



Synthesis of Glycerol Monostearate by Esterification on H₃PW₁₂O₄₀/MCM-41 Catalyst

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H₃PW₁₂O₄₀/MCM-41 solid-acid catalyst with different phosphotungstic acid (H₃PW₁₂O₄₀) loadings was prepared by impregnation method and used in the esterification of glycerol with stearic acid using N,N-dimethyl formamide as solvent. The catalyst was characterized by FT-IR spectroscopy, transmission electron microscopy and scanning electron microscopy. The effects of catalyst preparation and esterification parameters such as reaction time, stearic acid/glycerol ratio and reaction temperature on esterification were investigated simultaneously. The results showed that H₃PW₁₂O₄₀/MCM-41 had the best catalytic properties when the H₃PW₁₂O₄₀ loading was 30 % and the use of DMF had a significant improvement on the yield of monoglyceride. Under a reaction condition of 6 h, 433 K and glycerol/acid molar ratio 6:1, 91 % selectivity of glycerol monostearate was achieved with a stearic acid conversion of 98 %.

Keywords: Esterification, Glycerol monostearate, Tungstophosphoric acid, MCM-41.

INTRODUCTION

The increasing production of biodiesel generates a great amount of glycerol surplus. Converting glycerol into value-added products is a significant way to improve the economics of biodiesel production.

Glycerol monoesters have wide and significant applications in food, plasticizer, pharmaceutical and cosmetic products¹. Monoglycerides are usually synthesized from glycerolysis, the hydrolysis of triglycerides and the direct esterification of glycerol with fatty acids. The esterification reaction is generally catalyzed by strong mineral acids such as sulfuric acid and phosphoric acid which leads to a mixture of mono-, di- and triglycerides (40:50:10)^{2,3} and causes environmental problems.

Phosphotungstic acid (H₃PW₁₂O₄₀), the 12-tungstophosphoric acid, has shown the strongest acidity among the Keggin series. The Keggin structure can be supported on a high surface area carrier to improve its surface area, thus providing more acid sites. MCM-41 is the most well-known member of the M41S family of mesoporous molecular sieves. MCM-41 loaded with heteropoly acid was reported effective in a variety of esterification reactions. Juan *et al.*⁴ reported a conversion of 88 % for the esterification of fatty acid with butanol using 30 % H₃PW₁₂O₄₀/MCM-41 as catalyst. Chu⁵ found that H₄SiW₁₂O₄₀/MCM-41 catalysts had 100 % selectivity to *n*-butyl acetate with a conversion of 86.5 %.

The direct esterification of glycerol with fatty acid in the presence of solid acid materials has attracted more and more attentions in order to avoid side reactions. Pouilloux *et al.*⁶ studied the reaction between glycerol and fatty acid in the presence of ion-exchange resins. The oleic acid conversion increased to 90 % without any change of the monoglyceride selectivity 85 %. But the resins could not be used at high temperatures, which might prevent the further improvement of monoglyceride yields. Machado *et al.*⁷ described a process for the synthesis of monoesters from the esterification of glycerol with lauric acids in the presence of zeolites (H-beta, H-Y and H-MOR zeolites). More than 65 % selectivity of monolaurate could be obtained when the zeolite beta was used as catalyst although the activity and consequently monoglyceride yield were sometimes low. In the study of Bossaert *et al.*⁸, mesoporous silica functionalized with sulfonic groups was obtained to be more active than zeolites in the glycerol esterification with lauric acid, which led to more than 53 % of monoglyceride yield. However, the high selectivity of monoglycerides was only obtained at a relatively low conversion.

The potential of H₃PW₁₂O₄₀/MCM-41 for esterification of stearic acid and glycerol has not been reported yet. In this paper, the synthesis of glyceryl monostearate *via* direct esterification of glycerol with stearic acid catalyzed by H₃PW₁₂O₄₀/MCM-41 was studied. The influence of several catalyst properties and reaction conditions on the activity and selectivity was discussed.

