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Synthesis of monoglyceride through glycerol esterification with lauric acid over propyl sulfonic acid post-synthesis functionalized SBA-15 mesoporous catalyst

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ABSTRACT

Monoglyceride synthesis through glycerol esterification with lauric acid over a propyl sulfonic acid functionalized SBA-15 mesoporous catalyst (HSO_3SBA-15) was studied under reduced pressure to continuously remove water formed. Effects of various reaction parameters such as reaction temperature (413–433 K), catalyst loading (1–5%) and glycerol/lauric acid molar ratio (2:1 and 4:1) on lauric acid conversion and products selectivity were successfully elucidated and correlated with reaction scheme and kinetic model. The parent and functionalized SBA-15 were characterized using FT-IR, ammonia chemisorptions, surface analysis, TEM and SEM. Reusability behavior of the catalyst was also demonstrated. Glycerol esterification could be modeled as irreversible parallel reactions and the kinetic data were successfully fitted to a second order kinetic model. The apparent activation energy for monoglyceride formation using a catalyst loading of 5% and glycerol/lauric acid molar ratio of 4:1 was found to be 42 kJ/mol. The HSO_3SBA-15 catalyst could be reused up to four times without significant loss of catalytic activity.

1. Introduction

Monoglyceride has various applications in food products, cosmetics, pharmaceutical formulations, drug delivery systems, oil well drilling operations, etc. [1,2]. Synthesis of monoglyceride through glycerol transesterification with oleic acid methyl ester using solid basic catalysts in solvent free condition was found to be favourable at an elevated temperature (473 K) over rehydrated Al–Mg mixed oxides and Al–Li mixed oxides catalyst that had Bronsted basic sites and Lewis basic sites, respectively [3]. Meanwhile, glycerol transesterification with lauric acid methyl ester over montmorillonite intercalated with lithium hydroxide (LiK10) catalyst and in the presence of tetramethylammonium hydroxide (TMAOH) was recently reported to show excellent performance at a relatively lower temperature (403 K) [4]. However, the use of organic solvent will result in an extra step for its separation during product purification process. Residual solvent content in the product will also limit the application of the monoglyceride, especially when food products are considered [5–7]. Glycerol esterifications with fatty acids at low temperature in solvent free condition using solid acid catalysts such as acidic resins, conventional zeolites, and sulfated iron oxide were reported to be unfavourable for the reaction due to small pore diameters of less than 8 Å [8,9].

To accelerate the reaction involving bulky molecules such as fatty acids, effective solid acids having pore sizes between 20 and 100 Å are required [10,11]. HSO_3SBA-15 catalyst with a pore size of 67 Å synthesized via post synthesis route was found to be an active solid acid catalyst for monoglyceride formation through the glycerol esterification with lauric acid [12]. However, no sufficient information has been reported on the influence of important process variables, reaction pathway and kinetic model on the product formations in the esterification process. As such, a study on these aspects is deemed necessary for the purpose of advancement of knowledge in this research area.

Reaction pathway is essential to be used for constructing a kinetic model that can be applied to predict the changes in amount of specific product obtained during a reaction process. In order to obtain a better understanding of the reaction pathway, several researchers have undertaken various studies on glycerol esterification with different fatty acids and solid acid catalysts to produce monoglycerides [9,13–15]. Based on their observations, it can be concluded that the reaction pathways of glycerol esterification with fatty acid could be modeled either as consecutive reactions (Fig. 1) following the first order kinetic model with respect to glycerol or as irreversible parallel reactions (Fig. 2) following second order kinetic model with respect to fatty acid and glycerol. The reaction orders reported in the open literatures can be summarized in Table 1.

In the present work, glycerol esterification with lauric acid over the HSO_3SBA-15 is reported. The main focus is to investigate the effect of temperature, glycerol/lauric acid molar ratio and catalyst

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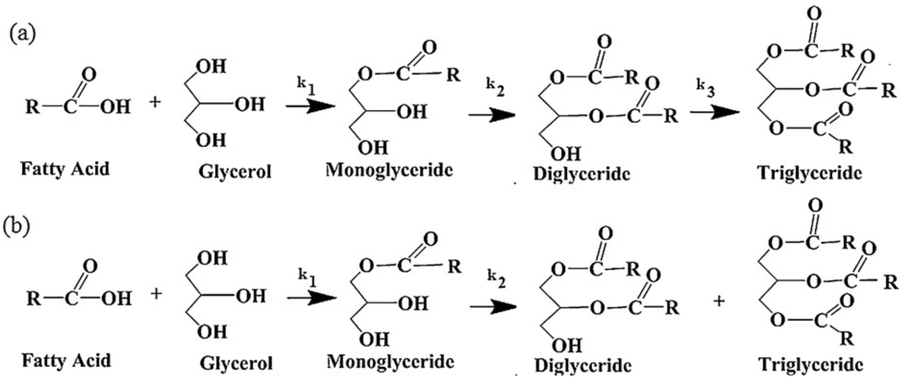

Fig. 1. Consecutive reactions of the glycerol esterification: (a) as proposed by Szelag and Zwierzykowski [13] and, (b) as proposed by Macierzanca and Szelag [14].

