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THE CATALYTIC PERFORMANCE OF Mg-Al CATALYST IN TRANSESTERIFICATION OF GLYCEROL WITH ETHYLENE CARBONATE

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ABSTRACT

The development of heterogeneous catalysts for oleochemical reactions is becoming very important, because such catalysts possess well defined catalytic active sites, which will increase catalytic activity and process efficiency. The use of hydrotalcites as heterogeneous catalyst has shown potentials in transesterification reaction due to their physico-chemical properties, such as good thermalstability, good mesoporous material, bigger surface area, good memory effect, and even balanced basicity/acidity active points. The catalytic performance of the calcined Mg-Al catalyst in the green process was developed for the conversion of glycerol to glyceryl carbonate using ethylene carbonate. The X-ray diffraction confirmed the calcined materials exhibit hydrotalcite pattern structure with surface area of 179 $m^2\ g^{-1}$*. The HT3.0c comprised of Mg:Al composition of 3:1 was the best catalyst. The catalyst is robust and reusable.*

Keywords: calcined hydrotalcites, co-precipitation, green chemistry, transesterification, glycerol.

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INTRODUCTION

Biodiesel has been successfully evaluated as a diesel substitute and has gained worldwide acceptance (Choo *et al*., 2005). However, every production of biodiesel will produce 10% w/w glycerol as co-product which needs to be utilised in order to make economics favourable (Fan *et al*., 2010). It was reported that 66.2% of the total glycerol was produced from biodiesel industry in 2011. Biodiesel consumption in US rose from 995.56 litres (263 million gallons) in 2010 to 3323.58 litres (878 million gallons) in 2011 to 1 billion litres in 2012. All these production came from 112 biodiesel plants with capacity of 2.2 billion gallons annually (Sonnati *et al*., 2013).

Therefore, making profit from glycerol, a by-product from the biodiesel production will be an important way forward to solve the economic and environmental challenges of biofuels production (Choo *et al*., 2005). There are various field of glycerol applications such as in cosmetic, pharmaceutical and food industries. Oxidation (Prati *et al*., 2009), etherification (Ruppert *et al*., 2008), esterification and transesterification (Corma *et al*., 2005) are examples of chemical processes involving glycerol for the production of value-added products and intermediates.

One important glycerol derivative is glyceryl carbonate (GC) which is widely used as a protic solvent in resins and plastics, a chemical intermediate in organic synthesis and it can also be used as an additive (Murase, 1987). It is a green substitute for important petro-derivative compounds (Shieh *et al*., 2002; Behr *et al*., 2008). Glyceryl carbonate is useful in the synthesis of polymers such as polyesters, polycarbonates, polyurethanes, polyamides,

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surfactants and lubricating oils (Yoo *et al*., 2001). GC offers several advantages. They are less toxic, less flammable, excellent biodegradability and high boiling point (Climent *et al*., 2010).

Conventionally, preparation of GC is based on the reaction of glycerol with urea, or with carbon monoxide and oxygen (Bell *et al*., 1959). Another method for the synthesis of GC described in the literature is via transesterification of propylene carbonate with glycerol (Aresta *et al*., 2009). Mouloungui *et al*. (1996) patented a process for the manufacture of GC by reacting glycerol with propylene carbonate in the presence of solvent and using zeolites as catalyst. Studies by Sugita *et al*. (1994) reported that the synthesis of GC using aluminum oxide (Al_2O_3) as catalyst was conducted under reduced pressure and mild temperature around 140°C. Wheres Vieville *et al*. (1998) used zeolite catalyst at 80°C with two molar ratio of ethylene carbonate to glycerol to give the desired GC. In this article, characterisation of calcined heterogeneous catalysts and their catalytic activities in the transesterification of glycerol with ethylene carbonate are described.

MATERIALS AND METHODS

Materials and Catalyst Preparation

Glycerol (≥99%), ethylene carbonate (≥99%), sodium hydroxide (≥99%) and sodium carbonate (≥99%) were purchased from Merck. Precursor salts $Mg(NO_3)_2.6\ H_2O$ (≥98%) and $Al(NO_3)_3.9\ H_2O$ (≥98%) were purchased from Bendosen Laboratory Chemicals and used as received. The hydrotalcite catalyst was prepared by adopting the well-known co-precipitation method in a single container of two diluted solutions A and B. Solution A contained divalent cation (288 g) and trivalent cation (140 g) dissolved in 1 litre deionised water.

