Hydrogenation of Palmitic Acid as Palm Oil Model Compound over Sulfided $NiMo/Al_2O_3$-TiO_2 Catalysts

Parinya Jitreewas, King Mongkut's University of Technology North Bangkok,
Bangkok, Thailand
Sabaithip Tungkamani, King Mongkut's University of Technology North Bangkok,
Bangkok, Thailand
Tanakorn Ratana, King Mongkut's University of Technology North Bangkok,
Bangkok, Thailand
Monrudee Phongaksorn, King Mongkut's University of Technology North Bangkok,
Bangkok, Thailand
Samitthichai Seeyangnok, King Mongkut's University of Technology North Bangkok,
Bangkok, Thailand

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Abstract

Bio-hydrogenated diesel (BHD) has always been an interesting alternative for renewable fuel. The hydrogenation of oils seems to be a very promising method in term of production of future fuels. The major advantage of this process is the formation of hydrocarbon products at the conventional fuel range with less sulfer containing. The aim of this present study is to investigate hydrogenation of Palmitic acid as the palm oil model compound is studied over sufided $NiMo/Al_2O_3$-TiO_2. The three catalysts are compared specifically based on different Ni loaded with Ni/(Ni+Mo) weight ratios of 0.2, 0.3 and 0.4 accordlingly. Then, sol-gel and NiMo complex co-impregnation procedure were prepared and being processed. The catalyst reactivity was investigated via the hydrogenation reaction of Palmitic acid in a stirred batch autoclave at a temperature of 240-320 °C for 1 hour with the support of 10 bars of H_2. The liquid parts of the products were then analyzed by Gas Chromatography-Mass Spectrometry and Gas Chromatography-Flame ionization detector. The change in the hydrogenation activity of catalyst and the effect of temperature (240-320 °C) on the yield and composition of product were also carefully investigated. The conversion of all catalysts in Palmitic acid to C 15 and C 16 hydrocarbons clearly showed that the hydrogenations had undergone both hydrodeoxygenation and decarboxylation procedures. The product selectivity of hydrodeoxygenation (C16) increased with the increases of Ni/(Ni+Mo), with the weight ratios from 0.2 to 0.3. But, the 0.4NiMo catalyst was the likely desirable choice with a higher selectivity of decarboxylation (C15).

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1. Introduction

The potential sources of fuel for transportation are natural gas and petroleum which are non-renewable fossil fuels with limited sources, unpredictable prices and increasing the emission of CO_x, NO_x and SO_x gases, which cause global warming and environmental problems [1,2]. These concerns lead to considerable efforts have been made to develop clean and renewable fuels technologies in order to secure the world energy reserves and gain environment benefits.

Bio-hydrogenated diesel (BHD) has been interesting for alternative renewable fuel. The hydrogenation of vegetable oils or fat is a promising route to the production of future fuels and the major advantage of this process is the formation of hydrocarbon products at the conventional fuel range with less sulfer and nitrogen containing.

This work attempted to investigate on the hydrogenation of Palmitic acid over sufided $NiMo/Al_2O_3$-TiO_2 in a stirred batch autoclave at 240-320 °C for 1 h with 10 bars of H_2. The effects of Ni loaded on product selectivity of decaboxylation were investigated.

2. Materials and Methods

2.1 Catalyst preparation

The mixed oxide Al_2O_3-TiO_2 support were synthesized by sol-gel method using Al(*s*-BuO)$_3$ and $Ti(OBu)_4$ as starting materials. The NiMo based catalysts were prepared by impregnation method. The solution of NiMo complex ($Ni(NO_3)_2.6H_2O$ and MoO_3 in water) was impregnated on Al_2O_3-TiO_2 support and impregnated support was dried under reduced pressure at 110 °C. Finally, the greenish powders were calcined at 550 °C for 2 h.

2.2 Catalyst characterization

- BET measurement

The prepared catalyst 0.2 g was purged under N_2 at 350 °C for 4 h. BET measurement was performed in N_2/He at -196 °C. Total surface area, pore size diameter and pore volume were obtained.