EXPERIMENTAL

Catalyst preparation and characterization: MCM-41 mesoporous material was purchased from Catalyst Factory of Nankai University. One gram of MCM-41 was dispersed in an aqueous solution of the desired amount of H₃PW₁₂O₄₀ crystals in 12 mL of water and stirred overnight at room temperature. Then the water was evaporated at 80 °C and the solid was dried in an oven at 110 °C overnight⁹. The prepared catalysts were denoted by their weight percentage of H₃PW₁₂O₄₀ signed as (X) H₃PW₁₂O₄₀/MCM-41. A series of H₃PW₁₂O₄₀/MCM-41 namely 10, 30 and 50 wt. % were prepared according to previous method.

The primary Keggin structure of H₃PW₁₂O₄₀ on MCM-41 was studied by means of FT-IR spectroscopy. The sample was pelletized with KBr and used to record the infrared spectra, ranging 4000-400 cm⁻¹.

Transmission electron microscopy (TEM) was performed on TecnaiG220 transmission electron microscope equipped with field emission gun operated at 200 kV. A small amount of samples were prepared by ultrasonically suspending the powder in ethanol and drops of the suspension were deposited on a copper grid dried at room temperature before analysis.

SEM studies of the catalysts were carried out using FEI Sirion2000 scanning electron microscope at 10-15 kV and 0.14-0.58 nA.

Esterification: The esterification was carried out in a four-necked flask reactor equipped with a mechanical stirrer, a thermometer and a condenser. Glycerol and stearic acid were stirred at 800 rpm with DMF as solvent and heated in an oil bath at required temperature. A N₂ steady flow was passed over the reaction mixture through one-flask opening. The catalyst was added to the reactants when the desired temperature was reached.

Product analysis: Reaction products, the mixture of fatty acid, monoglycerides, diglycerides and triglycerides were analyzed by gas chromatography. Gas chromatographic analysis was performed on a DB-5ht column with a GC9160 instrument with FID detector. The detector and injector temperatures were both 633 K. Samples were injected "on-column" at 323 K. The column was held at this temperature for 2 min and then heated to 653 K at a rate of 10 K/min.

Conversion (X_{SA} , referred to the total content of esters in the reactant), selectivity (S) and yield (Y) were calculated through the following equations (n_j , mol of product j ; MG = monoglycerides (both isomers), DG = diglycerides (both isomers), TG = triglycerides^{10,11}):

$$X_{SA} = \frac{n_{MG} + 2n_{DG} + 3n_{TG}}{n_{MG} + 2n_{DG} + 3n_{TG} + n_{SA}} \times 100\%$$

$$S_{MG} = \frac{n_{MG}}{n_{MG} + 2n_{DG} + 3n_{TG}} \times 100\%$$

$$Y_{MG} = X_{SA} \times S_{MG} \times 100\%$$

RESULTS AND DISCUSSION

Characterization of the H₃PW₁₂O₄₀/MCM-41 catalysts:

Fig. 1 showed the FT-IR spectra of MCM-41, H₃PW₁₂O₄₀ and

30 % H₃PW₁₂O₄₀/MCM-41. Curve a showed broad bands around 3426 and 1300-1000 cm⁻¹ which assigned to O-H and Si-O-Si stretching vibration of MCM-41, respectively. Bands at 801 and 458 cm⁻¹ were due to symmetric stretching vibration and bending vibration of rocking mode of Si-O-Si, respectively. These bands were also observed in curve c, which suggested the structure of MCM-41 was well retained after loaded with H₃PW₁₂O₄₀. Curves b and c in Fig. 1 showed the typical IR bands at 1080 cm⁻¹ (P-O in the central tetrahedra), 993 cm⁻¹ (terminal W = O), 885 and 798 cm⁻¹ (W-O-W) asymmetric vibrations associated to the Keggin ion¹², indicating that the primary structure of the heteropolyacid kept well after loaded on MCM-41. Weak bands at 993 and 798 cm⁻¹ corresponding to H₃PW₁₂O₄₀ in curve c were due to the low concentration of H₃PW₁₂O₄₀ caused by its dilution in the silica matrix¹³.

