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Hydrodeoxygenation of waste vegetable oil over sulfide catalysts

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ABSTRACT

Hydrodeoxygenation (HDO) of waste cooking oil and trapped grease over sulfide catalysts was examined to produce high quality transportation fuel from low-grade resources. The hydrodeoxygenation of waste oils was carried out in a high pressure batch reactor and a fixed bed flow reactor. Sulfide catalysts showed high HDO activity and all waste oils gave n-paraffins, isoparaffins and small amount of olefins. NiMo and NiW catalysts showed high and stable hydrogenation activity, whereas the deactivation of hydrogenation activity was observed using CoMo catalyst. NiW catalyst gave more hydrocarbons formed by decarboxylation or decarbonylation than NiMo and CoMo catalysts. The sulfur content in the product oil was low when catalytic activity showed constant.

1. Introduction

To reduce green house gas emission, the introduction of transportation fuel derived from renewable resources is strongly desired. Biodiesel is a transportation fuel produced from vegetable oils which are the most popular renewable resources. Edible vegetable oils such as rapeseed oil, soybean oil and palm oil have been usually used as resources of biodiesel. Recently, the utilization of nonfood biomass resources is recommended from the viewpoint of food supply.

Waste cooking oil is a useful nonfood biomass. In Japan, it is presumed that 100–140 kt waste cooking oil from household sector [1] and 310 kt trap grease from industrial sector are discarded every year. These low-grade waste oils can not be used as raw materials for the production of fatty acid methyl ester (FAME) type biodiesel because they sometimes contain high concentration free fatty acid. In this case, hydrodeoxygenation (HDO) is suitable for converting low-grade waste oils into hydrocarbons, so-called "2nd generation biodiesel", similar to the components in petroleum diesel. Hydrodeoxygenation of fatty acid esters [2] and virgin vegetable oils such as rapeseed [3–5], sunflower [6] and palm [7] has been reported. Sulfided supported NiMo and CoMo catalysts were used as HDO catalysts. However, HDO technology has not been applied for production of hydrocarbon fuels from low-grade waste oils. In this study, we examined hydrodeoxygenation of low-grade waste oils and clarified catalytic performances and properties of product oils.

2. Experimental

Three kinds of waste cooking oils supplied by house and school lunch center, and two kinds of trap greases supplied by an industrial section were used here. Their fatty acid compositions are summarized in Table 1. Solidified waste cooking oil used Section 3.2 was prepared by dissolving 3.2 g of commercial solidified reagent into 100 g of waste cooking oil (WCO2). To optimize the reaction conditions, hydrodeoxygenation of waste oil was carried out in a batch reactor using NiMo (NiO: 3.7 wt%, MoO_3: 14.0 wt%, surface area: 220 m^2/g), CoMo (CoO: 3.7 wt%, MoO_3: 14.0 wt%, surface area: 220 m^2/g) and NiW (NiO: 4.2 wt%, MoO_3: 29.0 wt%, surface area: 167 m^2/g) sulfide catalysts. All catalysts were prepared by impregnation method. 0.5 g of catalyst and 10 g of waste oil were introduced into a swing type 80 cm^3 stainless steel autoclave reactor and the autoclave was pressurized with 7 MPa of hydrogen. The reaction was carried out at 250–350 °C for 3 h. Hydrodeoxygenation of waste oil was also carried out in a high-pressure fixed-bed continuous-flow reactor to investigate catalyst deactivation. The hydrogen pressure and reaction temperature were 5 MPa and 350 °C, respectively. The amount of catalyst used was 2 g. The WHSV and hydrogen-to-feed ratio were 2.8 h^{-1} and 666 Nm^3/m^3, respectively. All catalysts were sulfided in the stream of $5\%H_2S/H_2$ gas at 360 °C for 3 h before reaction. Before analysis, the reaction products were treated with bistrimethylsilyltrifluoroacetamide (BSTFA) to silylate remained alcohols, free fatty acids, mono- and diglycerides.