- H_2-TPR

The prepared catalyst 0.2 g was packed in a reactor then pretreated under Ar at 200 °C for 30 min. The catalyst was cooled down to room temperature. The reducing gas 5%H_2/Ar was allowed to the reactor. Temperature programmed reduction was carried out from 40 °C to 900 °C and the hydrogen consumption was monitored by thermal conductivity detector as displayed as H_2-TPR profile.

2.3 Catalytic reactivity test and products analysis

Hydrogenation of palmitic acid over sufided $NiMo/Al_2O_3$-TiO_2 was performed in a high-pressure batch reactor (Parr autoclave reactor). The liquid mixture (palmitic acid, dodecane and dodecylcyclohexane) 20 g was filled in a batch reactor. Prior to the activity test, the prepared catalyst 0.4 g was sulfided at 400 °C under 10%H_2S/H_2

atmosphere at a flow rate of 25 ml/min for 4 h. Then, the sulfided catalyst was loaded into the reactor under N_2 atmosphere and catalytic activities was undergone at 240-320 °C under 10 bar of H_2 for 1 h. The liquid products were analyzed by GC-MS and GC-FID technique.

3. Results and Discussion

3.1 Catalyst characterization

- BET measurement

Total surface area, pore volume and pore size diameter of prepared catalyst are summarized in Table 1. Total surface area of catalysts decreases with the increasing of Ni loading, resulting from the blocking effect of Ni metal on porosity of support. The pore structures corresponding to Figure 1 are in the range of mesoporous materials [3,4,5].

Table 1: Physical properties of support and NiMo/Al_2O_3-TiO_2 catalysts

Catalyst	$a_{s,BET}$ m^2g^{-1}	total pore volume cm^3g^{-1}	mean pore diameter nm
support	308.43	0.553	7.178
0.2 NiMo	236.39	0.514	8.697
0.3 NiMo	176.47	0.337	7.642
0.4 NiMo	159.49	0.360	9.044

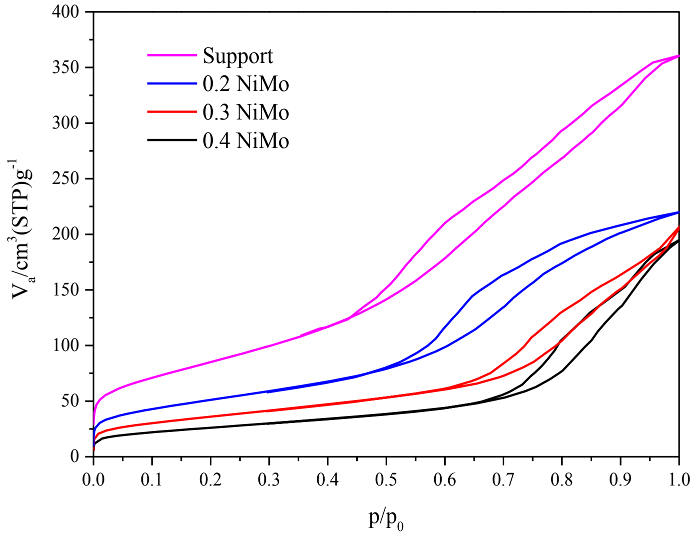

Figure 1. N_2 adsorption–desorption isotherms of support and NiMo/Al_2O_3-TiO_2 catalysts.

- H_2-TPR

H_2-TPR profiles of all catalysts were investigated and illustrate in Figure 2. A series of catalysts shows three reduction temperature regions. The first reduction peak appeared at low temperature (385–430 °C), was assigned to the reduction of Mo^{6+} to Mo^{4+} [6] of the well dispersed octahedral Mo species and also around 440-480 °C was assigned to the reduction of Ni^{2+} to Ni metal. The second peak around 550-563 °C could be attributed to the formation of $NiMoO_4$ phase [6,7]. The last reduction peak at higher temperature (730-843 °C) is generally associated with a further progress in the reduction of Mo species of the first peak, together with the partial reduction of strongly Al_2O_3 interacting with coordinated tetrahedral Mo species (Mo^{3+} to Mo^{2+})[6].