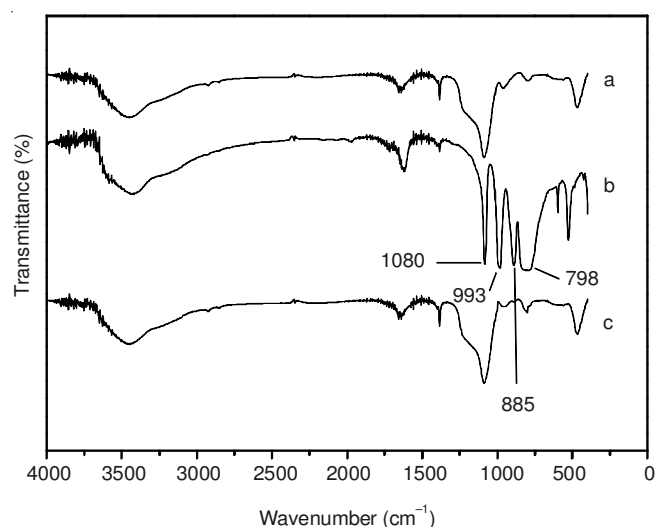


Fig. 1. FT-IR spectra of MCM-41(a), H₃PW₁₂O₄₀ (b) and 30 % H₃PW₁₂O₄₀/MCM-41 (c)

Fig. 2 showed the TEM images of MCM-41 and 30 wt. % H₃PW₁₂O₄₀/MCM-41 from which suggest the well-ordered pore space framework of mesoporous material. After MCM-41 loaded with H₃PW₁₂O₄₀, results still showed an evidence of MCM-41 mesoporous structure kept well at loading of 30 wt. %. In Fig. 2(b), there was no clear sign of bulk H₃PW₁₂O₄₀ species located outside MCM-41 particles. Although the long-range order was partially turned amorphous, the H₃PW₁₂O₄₀ was well dispersed and located inside the pores of MCM-41¹⁴.

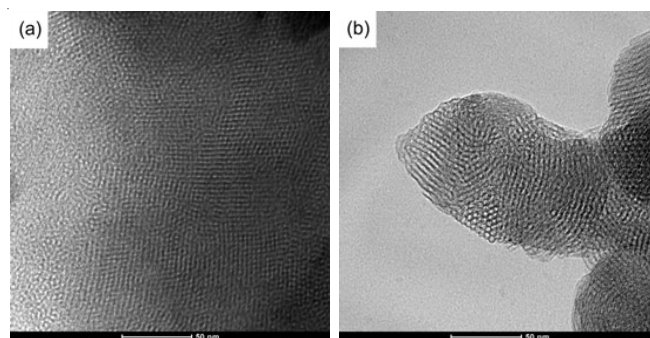


Fig. 2. TEM micrographs of MCM-41(a) and H₃PW₁₂O₄₀/MCM-41(b)

The SEM images of parent MCM-41 and the catalyst presented in Fig. 3(a) and (b) revealed that their structures had regular and orderly pore structure. Surface morphology had no obvious change after the loading with $\text{H}_3\text{PW}_{12}\text{O}_{40}$, which suggested that the mesoporous arrangement was preserved and the incorporation of Keggin-type structures had no adverse effects on the ordered structure of MCM-41. Meanwhile, it also showed a good dispersion of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ on the MCM-41 surface without clustering.