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Table 1
Fatty acid composition of low-grade waste oils.

Fatty acid	WCO1	WCO2	SWCO	LTG	STG
C12:0	0.02	0.01	0.01	0.03	0.09
C14:0	0.18	0.28	0.07	0.18	1.16
C16:0	6.98	11.02	7.45	8.22	19.91
C16:1	0.87	0.58	0.20	0.42	1.91
C17:0	0.07	0.11	0.07	0.08	0.47
C18:0	2.66	4.40	3.36	3.26	10.52
C18:1	57.55	25.10	43.26	43.30	45.26
C18:2	19.62	50.91	34.99	34.52	12.53
C18:3	7.89	5.78	6.84	5.97	0.96
C20:0	0.55	0.37	0.52	0.49	0.47
C20:1	1.25	0.89	0.81	0.85	0.88
C22:0	0.29	0.39	0.38	0.34	0.32
C24:0	0.16	0.16	0.18	0.18	0.17
Saturated	10.91	16.74	12.04	12.78	33.11
Unsaturated	87.18	83.26	86.10	84.04	61.54
C16 fatty acid	7.85	11.60	7.65	8.64	21.82
C18 fatty acid	87.72	86.19	88.45	87.05	69.27

WCO1, waste cooking oil (house); WCO2, waste cooking oil (school lunch center); SWCO, solidified waste cooking oil (house); LTG, liquid trap grease, STG, solid trap grease.

The compounds contained in the product were identified by GC–MS and quantified by gas chromatography which was equipped with a DB-5HT capillary column. Hydrodeoxygenation of low-grade oil (HDO) was calculated as follows:

$$\mathrm{HDO}\,(\%) = \left[\frac{T_{\mathrm{feed}} - T_{\mathrm{product}}}{T_{\mathrm{feed}}}\right] \times 100$$

where T_{feed} and T_{product} indicate the composition of total oxygenated compound determined by gas chromatograph analysis in the feed and products, respectively. Composition of n-paraffin was calculated as follows:

$$\text{n-Paraffin composition}\,(\%) = \left(\frac{C_{\mathrm{n-paraffin}}}{C_{\mathrm{all}}}\right) \times 100$$

where $C_{\text{n-paraffin}}$ and C_{all} indicate the concentration of n-paraffin and all compounds in the product determined by gas chromatograph analysis, respectively. Compositions of other compounds were calculated in a similar manner as above.

The content of total sulfur was measured by elemental analysis.

3. Results and discussion

3.1. Hydrodeoxygenation of low-grade oil in a batch reactor

Table 2 shows the effect of reaction temperature on the composition of product oil in the hydrodeoxygenation of waste cooking oil over $NiMo/B_2O_3–Al_2O_3$ catalyst. At 250 °C, all triglycerides were completely converted to other compounds and diglycerides and monoglycerides were not observed in the product. However, large amount of oxygenated compounds such as free fatty acid, alcohol and long chain esters such as octadecyl octadecanoate formed by esterification of free fatty acids and alcohols which are formed by hydrogenation of free fatty acids, remained. According to our previous work [8] and the proposed reaction mechanism [5,6,9], triglycerides are easily hydro-cracked and give free fatty acid. At lower temperature, hydrogenation and decarboxylation of oxygenated products did not proceed completely. More than 300 °C, hydrodeoxygenation proceeded completely and main component in product oil was n-paraffin. The concentration of isoparaffin increased with increasing reaction temperature. This means that isomerization of n-paraffin was accelerated at higher temperature.

Table 2
Effect of reaction temperature on hydrodeoxygenation of waste cooking oil.

Temperature	250 °C	300 °C	350 °C
HDO (%)	55.4	99.4	99.9
n-Paraffin	49.0	97.2	91.4
Isoparaffin	3.0	1.4	7.5
Olefin	3.4	0.8	1.0
Alcohol	3.9	0.1	0
Free fatty acid	9.5	0	0
Long chain ester	29.0	0	0
C15 + C16 n-paraffin	4.0	7.6	7.7
C17 + C18 n-paraffin	42.8	85.0	79.4

Oil, WCO1; catalyst, $NiMo/B_2O_3–Al_2O_3$; hydrogen pressure, 7 MPa; reaction time, 3 h.