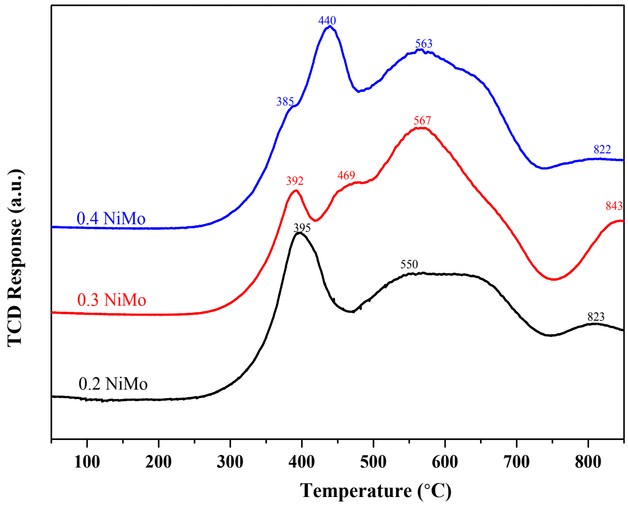

Figure 2. H_2-TPR profile of NiMo over Al_2O_3-TiO_2 supported catalyst.

3.2 Catalytic reaction test and product analysis.

The hydrogenation of Palmitic acid in mixed of dodecane and *n*-hexadecane over 0.2, 0.3 and 0.4 weight ratios of Ni:Mo catalysts are reported in term of activity, were shows in Figure3. The results shows that all catalysts were achieved 100% conversion of Palmitic acid to C15 and C16 hydrocarbons at 300°C.

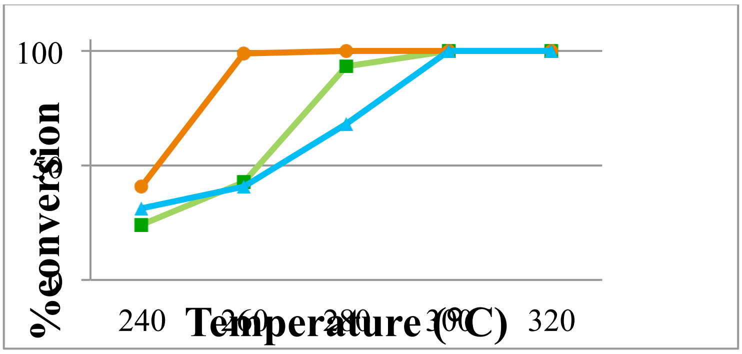

Figure 3. % Conversion of NiMo/Al_2O_3-TiO_2 catalyst.

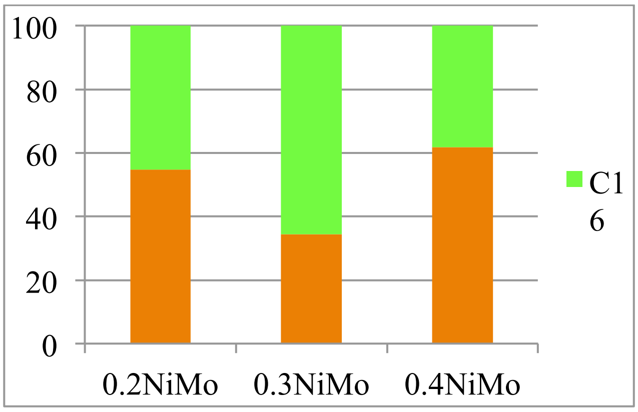

Figure 4. Selectivity of NiMo over Al_2O_3-TiO_2 supported catalyst.