Effects of reaction parameters on the catalyst performance

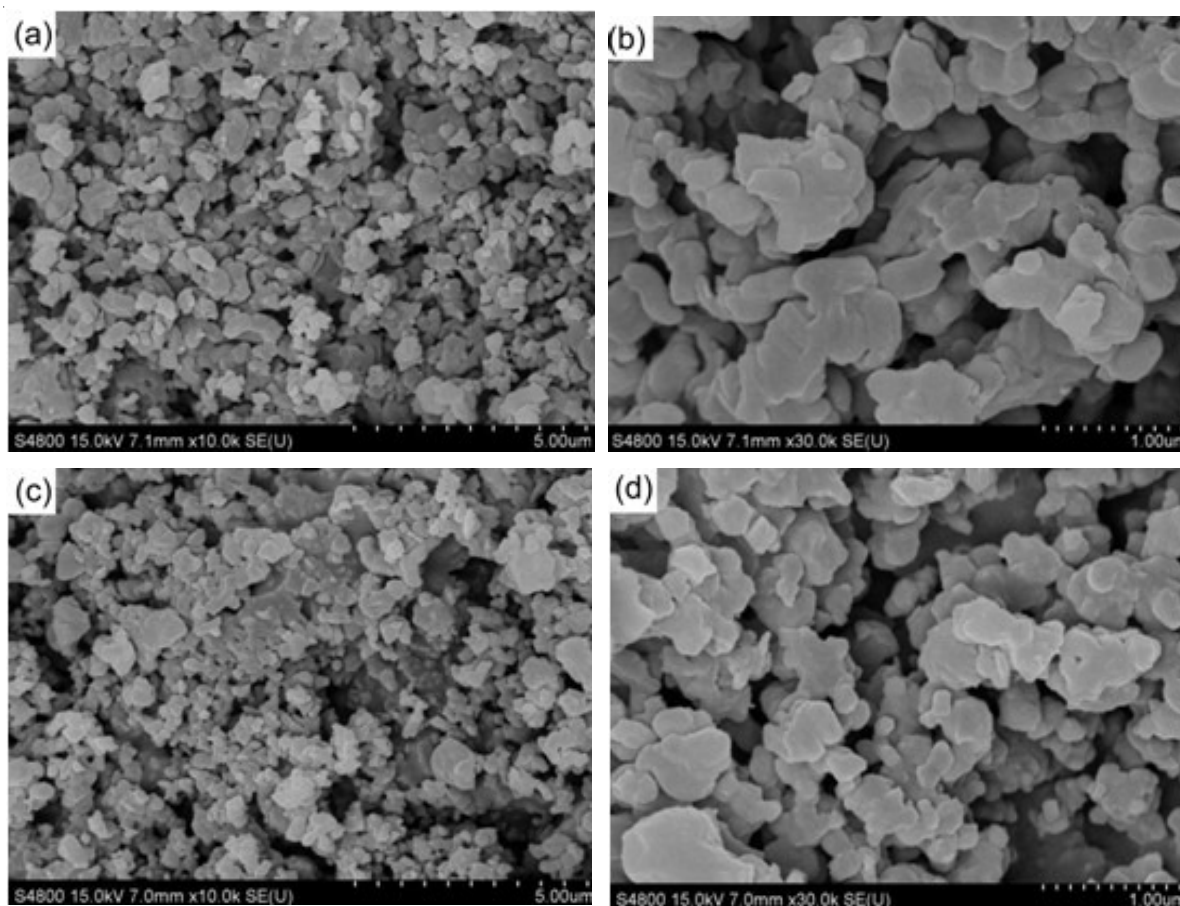


Fig. 3. Low-magnification (a) and high-magnification (b) SEM images of MCM-41; low-magnification (c) and high-magnification (d) SEM images of 30 % $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{MCM-41}$