Solution B acting as precipitating reagent was prepared by dissolving Na_2CO_3 (40 g) and NaOH (15 g) in 0.5 litres deionised water. The prepared solutions A and B were then mixed with a high supersaturation technique for 18 hr at 80°C under vigorous stirring. Precipitation occurred and the precipitate was later filtered, washed with hot deionised water until pH 7 and dried overnight at 120°C. The fresh catalyst obtained, denoted as HT3.0f, was then calcined by heating to 500°C in an oven at ramping rate 5°C min^{-1} for 5 hr under nitrogen. The calcined HT3.0f is denoted as HT3.0c.

Catalyst Characterisation

The synthesised hydrotalcite-type compound HT3.0f and HT3.0c were analysed by X-ray diffraction (XRD) using Bruker D8 ADVANCE diffractometer with a secondary monochromator (Model: Bruker D8 ADVANCE, Germany), using Cu Kα1 radiation and interface to a DACO-MP data aquisition microprocessor provided with Diffract/AT software, 2006.

Nitrogen adsorption/desorption isotherms were performed in Micromeritics apparatus (Model: ASAP 2010, USA) after pre-treating the samples under vacuum at 400°C overnight and surface areas were obtained through the Brunauer-Emmett-Teller (BET) technique. The pore size distributions were obtained according to the Barret-Joyner Halenda (BJH) method from the adsorption branch data.

The investigation on thermal stability of the two catalysts was carried out via Mettler Toledo TGA/SDTA 851^{e} thermo balance using an open alumina crucible of 100 µl. The TGA temperature was programmed dynamically from ambient to 700°C at heating rate of 5°C min^{-1} under nitrogen with flow rate of 50 ml min^{-1}. The elemental content of the catalysts was analysed on an Energy-dispersive X-ray (HITACHI S530, Japan).

Attenuated total reflection Fourier transform infra-red (ATR-FTIR) spectra were recorded on a Thermo Scientific Nicolet 6700 FT-IR spectrometer (Waltham, MA, USA) at room temperature with a resolution of 4 cm^{-1} and a 64-scan signal from 600-4000 cm^{-1} in absorbance mode.

Catalytic Activity Measurements

The catalytic activity of HT3.0f and HT3.0c were tested on the transesterification of glycerol with ethylene carbonate using a 250 ml three-necked round-bottom flask. The system was equipped with a stirring bar, a thermometer and a reflux condenser. Eighteen grams of glycerol (0.2 mole) and 17.6 g of ethylene carbonate (0.2 mole) together with 2.5 g of HT3.0f catalyst were charged into the flask. The mixture was heated to 180°C under stirring for 5 hr. The mixture was then cooled to room temperature. It was filtered off to remove the catalyst. The same procedure was repeated using HT3.0c catalyst.

Product Analysis

The product mixture compositions were quantitatively analysed on a gas chromatography (HP 6980 Agilent Technologies, US) spectrophotometer equipped with a non-polar HP-Innowax capillary column (30 m × 0.25 mm × 0.25 μm) and a flame ionisation detector. The initial temperature of the column was set at 80°C and raised up to 250°C with a programming rate of 10°C min^{-1} for 30 min. The injection and detector temperatures were kept at 250°C and 260°C, respectively with Helium (He) as the carrier gas. The method development used as reported by Mariam *et al.* (2016) where qualitative and quantitative evaluation were identified.

RESULTS AND DISCUSSION

Catalyst Characterisation

The structural and chemical properties of the HT3.0f and HT3.0c were analysed via various physico-chemical characterisation techniques. *Figure 1* shows the XRD profiles of HT3.0f and HT3.0c. For HT3.0f, the presence of peaks at 12°, 23°, 35°, 40°, 47°, 62° and 63° confirmed a crystalline patterns characteristic of Mg/Al hydrotalcite. These observations were also reported by Cavani *et al.* (1991).

The characteristic reflections of HT3.0c was clearly observed at 45° and 65° which corresponded to a MgO-like phase for all the calcined samples. Based on the 'search and match' technique in XRD database, the prepared HT3.0f and HT3.0c diffractogram matched with the results from the study of Magnesium Aluminum Hydroxide Carbonate Hydrate carried out by Vaccari *et al.* (1995).

The catalyst has a MgO-like structure, where Al^{3+} cation dissolved in the lattice to form a solid solution as described by Millange *et al.* (2000). Studies by Kustrowski *et al.* (2004), confirmed that all the XRD patterns of the mixed oxides (calcined hydrotalcites) exhibited the typical features of a mixed oxide of an MgAlO type.

