Technical Report

Catalytic Activity of Intercalated Montmorillonite Clay for Glycerol Conversion to Oligomers via Microwave Irradiation

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Short-chain oligomers such as dimers and trimers are highly valued products because of their excellent biocompatibility caused by the presence of multi-hydrophilic groups within their structures. Conventionally, oligomers are produced via solvent-free glycerol etherification reactions using a simple heating process. However, the process requires a long reaction time (>7 h). Therefore, this work aims to minimize the reaction time by using microwave irradiation as a heating source and to enhance the yield of dimers and trimers by using a catalyst prepared from clay as an economical material for glycerol etherification. Thus, lithium-intercalated montmorillonite clay (Li/mk-10) was prepared via the wet impregnation method. The maximum 98% glycerol conversion was achieved in 4 h with the maximum dimer yield of 45% in 3 h.

Key Words

Glycerol, Clay, Microwave

1. Introduction

Glycerol is a renewable source used as a building block precursor to produce dimers and trimers via solvent-free glycerol etherification reactions. These oligoglycerols have wide-ranging potential applications in various fields, such as cosmetics, pharmaceuticals, and food industries¹⁾. Over the past decade, various homogenous and heterogeneous catalysts have been used to convert glycerol into valuable oligomers via conventional heating processes²⁾.

Using a homogenous Na_2CO_3 catalyst under reaction conditions of 9 h and 240 °C, 76% glycerol conversion with 46% dimer and 34% trimer selectivities was achieved³⁾. However, reactions involving homogenous catalysts are highly active but are less selective of the

dimers as compared to the reactions using heterogeneous catalysts. Moreover, whether homogeneous catalysts can control glycerol etherification reactions has not yet been investigated. Hence, the industrial utilization of homogenous catalysts complicates the purification process⁴⁾.

To enhance catalyst selectivity toward a desired product, several researchers^{2) 5) 6)} designed a porous solid catalyst and suggested that the catalysts with microporous and mesoporous crystalline structures are highly applicable to glycerol conversions. Rupert *et al.*⁷⁾ reported 60% glycerol conversion with 90% selectivity for the desired product using 1 wt.% metal oxide catalyst (i.e. magnesium oxide (MgO), calcium oxide (CaO), strontium oxide (SrO), and barium oxide (BaO)) in a batch stirred reactor at 220 °C. Moreover, the selectivity of the oligomers was enhanced by an increase in the oxide basicity as: $\text{MgO} < \text{CaO} < \text{SrO} < \text{BaO}$. Meanwhile, CaO colloid had a higher activity during the glycerol etherification reaction.

Zahra *et al.*⁸⁾ carried out the catalytic etherification of glycerol under reaction conditions of 8 h and 250 °C, and reported 91% conversion and 43% dimer and 25% trimer yields by using a basic catalyst (20% $\text{Ca}_{1.6}\text{La}_{0.6}$ /MCM-41). The product selectivity was higher for the ordered mesoporous silica surface than homogeneous catalyst. However, there

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was a loss in the selective shape caused by leaching of the active component from the surface of the microporous and mesopore system due to the use of hot glycerol. Ayoub *et al.*⁹⁾ reported 98% glycerol conversion with maximum 80% yield of polyglycerols using 3 wt% of sodium intercalated aluminum pillared clay (Na/AlPC) catalyst with reaction conditions of 12 h and 260 °C.

More promising potential green catalytic pathways have been reported for optimized glycerol conversions with/without solvents by using different solid catalysts via the conventional heating process. However, achieving higher selectivity for the dimer and trimer has remained the main challenge during higher glycerol conversion over a short reaction time. Therefore, to overcome these challenges, an efficient and environmentally friendly catalyst must be developed. Moreover, the utilization of nonconventional heating sources as microwave irradiation or ultrasonic irradiation may significantly reduce the reaction time for converting biodiesel waste glycerol to valuable products.

Therefore, the objective of this study is to synthesize the lithium-intercalated montmorillonite clay (Li/mk-10) catalyst to enhance selective glycerol conversion using microwave irradiation as the heating source. A modified clay catalyst is preferred because of its stable layered structure and interlayer spacing, which can potentially promote higher dimer and trimer yields. The conversion was carried out in the presence of 2 wt.% Li/mk-10 catalyst at atmospheric pressure, a reaction temperature of 260 °C, and a reaction time of 4 h. The reaction product samples were withdrawn every 30 min and characterized using high pressure liquid chromatography (HPLC) to determine the product yield and composition.

2. Experimental

2.1 Materials

Lithium hydroxide (99%), Montmorillonite clay (mk-10), glycerol from Sigma Aldrich (Malaysia), and deionized water for mixing were used in this work.

