Production of Higher Olefins via Selective Hydrodeoxygenation of Methyl Palmitate over Bifunctional Re-Based Catalysts

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Abstract: The catalytic activities of bifunctional 4 wt% Re/SAPO-11 and 4 wt% Re/ALPO-11 in hydrodeoxygenation of methyl palmitate were evaluated. The higher deoxygenation activity and the selectivity of C_{15-16} olefins were achieved over 4 wt% Re/SAPO-11 because of the abundance of acid sites and the existence of Brønsted acid sites. The effect of Re content (x = 0.3, 1, 4 wt%) on the activity of Re/SAPO-11 was investigated. The higher conversion and the selectivity of C_{15-16} hydrocarbons were achieved with increasing x. The highest selectivity of C_{15-16} olefins was obtained over 1 wt% Re/SAPO-11 because of its moderate hydrogenation activity.

Keywords: Hydrodeoxygenation, Higher olefin production, Re-based catalyst.

1. Introduction

Higher olefins are industrially valuable as raw materials for various chemical products such as lubricants and detergents, have so far been produced in the petrochemical process. However, because of the depletion of fossil resources, a new sustainable production of higher olefins from fatty acid esters derived from the vegetable oil has recently received broad attention. Hydrodeoxygenation of fatty acid esters is currently investigated as a promising route to produce hydrocarbons[1]. The potential pathways to produce higher olefins are the selective hydrodeoxygenation of fatty acid esters to higher alcohols, followed by the alcohol dehydration to higher olefins. However, most of the researches have focused on the production of saturated hydrocarbons for transportation fuels[2], and the production of higher olefins have hardly been investigated. In the present study, a novel catalyst based on Re for the production of higher olefins was developed, and the effects of Re content and the acidity of SAPO-11 supports on the selectivity of C_{15-16} olefins in hydrodeoxygenation of methyl palmitate were investigated.

2. Experimental

SAPO-11 (Si/Al = 0.2) and ALPO-11 (Si/Al = 0) were used as supports. The catalysts were prepared by an incipient wetness impregnation method. After the impregnation, the catalysts were dried at 120 °C overnight and calcined at 450 °C for 6 h in air. The prepared catalysts are coded as xRe/SAPO and xRe/ALPO (x is Re content [wt%]). Prior to the activity test, the catalysts were reduced by H_2 at 450 °C for 3 h. The hydrodeoxygenation reaction of methyl palmitate was performed in a fixed-bed flow reactor at 300-350 °C, under 3 MPa of H_2 pressure, with a WHSV of 5 h^{-1}, and H_2/feed ratio of 800 (ml/ml). The supports and catalysts were characterized using H_2-TPR, NH_3-TPD, TEM, CO chemisorption, and FT-IR of pyridine adsorption.

3. Results and discussion

3.1. Activity of bifunctional 4Re/SAPO and 4Re/ALPO

The hydrodeoxygenation results over 4Re/SAPO and 4Re/ALPO are listed in **Table 1**. With increasing reaction temperature, the selectivity of oxygenates significantly decreased over 4Re/SAPO compared to 4Re/ALPO, which means the increase in HDO activity. On the other hand, both the selectivity of C_{16} hydrocarbons and the selectivity of C_{15} hydrocarbons increased over 4Re/SAPO because of its higher catalytic activity. Also, the selectivities of C_{15-16} olefins and C_{15-16} isomers increased over 4Re/SAPO with increasing temperature.

Table 1 Conversion and product selectivity in hydrodeoxygenation of methyl palmitate over 4Re/SAPO and 4Re/ALPO.