The spectroscopic data of HT3.0f and HT3.0c catalysts were tabulated in *Table 1*. The N2 adsorption of HT3.0c exhibited type IV isotherm with a hysteresis loop indicating the characteristics of a mesoporous solid (Gubbins *et al.*, 2009). The BET surface area of HT3.0c and HT3.0f catalysts were found to be 179 $m^2 g^{-1}$ and 81 $m^2 g^{-1}$, respectively. The pore volume measured for both HT3.0c and HT3.0f catalysts were 0.59 $cm^3 g^{-1}$ and 0.19 $cm^3 g^{-1}$, respectively.

Cavani *et al.* (1991) reported that a bigger surface area and pore volume were obtained upon calcination due to metal migration from the bulk to the surface of the mixed oxides medium. The pore size distributions of the HT3.0f and HT3.0c catalyst gave average pore diameters between 10 and 80 Å, respectively as shown in *Figure 2*.

Based on the thermogram in *Figure 3*, the thermal behaviour of HT3.0c catalyst was observed. The loss occurred between 25°C to 250°C, could be attributed to water elimination from the interlayer, which gave losses of about 12.5% in the catalyst. The anionic species present in the HT3.0c catalyst were traces of CO_3^{2-} resulted from adsorption of atmospheric carbon dioxide and decarboxylation at temperature above 250°C. Above temperature 250°C, the cation layers (Mg^{2+} and Al^{3+}) started to decompose to carbonate ions, with weight loss of 31.26%. The phase transformation took place at temperature above 420°C.

The differences in IR transmittance pattern for HT3.0f and HT3.0c catalysts can be observed in *Figure 4*. Upon calcination of catalyst HT3.0f to HT3.0c, we can clearly observe -OH absorption at

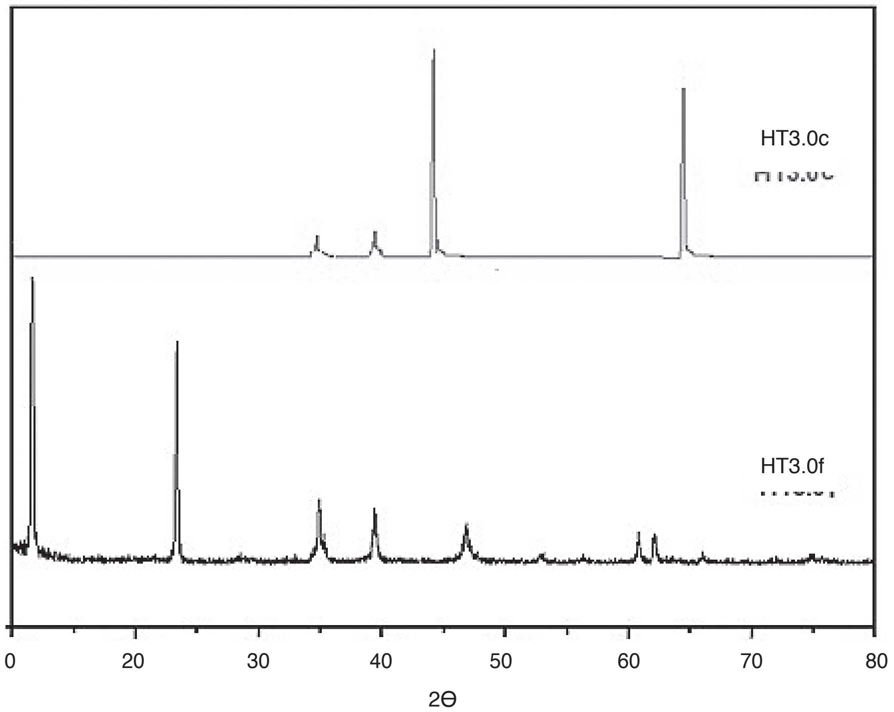

Figure 1. The X-ray diffraction (XRD) pattern of HT3.0f and HT3.0c catalysts.

TABLE 1. THE BRUNAUER-EMMETT-TELLER (BET) SURFACE AREA AND PORE SIZE DISTRIBUTION OF HT3.0f AND HT3.0c CATALYST

Catalyst	aSBET (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore diameter (nm)	Atomic ratio Mg/Al
HT3.0f	81	0.19	3.81	3.04:1.00
HT3.0c	179	0.59	7.74	2.35:1.00

Note: aSBET-BET surface area.

