein as an indicator. The base amount was calculated using the same standard equation reported in Ref. [24].

Temperature-programmed desorption using CO_2 (TPD- CO_2) as the probe molecule was used to investigate the base amount and the basic sites strength of the catalyst samples. Impurities and trapped gasses were removed by heating 50 mg of the samples under helium flow (10 °C/min, 50 mL/min) for 2 h and from ambient temperature to 800 °C. The samples were cooled to 90 °C, and CO_2 gas was allowed to adsorb (50 mL/min) for 1 h. The thermal desorption of adsorbed CO_2 molecules was conducted from 90 to 900 °C under helium flow and the desorbed CO_2 was monitored online using gas chromatography fitted with a thermal conductivity detector.

Hammett indicators which include phenolphthalein ($H_- = 9.3$), 2,4-dinitroaniline ($H_- = 15.0$), 4-nitroaniline ($H_- = 18.4$), and aniline ($H_- = 27.0$) were used to investigate the basic strength distribution of LF, NaOH impregnated LF samples (5–15 wt.%) and five times reused catalyst [14,23,27]. Samples powder (50 mg) was transferred into 10 mL cyclohexane and sonicated for 2 h. Thereafter, indicator dissolved in benzene (0.75 wt.%) was added dropwise to the catalyst suspension in cyclohexane. Then, it was left to equilibrate for 3 h, until no further color changes were observed. The color changes on the catalyst were monitored virtually, and the relative base strength is described as being stronger than the weakest indicator that produces a color change but weaker than the strongest indicator that shows no color change.

Fourier transform infrared spectrometer (FTIR; Perkin Elmer Spectrum GX) was utilized to analyze the surface functional groups over a range of 4000 cm^{-1} to 400 cm^{-1} and a resolution of 4 cm^{-1} . The KBr method was employed by mixing 7 mg of the sample with 100 mg of KBr, followed by grinding and pressing to form a transparent pellet.

X-ray diffraction (XRD; SIEMENS D5000) for the samples and five times reused NaOH-impregnated LF were conducted using $\text{Cu K}\alpha$ radiation at 30 mA/40 kV with a scanning rate of 2°/min over a 2θ range of 5–90°.

2.4. Glycerol transesterification reaction with DMC

Transesterification reaction was conducted in a 50 mL glass reactor equipped with a K-type thermocouple for temperature

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