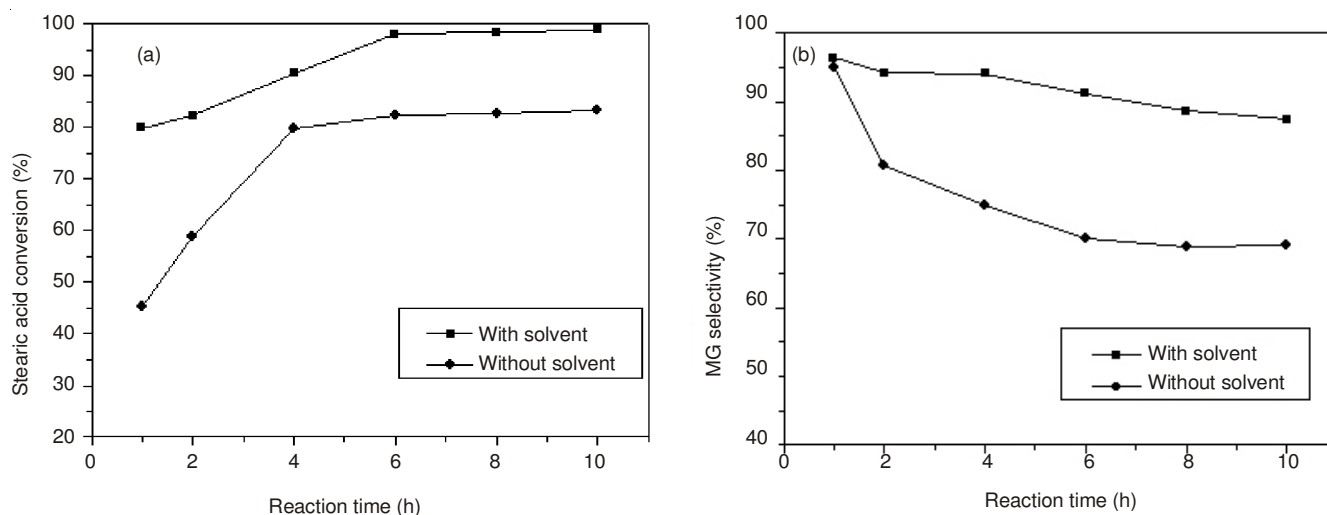


Fig. 4. Effect of solvent (DMF) on steric acid conversion (a) and monoglyceride selectivity (b)

Effect of solvent: The activity of the catalyst in the esterification of glycerol with stearic acid under solvent condition was plotted in Fig. 4. The use of DMF increased the activity and the monoglyceride selectivity of $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{MCM-41}$ due to the homogenisation of the reaction mixture. Glycerol created a system of high viscosity in which glycerol molecules could not contact fully with stearic acid that inhibiting the collision between reactant molecules without the solvent. On the contrary, the addition of a solvent can modify the catalytic

properties of the solid acid significantly in changing the miscibility of reactants and products. Adsorbed at the surface of the catalyst, the solvent modified the coverage of reactants and products, moreover, the rate of the esterification¹⁵. The results showed that the esterification rate was strongly depended on both the catalyst and solubility.

Reaction conditions: 5.68 g steric acid, 11.04 g glycerol, 0.84 g catalyst (30 % $H_3PW_{12}O_{40}/MCM-41$), 433 K.

Effect of the glycerol/stearic acid molar ratio: Fig. 5 showed the effect of glycerol/stearic acid molar ratio on the stearic acid conversion and monoglyceride selectivity. As can be seen in the figure, the conversion rate increased with time before reaction time of 6 h. when glycerol/acid molar ratio rose to 6:1, stearic acid conversion was faster and higher on the overall trend. This was attributed to a higher chance for stearic acid to react with glycerol while using excess glycerol which would be possible to increase the monoglyceride yield by shifting the reaction equilibrium. But a higher glycerol/fatty acid ratio resulted in a low effective collision of reactant and catalyst, an increase in the viscosity of the reaction system, thus not having a positive effect on the acid conversion

percentage. After reaction time of 6 h, the conversion of the reaction tended to be steady, proving the reaction reached equilibrium. The slight decline of conversion at glycerol/stearic acid molar ratio 6:1 after 6 h was due to the partial decomposition of monoglycerides. The monoglyceride selectivity decreased in the process, which was caused by the monoglycerides transformed to diglycerides and triglycerides. Considering the conversion and selectivity, we chose the molar ratio of 6:1 and 6 h of reaction time as the best condition.

Effect of $H_3PW_{12}O_{40}$ loading on MCM-41: Several catalytic tests were conducted at 433 K with different $H_3PW_{12}O_{40}$ loadings (10, 30 and 50 wt. % with respect to MCM-41) using a constant glycerol/stearic acid molar ratio of 6:1, presented in Fig. 6. Results indicated that the 30 % $H_3PW_{12}O_{40}/MCM-41$ was more active. When the $H_3PW_{12}O_{40}$ loading increased from 10 to 30 wt. % at reaction time of 6 h, stearic acid conversion increased from 80 to 98 %. The 30 % $H_3PW_{12}O_{40}/MCM-41$ exhibited higher catalytic activity owing to its strong acidity and large acid amount. However, when the $H_3PW_{12}O_{40}$ loading amount increased to 50 wt. %, no further increase in the conversion was observed, even at a longer reaction time.

