



## Improved production of fuel oxygenates via glycerol acetylation with acetic acid



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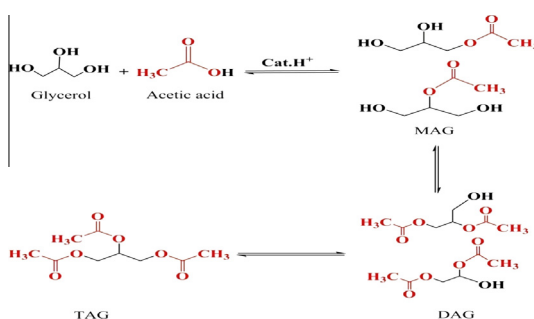
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### HIGHLIGHTS

- The selective acetylation of glycerol with acetic acid was investigated.
- TAG was produced with very high selectivity of 55% with minimal MAG formed.
- 3%Y/SBA-3 catalyst was the best catalyst to achieve glycerol conversion of 100%.
- The best reaction conditions are:  $T = 110\text{ }^{\circ}\text{C}$ , time = 2.5 h, catalyst loading = 0.05 g.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The selective formation of fuel oxygenates via glycerol acetylation with acetic acid over a series of yttrium containing SBA-3 catalysts is reported. The products of glycerol acetylation are mono-, di- and triacetyl glycerol (MAG, DAG, and TAG, respectively) with TAG being the favored. The Y/SBA-3 was prepared by grafting yttrium into the framework of SBA-3. XRD, SAXS, FTIR, SEM–EDX, and surface area and porosity analyzer were used to confirm the properties of the catalysts. The 3%Y/SBA-3 presented unique catalytic performance achieving complete glycerol conversion with corresponding selectivity of 34% and 55% toward DAG and TAG. Over 0.05 g of this catalyst, the reaction conditions were economized to reaction temperature of  $110\text{ }^{\circ}\text{C}$ , molar ratio of glycerol to acetic acid of 1:4, and reaction time of 2.5 h. The catalytic activity was mainly attributable to the catalyst' strong acidity and its high surface area with large pore size that facilitate the diffusion of substrates and products. The reaction kinetics model over this catalyst has been developed using experimental data. The stability of the catalyst was examined via leaching and reusability tests through four consecutive batch runs.

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## 1. Introduction

The importance of bio-based fuels to partially replace the fossil fuels and for sustainable growth cannot be overemphasized. Today,

the increasing concern about the global warming and the dwindling of global energy supplies have motivated the search for alternative fuels that can partially replace the finite fossil fuels and assist to reduce the noxious emissions. As an alternative to the petro-diesel, biodiesel is acquiring a peerless interest due to its sustainability, low toxicity, high BTUs per gallon and high cetane number, which translated into higher combustion efficiency in an internal combustion engine [1]. Commercially, biodiesel is produced via the catalytic transesterification of triglycerides of fatty

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acids ( $C_{12}$ – $C_{22}$ ) with short chain alcohol such as methanol [2]. Inevitably, the process generates about 100 kg of glycerol as a byproduct for each ton of biodiesel produced [3].

A surplus of glycerol has been produced as a consequence of the biodiesel industry growth, leading to the depreciation of its commercial value and thereby, affecting the industrial feasibility of biodiesel. Therefore, the valorization of this glycerol is intimately intertwined with the new and emerging solutions to ameliorate the biodiesel economy and to cut down its global prices [4]. Recently, great interest has been devoted to convert this polyol into value-added products via different routes such as valorization [5], dehydration [6,7], esterification [8], hydrogenolysis [9], and acetalization [10]. Besides, glycerol acetylation with acetic acid is acquiring special attention due to the industrial importance of the final products. Mono-, di-, and triacetyl glycerol (MAG, DAG and TAG, respectively) are the reaction products, which have found various applications ranging from moisturizers to fuel additives. Particularly, TAG is the most attractive acetyl due to its importance as an antiknock agent to gasoline and to its role in improving the cold flow properties and the viscosity of biodiesel [11].