From Figure 4 showed that to the selectivity of NiMo over Al_2O_3-TiO_2 supported catalyst. The result were showed that the formation of hydrocarbons with one carbon less than the corresponding Palmitic acid to *n*-pentadecane was the main product in the decarboxylation (C15) pathway, while *n*-hexadecane was formed in the hydrodeoxygenation (C16) of Palmitic acid. The reaction pathways for hydrogenation are presented in Figure 5. Related, in our research showed that the hydrogenation had undergone both hydrodeoxygenation and decarboxylation pathways. The product selectivity of hydrodeoxygenation (C16) increased with the increases of Ni/(Ni+Mo) weight ratios from 0.2 to 0.3. But the 0.4NiMo catalyst was the desirable choice with a higher selectivity of decarboxylation (C15).

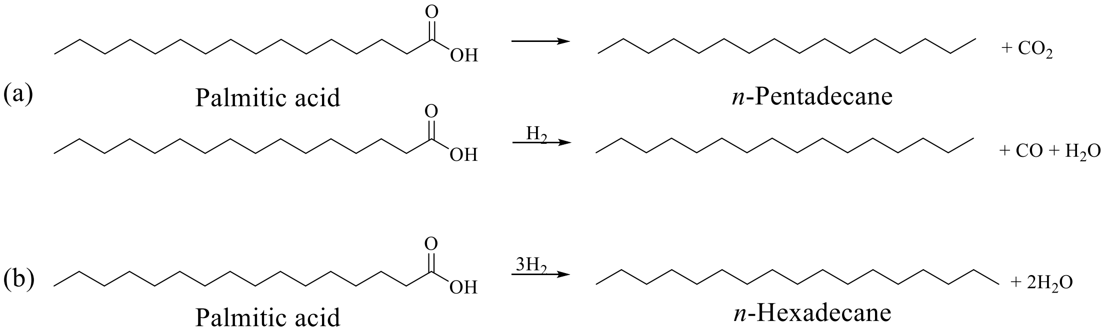

Figure 5. Reaction of Palmitic acid on sulfided NiMo/Al_2O_3-TiO_2 catalysts (a) decarboxylation (C15) and (b) Hydrodeoxygenation (C16)

4. Conclusions

The hydrogenation reactions over catalysts with different Ni loading by Ni/(Ni+Mo) weight ratios of 0.2, 0.3 and 0.4 respectively, were performed in a batch reactor at 240-320 °C under 10 bar of H_2. The conversion of Palmitic acid to C15 and C16 hydrocarbons in all catalysts was completed at 300 °C and clearly showed that the hydrogenation had undergone both hydrodeoxygenation and decarboxylation pathways. The product selectivity of hydrodeoxygenation (C16) increased with the increases of Ni/(Ni+Mo) weight ratios from 0.2 to 0.3. But the 0.4NiMo catalyst was the desirable choice with a higher selectivity of decarboxylation (C15).

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References

[1] J. K. Satyarthi, T. Chiranjeevi, D. T. Gokak and P. S. Viswanathan, An overview of catalytic conversion of vegetable oils/fats into middle distillates, Catal. Sci. Technol., 3 (2013), pp. 70-80.

[2] M. Mohammada, T. K. Hari, Z. Yaakob, Y. C. Sharma, K. Sopian, Overview on the production of paraffin based-biofuels via catalytic hydrodeoxygenation, Renewable and Sustainable Energy Reviews, 22 (2013) pp. 121–132.

[3] I.K. Mbaraka and B.H. Shanks, J. Catal., 229 (2005), pp. 365–373.

[4] I.K. Mbaraka, D.R. Radu, V.S.Y. Lin and B.H. Shanks, J. Catal., 219 (2003), pp. 329–336.

[5] G. Leofanti, M. Padovan, G. Tozzola, B. Venturelli, Surface area and pore texture of catalysts, Catalysis Today 41 (1998), pp. 207-219.

[6] Support effects on hydrotreating activity of NiMo catalysts, Materials Characterization 58 (2007), pp. 864–873.

[7] A. Spojakina, S. Damyyanova, K. Jiratova, L. Nogueira, Y.L. Zam, proceedings of XII simposio iberoamericano de catálisis; (1990). pp. 571.