Catalyst	Temperature [°C]	Conversion [%]	Selectivity [C%]										
			CO + CO_2 + CH_4	C_2-C_{14}	$C_{15=}$	iso-C_{15}	n-C_{15}	$C_{16=}$	iso-C_{16}	n-C_{16}	C_{16+}	C_{16}-OH	Oxy.[a]
4Re/SAPO	275	65.2	0.4	1.5	0.3	0.0	5.9	3.0	0.9	22.4	0.4	7.3	58.1
	300	85.9	1.6	2.0	3.6	0.3	2.8	9.9	20.1	45.4	0.5	1.2	12.6
	325	97.6	4.1	3.2	17.0	2.4	4.4	2.2	39.2	25.5	0.4	0.1	1.5
4Re/ALPO	275	57.9	0.7	1.2	0.9	0.0	1.6	0.4	0.4	8.9	0.7	5.4	79.8
	300	77.3	1.9	1.4	0.3	0.0	2.5	0.9	0.1	13.3	0.7	7.3	71.5
	325	91.4	3.2	1.8	0.4	0.0	5.9	4.1	0.3	32.7	0.7	8.1	42.7

Reaction condition: WHSV = 5 h^{-1}, P_{H2} = 3 MPa, H_2/Reactant = 800 (ml/ml)

[a] Oxygen containing compounds except for C_{16} alcohols and unreacted feed.

The acidity of SAPO-11 and ALPO-11 supports were investigated by means of FT-IR of pyridine adsorption and NH_3-TPD. The results indicate that SAPO-11 had more Brønsted acid sites and Lewis acid sites than ALPO-11. Therefore, the higher activity of 4Re/SAPO was probably due to the abundance of acid sites. The increases in the selectivity of $C_{15\text{-}16}$ olefins and $C_{15\text{-}16}$ isomers indicates that Brønsted acid sites of 4Re/SAPO were not only active in isomerization but also more active in alcohol dehydration at higher temperature.

3.2. Effect of loading content of Re on catalytic activity

Figure 1 shows the conversion and the selectivities of various products over *x*Re/SAPO (*x* = 0.3, 1, 4) at 325 °C. The selectivity of oxygenates significantly decreased while the conversion increased with increasing *x* from 0.3 to 1, which means the increase in HDO activity. However, conversion showed moderate increase when *x* > 1. The selectivity of $C_{15\text{-}16}$ olefins slightly increased with increasing *x* from 0.3 to 1, but it decreased when *x* > 1. Meanwhile, the selectivity of saturated $C_{15\text{-}16}$ hydrocarbons constantly increased, which indicates the further hydrogenation of $C_{15\text{-}16}$ olefins.

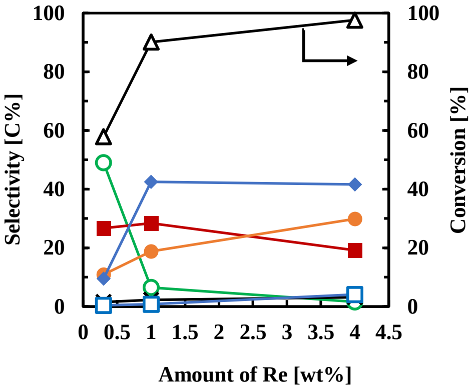

Figure 1. Conversion and selectivities over Re/SAPO at 325°C. △ Conversion, ○ Oxygenates, ■ $C_{15\text{-}16=}$, ● n-$C_{15\text{-}16}$, ◆ iso-$C_{15\text{-}16}$, ✕ Cracking ($C_{2\text{-}14}$), □ Gas (CO + CO_2 + CH_4).

The TEM images and the results of H_2-TPR of *x*Re/SAPO showed the increase in particle size of Re and the shift of reduction peaks to higher temperature with increasing *x*. The moderate increase in conversion was due to the particle size growth and the difficulty of reduction of Re oxides when *x* > 1. The CO pulse chemisorption results showed that the Re active sites of catalysts increased with increasing *x*. The decrease in the selectivity of $C_{15\text{-}16}$ olefins was because of the increase of active sites which was responsible for further hydrogenation of olefins produced. These results indicate that the selectivity of $C_{15\text{-}16}$ olefins could be improved by controlling the hydrogenation activity.

4. Conclusions

4Re/SAPO showed higher conversion of methyl palmitate and the selectivity of $C_{15\text{-}16}$ olefins compared with 4Re/ALPO, because of the abundance of acid sites and the higher alcohol dehydration activity of Brønsted acid sites on SAPO-11. In addition, the hydrogenation activity of *x*Re/SAPO catalysts was tuned by changing Re content, and 1Re/SAPO showed higher conversion (90.1%) and the selectivity of $C_{15\text{-}16}$ olefins (28.4C%) at 325°C.

References

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