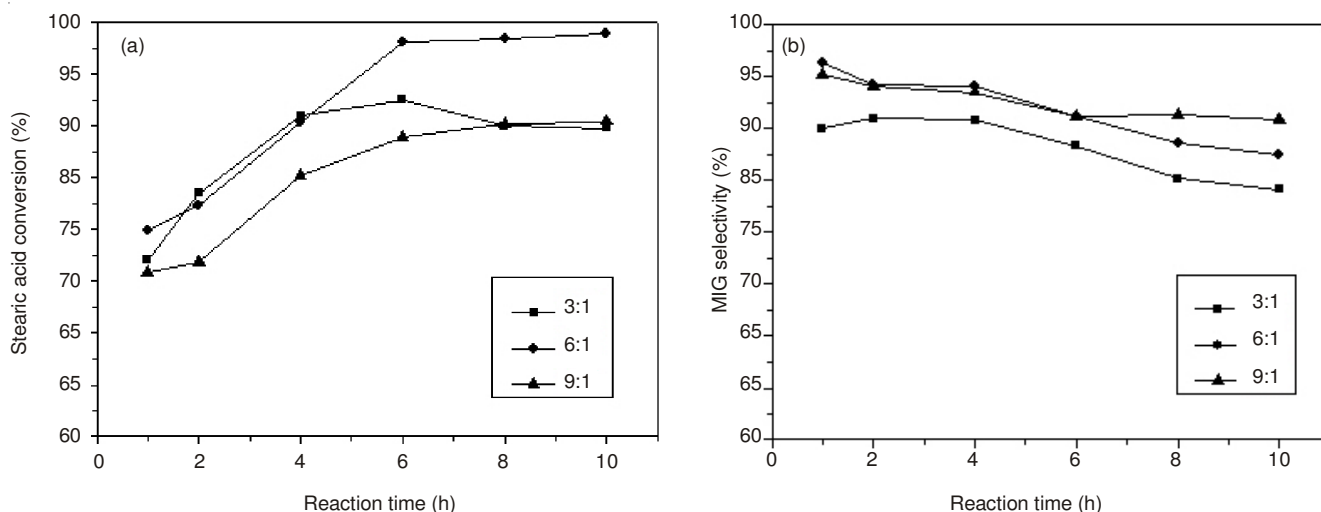


Fig. 5. Effect of glycerol/stearic acid molar ratio on steric acid conversion (a) and monoglyceride selectivity (b) Reaction conditions: 0.84 g catalyst (30 % $H_3PW_{12}O_{40}/MCM-41$), 50 mL DMF, 433 K