2.2 Catalyst Preparation

The wet impregnation method was adopted to prepare the lithium-intercalated montmorillonite clay (Li/mk-10) catalyst. The procedure involves mixing 15.8 g LiOH, 10 g mk-10, and 100 mL deionized water in a 250 mL capacity round bottom flask equipped with a reflux condenser. Montmorillonite clay as a support material was first suspended in deionized water and then heated to 60 °C. Upon reaching 60 °C, LiOH was slowly added while maintaining rigorous stirring. The evaporated water was refluxed using the condenser. After 8 h of mixing, the

mixture was filtered, the filtrate (slurry) was rinsed using deionized water, and the rinsed slurry was dried at 120 °C in an oven for 24 h. Finally, the prepared catalyst was calcined at 550 °C in a muffle furnace (Programmable digital muffle furnace FP-12).

2.3 Glycerol conversion

The glycerol etherification reaction was carried out in a 500 mL three-neck flask using the 2 wt.% Li/mk-10 clay catalyst at atmospheric pressure and 260 °C. Microwave irradiation was used as a heating source for the reaction. Glycerol (50 g) was added as feedstock. Then, 60 mL/min inert nitrogen gas flow was maintained throughout the experiment to avoid glycerol oxidation. The water vapor formed during the etherification of glycerol was separated using a Dean-Stark apparatus (Thermo Fisher scientific D95). The experimental setup for this reaction is shown in Fig. 1. The microwave reactor temperature was controlled via a proportional integral derivative controller with the maximum operation time of 4 h. Upon completion of the reaction, the reactor was shut down and left to cool down. The samples were collected every 30 min for further characterization.

The yield and composition of the etherification products (di to hexa oligomers) were analyzed using by HPLC (Thermo Fisher Scientific) with column specifications of 250 × 4.6 mm, and 5 µm hypersil gold amino.

3. Results and Discussion

The glycerol conversion experimental results are shown in Fig. 2. The glycerol conversion reached 98% after 4 h in the presence of the Li/mk-10 clay catalyst at 260 °C

Fig. 1 Microwave reactor setup for the glycerol etherification

Fig 2 Glycerol conversion to polyglycerols by Li/mk-10 catalyst

in an inert nitrogen gas environment when microwave irradiation was used as the heating source. The polyglycerol yield was calculated on the basis of the initial weight percentage of glycerol. The maximum yield (45%) of the dimer was observed at 3 h of the glycerol etherification reaction time, beyond which the yield decreased gradually due to further conversion of dimers into higher oligomers. Moreover, the dimer and trimer yields were determined to be 32% and 4% after 1 h, respectively. At this particular reaction time, higher oligomers such as tetramers, pentamers, and hexamers were not formed.

The catalyst activity was evaluated using glycerol conversion rate and the corresponding dimer and trimer yields. The limitations of the conventional heterogeneous catalysts included the leaching of active components in the hot glycerol and the formation of acrolein at high reaction temperatures. The acidic nature of montmorillonite clay (mk-10) hinders its activity for its application in glycerol conversion reactions. Glycerol conversion of 8% occurred with 6% yield of oligoglycerols at a 4 h reaction time. These low conversion yields are attributed to the presence of acidic sites rather than basic sites on the studied clay material. As previous studies have shown²⁾, a glycerol conversion reaction favors basic sites and is more selective when basic solid catalysts are utilized. Therefore, clay was intercalated with lithium to enhance the basicity of the clay. Moreover, lithium intercalation affects the interlayer spacing of montmorillonite. The changes in the interlayer

spacing of montmorillonite can be measured via X-rays diffraction (XRD)⁹⁾. The effects of lithium on the d-spacing of montmorillonite will be presented in our next article. Generally, metal cations adhere to the outer surface of clay due to electrostatic and van der Waals forces formed during the intercalation with mk-10. The use of alkaline modified montmorillonite clay in the glycerol etherification reaction resulted in the adsorption of glycerol on the surface, which reduced the initial Li/mk-10 activity for the selective formation of the dimers after 3 h. The formation of higher oligomers were likely because of subsequent reactions at higher temperature (260 °C). After 2 h of the glycerol etherification reaction, the formation of tetramers and pentamers was observed by 6% and 1%, respectively. Moreover, the formation of higher oligomers (tetramers, pentamers, hexamers) was increased with the increase in reaction time. After 4 h, the formation of tetramers, pentamers, and hexamers was calculated as 15%, 10%, and 6%, respectively.

The higher glycerol conversion to the desired oligomers using the Li/mk-10 catalyst over a short reaction time suggests that the basal spacing, pore size, and basic strength of the catalyst significantly affected the selective product yield. Moreover, the use of microwave irradiation as the heating source can one of the factors that affect product selectivity.

4. Conclusion

The objective of this study was to synthesize a lithium-intercalated montmorillonite clay (Li/mk-10) catalyst to enhance the selectivity toward glycerol conversion. The modified clay catalyst is preferred for its stable layered structure and interlayer spacing, which can potentially promote higher dimer and trimer yields. The conversion was carried out with 2 wt.% Li/mk-10 catalyst at atmospheric pressure, a reaction temperature of 260 °C, and a reaction time of 4 h. The reaction product samples were withdrawn every 30 min and characterized by HPLC to determine the product yield and composition. Maximum 98% glycerol conversion was achieved in 4 h with maximum dimer yield of 45% in 3 h.

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