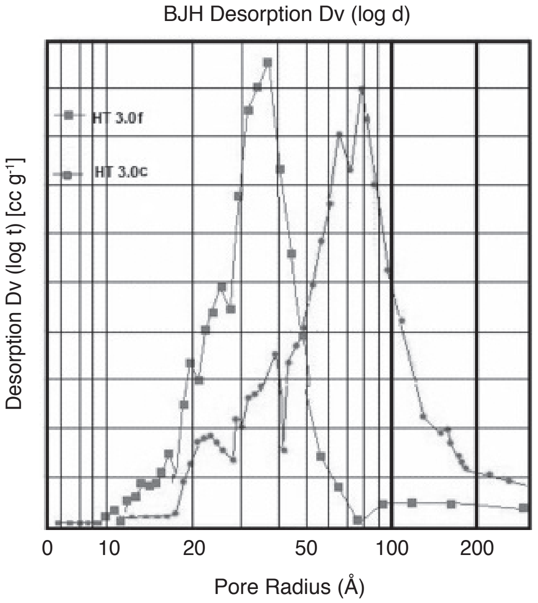

Figure 2. Pore size distribution of the HT3.0f and HT3.0c catalysts from N_2 *desorption branch using Barrett-Joyner-Halenda (BJH) method.*

3449 cm^{-1}. The vibrations of the interlayer CO_3^{2-} is attributed by the presence of sharp peak at 1370 cm^{-1}. Prior to calcination, synthesised catalyst (HT3.0f) contained traces of NO_3^- from the peak at 1384 cm^{-1} (Parida and Das, 2000). This impurity was completely removed after calcination. Again, Parida and Das (2000) reported that the band appearing between 450 and 800 cm^{-1}, represented the characteristics stretching vibration of Mg^{2+} -OH^- bond in Mg-Al-hydroxy-carbonate.

Catalytic Activity of HT3.0c Catalyst

The base-catalysed transesterification between ethylene carbonate and glycerol to produce glyceryl carbonate using HT3.0c catalyst is shown in *Figure 5*.

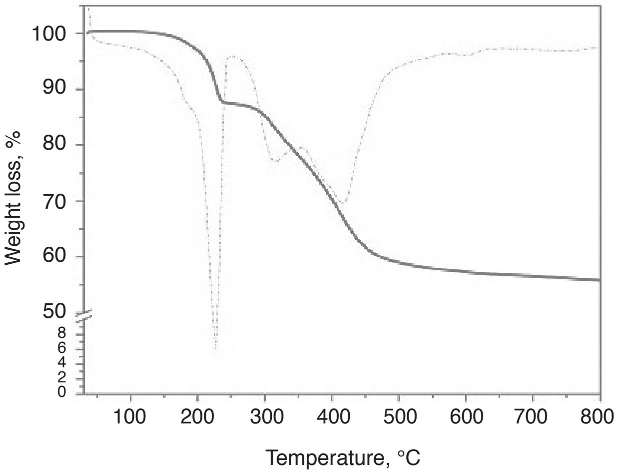

Figure 3. Thermogram spectra of HT3.0c catalyst.