Commercially, glycerol acetylation is performed under batch processes that are catalyzed by conventional Brønsted acids like  $H_2SO_4$ ,  $H_3PO_4$  or HCl as homogeneous catalysts. Such processes are usually accompanied by several technical and environmental drawbacks such as the catalyst separation, product purity, reactor corrosion, and the effluent disposal. As an alternative, different solid acid catalysts including supported heteropolyacids,  $\beta$ - $MoO_3/SBA-15$ ,  $WO_3/TiO_2-ZrO_2$ , sulfated Zirconia, sulfated activated carbon, and mesoporous silica functionalized with sulfonic acid groups have been employed for this reaction. It was found that the acidity of the catalyst (especially the Brønsted acid sites) has a key role toward the selective formation of the favored DAG and TAG products. Despite that these reported catalysts have shown high activity for glycerol acetylation; the low thermal stability and the unsatisfactory selectivity to TAG are still big challenges to the proper design of suitable heterogeneous catalyst for this reaction. In fact, the inevitable water formation in this reaction may lead to weakening the acidic sites [8] and thus, the water-tolerant property of solid acid catalyst is a necessity to perform glycerol acetylation well. In addition, the leaching of the active components to the reaction medium (due to the high polarity of the reaction mixture) is another unresolved problem in many of the previously reported catalytic systems [12,13]. The main reason for the poor hydrothermal stability and the leaching of the metallic species could be assigned to the catalyst preparation techniques. It was reported that catalysts prepared by wet impregnation (WI) method suffered a notable leaching and showed low selectivity to TAG [12]. Contrary to the WI which proceeds through the adsorption (chemi- and/or physisorption) of metal clusters onto the support surface, grafting technique proceeds through surface reaction (condensation, protolysis) of the supports' functional groups (e.g.  $OH^-$ ) and the metal precursor. Therefore, it is widely accepted that catalyst preparation by grafting of metal species may result in hindering of migration, agglomeration and sintering during the subsequent thermal treatments. Moreover, the catalyst would be of highly dispersed metal ions within its structure or framework. We have reported in our earlier contribution in the preparation and characterization of the yttrium containing SBA-3 catalyst along with its application during the transesterification of glycerol with methyl acetate [14]. Thus, this work emphasizes on the application of an outstanding heterogeneous catalyst of strong Brønsted acidity during the selective acetylation of glycerol toward the formation of DAG and TAG under economized process conditions.

## 2. Materials and methods

### 2.1. Materials

Anhydrous glycerol of high purity (>99%) was obtained from Sigma, Germany. Glacial acetic acid (100%) and HPLC grade ethanol (99.7%) were supplied by Merck, Malaysia. Tetraethylorthosilicate (TEOS), Yttrium nitrate hexahydrate ( $Y(NO_3)_3 \cdot 6H_2O$ ) of 98% purity, Cetyltrimethyl ammonium bromide (CTMABr), and Pluronic F127 ( $EO_{106}PO_{70}EO_{106}$ ) were purchased from Sigma–Aldrich, Malaysia. Hydrochloric acid (HCl 37%) was obtained from Mallinckrodt, USA. Standard diacetyl glycerol (~50%) and triacetyl glycerol (~99%) were supplied by Sigma–Aldrich, Germany. All reagents were used without further purification. Deionized water was used throughout this work.

### 2.2. Preparation of the heterogeneous catalysts

In this work, the mesoporous silicate material (SBA-3) was prepared by hydrothermal method and used as catalysts' support. The synthesis details of the mesoporous SBA-3 support and its functionalizing with yttrium species was explained in our previous report [14]. The Y-grafted SBA-3 was prepared by grafting of yttrium species into the lattice of the SBA-3 support, being  $Y(NO_3)_3 \cdot 6H_2O$  was added during the support preparation. The obtained catalysts were denoted as (X%)Y/SBA-3, where X refers to the Y mass fraction in the catalyst. To assess the effectiveness of the preparation technique, another group of catalysts prepared by impregnation technique were considered in this study.

### 2.3. Characterization of the catalysts

The prepared catalysts were characterized for their textural properties (BET surface area, pore volume, and pore size) over Micromeritics ASAP 2020 (USA) surface area and porosity analyzer. X-ray diffraction (XRD) patterns of the pristine SBA-3 and the Y functionalized catalysts (fresh and reused catalysts) were acquired on Bruker D8 Focus X-ray diffractometer (Bruker, Germany) over  $10^\circ \leq 2\theta \leq 90^\circ$ . Small angle X-ray scattering (SAXS) diffractograms were used to provide useful information about the repeating unit of the crystallite structure and the interplanar spacing which may be necessary in understanding the crystalline system of ordered materials. The X-ray tube was operated at 40 kV and 30 mA over scattering angle range of  $0.5^\circ \leq 2\theta \leq 5^\circ$  with scan speed of  $0.01^\circ/\text{min}$  at room temperature. FTIR spectra of the support and catalyst samples (fresh and reused catalysts) were acquired on Perkin–Elmer System 2000 spectrometer by using the standard KBr technique over the range of  $1500$ – $400\text{ cm}^{-1}$ . Scanning electron microscopy (SEM) was used to study the morphology of the synthesized materials using Zeiss Supra TM 35 VP scanning electron microscope (Zeiss, Jena, Germany) coupled with FEI as a source of electrons and accelerated at 300 kV. Energy-dispersive X-ray spectroscopy (EDX) was performed in conjunction with SEM to determine the metallic composition of the catalyst. It is important to mention that the results of SEM characterization for the pristine SBA-3 support and the so modified Y/SBA-3 catalysts were reported in our earlier report [14].

The acidity of prepared catalysts was determined by a neutralization titration procedure. Catalyst powder (0.12 g) was dispersed in 25 mL of 0.02 M NaOH solution and the resulting suspension was gently stirred at room temperature for 48 h. Finally, the mixture was filtered off using membrane filter (0.2  $\mu\text{m}$  pore size) fitted to vacuum system, and the alkali filtrate solution was titrated against 0.02 M HCl solution. The following formula was used to calculate the concentration of acidic sites (C):

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