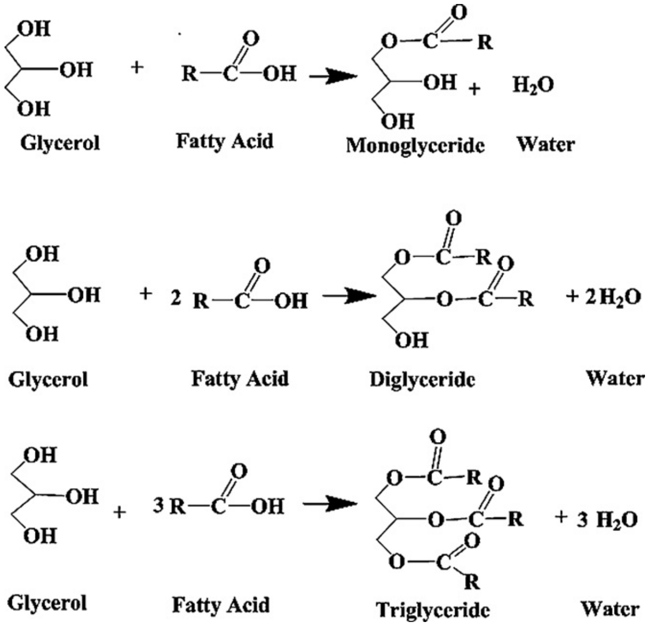

Fig. 2. Irreversible parallel reactions for glycerol esterification with fatty acid as adopted from Sanchez et al. [15].

loading on the products selectivity to gain better understanding of reaction pathway to eventually build a kinetic model for monoglyceride formation. The work also includes model verification, determination of the apparent activation energy of the reaction and reusability study of the catalyst.

2. Experimental

2.1. Catalyst preparation and characterization

SBA-15 mesoporous material was synthesized in the presence of Pluronic P123 which is a triblock co-polymer with a molecular formula of $HO(CH_2CH_2O)_{20}(CH_2CH(CH_3)O)_{70}(CH_2CH_2O)_{20}H$ and a molecular weight of 5800 as the structure-directing agent. After that, the SBA-15 mesoporous material was functinonalized with propylsulfonic acid by refluxing 2 g of SBA-15 materials with 2 mL of 3-mercaptopropyl trimethoxysilane (MPTMS). Then, soxhlet extraction was carried out for 20 h, followed by mild oxidation using H_2O_2 to form HSO_3SBA-15. The preparation methods of SBA-15 material and HSO_3SBA-15 catalyst were thoroughly described in a previously published article [15]. The parent SBA-15 mesoporous material and HSO_3SBA-15 catalyst were then characterized using FT-IR spectroscopy, pulse chemisorption followed by temperature programmed desorption (TPD) of NH_3, surface area analysis, TEM analysis and SEM analysis. Meanwhile, Fourier transform infrared (FT-IR) spectrum was used to detect the presence of organosulfonic acid group which was grafted on SBA-15 mesoporous material. The FT-IR spectroscopy was performed using a Perkin Elmer 2000 Fourier transformed infrared (FT-IR) system.

Acidity characterization of the catalysts involved pulse chemisorption of ammonia followed by its temperature-programmed desorption (TPD) using micromeritics Autochem II 2920 instrument. The sample was first activated by heating to 150 °C in helium for 2 h, and then cooled down to 127 °C. During the ammonia chemisorption step, 5 injections of ammonia were dosed onto the sample (to ensure the sample was saturated). After saturation, the temperature was subsequently increased from 127 to 427 °C to perform the TPD of NH_3 analysis.

Pore size distribution was obtained from N_2 adsorption–desorption isotherms of the prepared SBA-15 and HSO_3SBA-15 samples. The N_2 adsorption–desorption measurements were performed using a Quantachrome Autosorb-1 equipment. Prior to the experiment, the samples were degassed ($P < 10^{-1}$ Pa) at 270 °C for 6 h. Surface area was calculated using the BET method (S_{BET}) and pore size distribution was determined using the Barrett–Joyner–Halenda (BJH) model applied to the desorption branch of the isotherm. The micropore area (S_{μ}) was estimated using the correlation of *t*-Harkins and Jura (*t*-plot method).

The TEM images were obtained using Philips CM 12 transmission electron microscope. The sample of about 0.08 g was first dispersed in 5 ml ethanol. Then, the solution was vigorously shaken for a while. Subsequently, a small amount of the solution was taken

Table 1
Summary of published kinetic models for glycerol esterification with fatty acids reaction over various solid acid catalysts.

Type of catalysts	Fatty acids (FA)	G/FA[a] molar ratio	Reaction pathways	Rate reaction expression[b]	Refs.
Na or K soaps	Lauric acidMyristic acidPalmitic acidStearic acid	1:1	Consecutive reactions	$-r_G = k_1 C_G \, r_{Mono} = k_1 C_G - k_2 C_{Mono}$	[13]
Zinc carboxylates	Lauric acidMyristic acidPalmitic acidStearic acid	1:1	Consecutive reactions	$-r_G = k_1 C_G \, r_{Mono} = k_1 C_G - k_2 C_{Mono}$	[14]
Sulfated iron oxide	Oleic acid	1:1	Parallel reactions	$-r_{FA} = -(1/W)(dC_{FA}/dt) = k_1 C_G C_{FA}$	[9]
Zeolite (faujasite)	Oleic acid	1:3, 1:1 and 3:1	Parallel reactions	$-r_{FA} = -(1/W)(dC_{FA}/dt) = k_1 C_G C_{FA}$	[15]

[a] G/FA = glycerol/fatty acid molar ratio.
[b] $-r$ = rate of reaction, C_x = concentration of reactant x, k_1 = rate constant for forward reaction, k_2 = rate constant for reverse reaction, W = weight of catalyst.