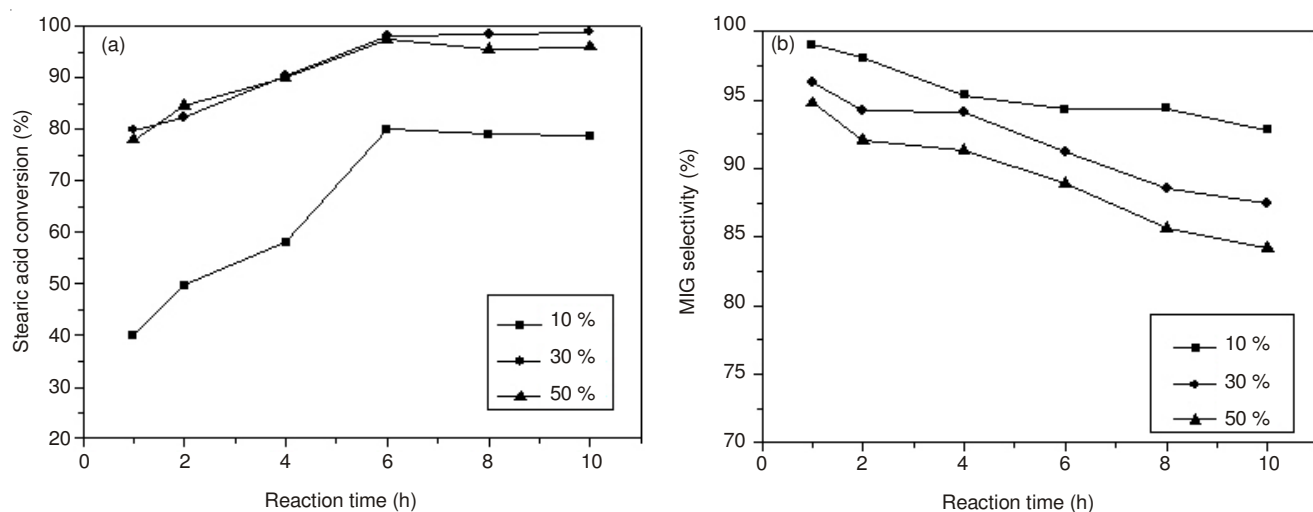


Fig. 6. Effect of $H_3PW_{12}O_{40}$ loading on MCM-41 on stearic acid conversion (a) and monoglyceride selectivity (b) Reaction conditions: 5.68 g steric acid, 11.04 g glycerol, 0.84 g catalyst, 50 mL DMF, 433 K

Fig. 6(b) showed a decline in monoglyceride selectivity with the increase of $H_3PW_{12}O_{40}$ loading. This observation suggested that at a low phosphotungstic acid capacity, the weak activity of catalyst was not able to lead to the synthesis of diglyceride or triglyceride. When phosphotungstic acid loading was too high, the big grain of phosphotungstic acid formed, blocking the molecular sieve pore structure where the formation of monoglyceride was probably more favourable than that of diglyceride and triglyceride. Therefore, 30 wt. % was chosen as the optimal $H_3PW_{12}O_{40}$ loading.

Effect of reaction temperature: Temperature effects on stearic acid conversion and monoglyceride selectivity were illustrated in Fig. 7. Stearic acid conversion increased with the increase of reaction temperature. For instance, it increased from 78 % at 393 K to 89 % at 413 K then to 98 % at 433 K at a reaction time of 6 h. This result suggested that by increasing the temperature, kinetic energy of glycerol and stearic acid

was higher, which made the stearic acid and glycerol molecules collision probability increase, thereby enhancing the effective interaction between the reactant molecules. With the presence of more acid sites either in the inner or the outer pores of $H_3PW_{12}O_{40}/MCM-41$ catalyst, the higher effective collisions led to the increase in stearic acid conversion.

Effects on monoglyceride selectivity were less significant. With the increase of temperature, monoglyceride selectivity decreased slightly. This might suggest that at lower temperature, fewer degradation products were formed. Fig. 7 showed that it achieved the best reaction effect when the reaction temperature was 433 K.

Conclusion

The solid acid catalyst $H_3PW_{12}O_{40}/MCM-41$ was prepared and used in the esterification of glycerol with stearic acid in the presence of DMF. In conclusion, $H_3PW_{12}O_{40}/MCM-41$ is an appropriate catalyst, coupling large conversion rates to high monoglyceride yields. Under a reaction condition of 6 h, 433 K and glycerol/acid molar ratio 6:1, 91 % selectivity of glyceryl monostearate was achieved with a stearic acid conversion of 98 %.