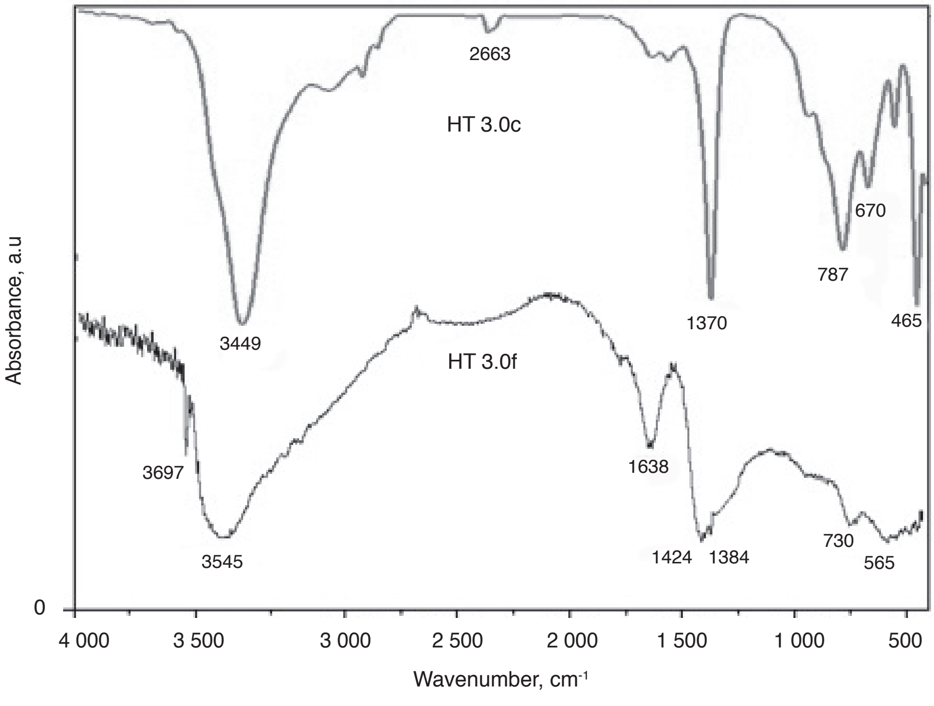

Figure 4. The differences in IR transmittance deformation band for HT3.0f and HT3.0c catalysts.

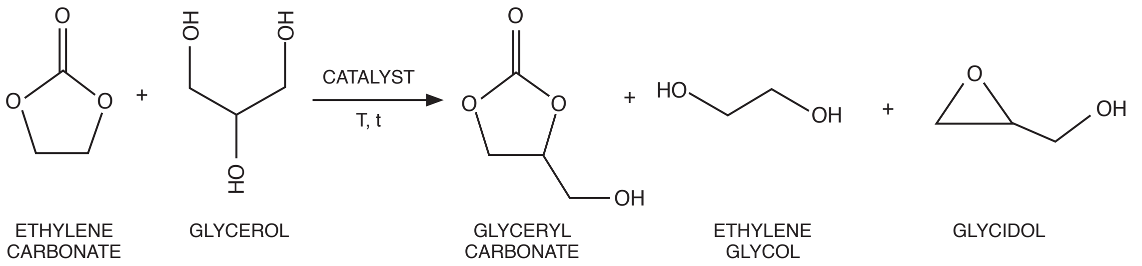

Figure 5. Synthesis of glyceryl carbonate from glycerol and ethylene carbonate.

The percentage composition of the product mixtures obtained after 5 hr of reaction at 80°C is shown in *Table 2*. The reaction without catalyst (Blank) was found to be slow, giving only 6.39% of GC. Catalyst HT3.0c was found to significantly improve the yield of GC to 71.58%. When using HT3.0f, only 39.35% of GC was obtained.

TABLE 2. THE PERCENTAGE OF PRODUCTS FROM GAS CHROMATOGRAPHY OF TRANSESTERIFICATION OF GLYCEROL WITH ETHYLENE CARBONATE

Sample	Unreacted glycerol (%)	Glyceryl carbonate (%)	Ethylene glycol (%)	Glycidol (%)
Blank (no catalyst)	74.91	6.39	8.06	10.64
Catalyst HT3.0f	41.48	39.35	11.93	7.24
Catalyst HT3.0c	11.57	71.58	16.05	0.80

Note: Operating condition: temperature, 180°C; ethylene carbonate, 0.2 mole; glycerol, 0.2 mole; catalyst loading, 7% by weight of total reactants; reaction duration, 5 hr.

Reusability Study of HT3.0c

The reusability test of HT3.0c catalyst was assessed for 10 reaction cycles. Based on the XRD diffractogram pattern of reused HT3.0c catalyst for three reaction cycles in *Figure 6*, revealed that HT3.0c did not change chemically nor it involved in leaching matters as the diffractogram profile was all consistent with the original HT3.0c. The pattern shape was in accordance to the diffractogram of pure hydrotalcite obtained by Cavani *et al*. (1991).

Reusability is one of the advantages of heterogeneous catalysts over homogeneous catalysts. In this study, reusability of HT3.0c catalyst was investigated by recycling the catalyst from one reaction to another without washing or drying of the catalyst cake obtained via vacuum filtration separation from the reaction mixture. Based on *Figure 7*, the reusability of HT3.0c catalyst was successfully tested for 10 subsequent cycles, where the conversion and GC compositions obtained for the second and third cycles were close to the first cycle using fresh HT3.0c catalyst. After the eight cycle, conversion was reduced and GC compositions