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REFERENCES

1. T.Y. Wibowo, A.Z. Abdullah and R. Zakaria, *Appl. Clay Sci.*, **50**, 280 (2010).
2. L. Hermida, A.Z. Abdullah and A.R. Mohamed, *J. Appl. Sci.*, **10**, 3199 (2010).
3. R. Nakamura, K. Komura and Y. Sugi, *Catal. Commun.*, **9**, 511 (2008).
4. J.C. Juan, J. Zhang and M.A. Yarmo, *J. Mol. Catal. A*, **267**, 265 (2007).
5. W. Chu, X. Yang, Y. Shan, X. Ye and Y. Wu, *Catal. Lett.*, **42**, 201 (1996).
6. Y. Pouilloux, S. Abro, C. Vanhove and J. Barrault, *J. Mol. Catal. A*, **149**, 243 (1999).
7. M.S. Machado, J. Pérez-Pariente, E. Sastre, D. Cardoso and A.M. de Guereñu, *Appl. Catal.*, **203**, 321 (2000).
8. W.D. Bossaert, D.E. De Vos, W.M. Van Rhijn and J. Bullen, *J. Catal.*, **182**, 156 (1999).
9. F.J. Méndez, A. Llanos, M. Echeverría, R. Jáuregui, Y. Villasana, Y. Díaz, G. Liendo-Polanco, M.A. Ramos-García, T. Zoltan and J.L. Brito, *Fuel*, **110**, 249 (2013).
10. C.A. Ferretti, A. Soldano, C.R. Apesteigua and J.I. Di Cosimo, *Chem. Eng. J.*, **161**, 346 (2010).
11. L. Hermida, A.Z. Abdullah and A.R. Mohamed, *Chem. Eng. J.*, **174**, 668 (2011).
12. T. Blasco, A. Corma, A. Martinez and P. Martinezcolano, *J. Catal.*, **177**, 306 (1998).
13. B.R. Jermy and A. Pandurangan, *Appl. Catal. A*, **295**, 185 (2005).
14. B. Rabindran Jermy and A. Pandurangan, *Catal. Commun.*, **9**, 577 (2008).
15. Y. Pouilloux, S. Métayer and J. Barrault, *Comptes Rendus de l'Académie des Sciences-Series IIC-Chemistry*, **3**, 589 (2000).

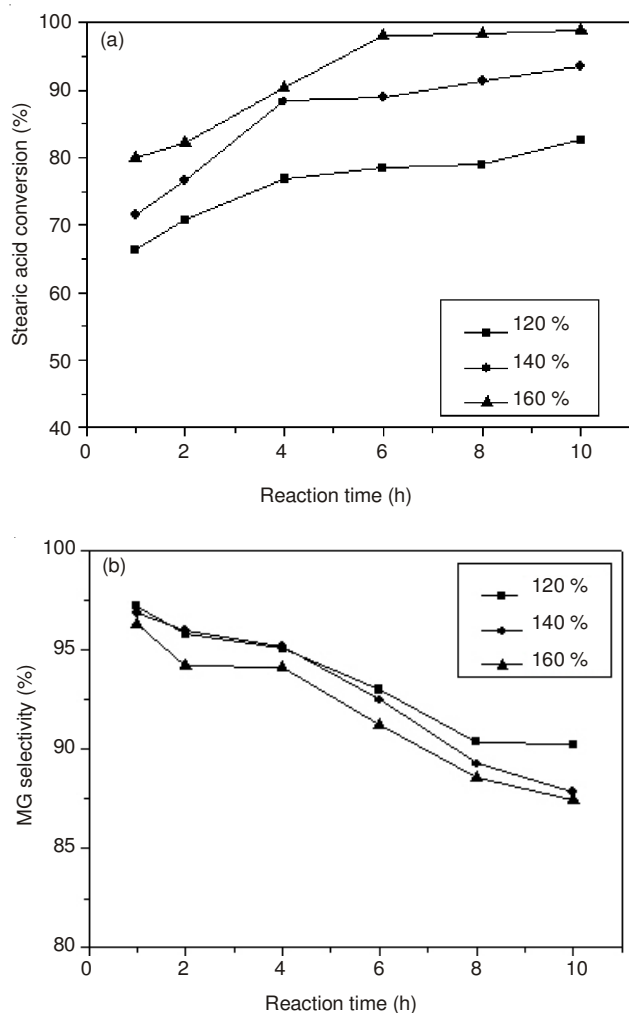


Fig. 7. Effect of reaction temperature on stearic acid conversion (a) and MG selectivity (b), Reaction conditions: 5.68 g stearic acid, 11.04 g glycerol, 0.84 g catalyst (30 % $H_3PW_{12}O_{40}/MCM-41$), 50 mL DMF