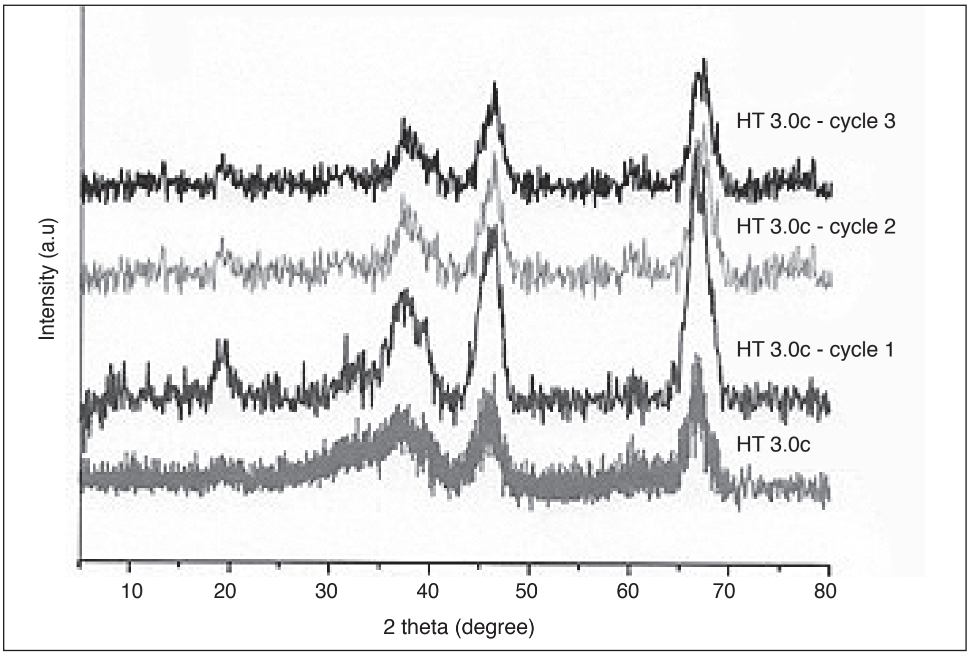

Figure 6. The X-ray diffraction (XRD) analysis for recycle HT3.0c catalyst.

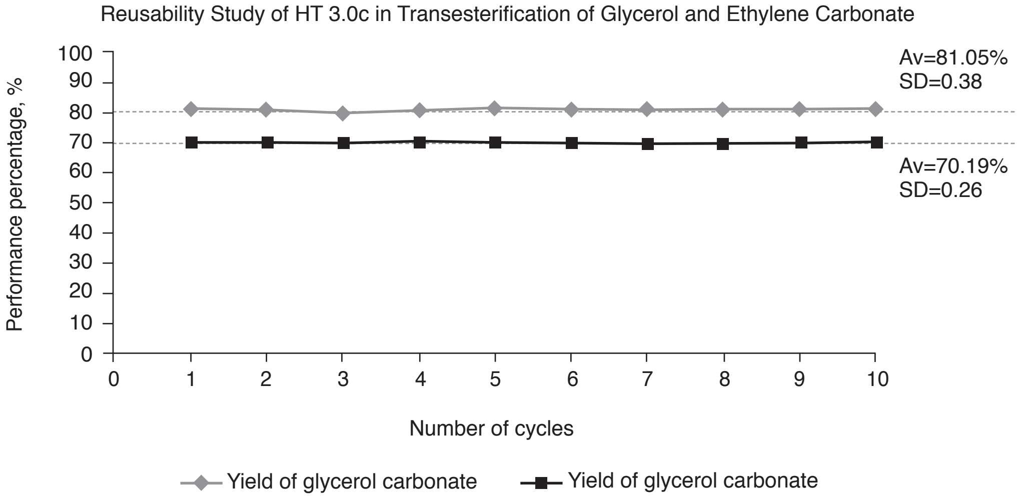

Figure 7. Reusability study profile of HT3.0c catalyst.

seemed to change dramatically. Hence, HT3.0c catalyst was found to have good stability as a reusable heterogeneous catalyst as its catalytic activity was unchanged for eight subsequent cycles in the production of GC via transesterification of glycerol with ethylene carbonate.

CONCLUSION

Transesterification of glycerol with ethylene carbonate was successfully carried out by employing HT3.0c catalyst (hydrotalcite) for glyceryl carbonate production. The optimum reaction conditions were established as 180°C, 7% catalyst, a mole ratio of 1:1 (glycerol:ethylene carbonate) and a duration of 5 hr. The uneconomical process, tedious separation technique and issue on safety of the conventional approach using homogeneous catalyst can now be replaced with a more environmental-friendly heterogeneous catalyst and a better separation process. The catalyst was reusable and the conversion of glycerol to GC was reproducible for eight subsequent cycles of reaction.

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