Table 3
Effect of catalyst species and reaction temperature on hydrodeoxygenation of waste cooking oil.

Catalyst	$NiMo/Al_2O_3$	$CoMo/Al_2O_3$	NiW/Al_2O_3
Reaction temperature 300 °C			
HDO (%)	99.6	99.3	~100
n-Paraffin	97.5	89.7	97.3
Isoparaffin	1.4	6.4	2.2
Olefin	0.7	3.2	0.9
Alcohol	0.1	0.1	0
Free fatty acid	0	0	0
Long chain ester	0	0	0.1
C15 + C16 n-paraffin	7.6	7.5	7.6
C17 + C18 n-paraffin	85.4	77.2	85.2
Reaction temperature 350 °C			
HDO (%)	99.8	99.6	99.6
n-Paraffin	94.8	82.8	96.0
Isoparaffin	3.8	11.8	2.7
Olefin	1.2	5.0	0.9
Alcohol	0	0	0
Free fatty acid	0	0	0
Long chain ester	0	0	0
C15 + C16 n-paraffin	7.6	7.8	7.9
C17 + C18 n-paraffin	83.1	70.1	84.0

Oil, WCO1; hydrogen pressure, 7 MPa; reaction time, 3 h.

In order to investigate the hydrotreating activity of the sulfide catalyst with different metals, hydrotreating reactions of waste cooking oil were carried out. As shown in Table 3, all catalysts showed high hydrodeoxygenation activity at 300 °C and 350 °C, and the conversions into n-paraffin + isoparaffin were 96.1–99.5%. The yields of isoparrafin at 350 °C were higher than those at 300 °C. $CoMo/Al_2O_3$ catalyst gave higher olefin yields because hydrogenation activity of $CoMo/Al_2O_3$ is lower than $NiMo/Al_2O_3$ and NiW/Al_2O_3. Oxidation stability of olefin is lower than that of paraffin. Therefore, NiMo and NiW are more suitable for hydrodeoxygenation catalyst to produce stable oil against oxidation.

The effect of catalyst support on the composition of HDO product is shown in Table 4. Isoparaffin yield was affected by catalyst support. It was in the order $NiMo/B_2O_3–Al_2O_3$ (B_2O_3/Al_2O_3 = 15/85, wt%/wt%) > $NiMo/Al_2O_3$. The acidity of $B_2O_3–Al_2O_3$ is higher than that of Al_2O_3 [10]. Cold flow property of isoparaffin is better than that of n-paraffin with same carbon number. Acid support accelerates the formation of isoparaffin and is suitable for the production of oil with good cold flow property.

Hydrodeoxygenation of various low-grade-oils was examined over $NiMo/B_2O_3–Al_2O_3$. As shown in Table 5, all low-grade-oils gave hydrocarbons with high yield. Main component of waste cooking oil (WCO1), waste cooking oil solidified by a commercial reagent (SWCO) and liquid trap grease (LTG) are triglycerides (WCO1 87.9%, SWCO 90.4%, LTG 84.1%), while main component of solid trap grease (STG) is free fatty acid (80.5%). These results indicate that the activ-

Table 4
Effect of support species on hydrodeoxygenation of waste cooking oil.

	$NiMo/Al_2O_3$	$NiMo/B_2O_3–Al_2O_3$
HDO (%)	99.8	99.9
n-Paraffin	94.8	91.4
Isoparaffin	3.8	7.5
Olefin	1.2	1.0
Alcohol	0	0
Free fatty acid	0	0
Long chain ester	0	0
C15 + C16 n-Paraffin	7.6	7.7
C17 + C18 n-Paraffin	83.1	79.4

Oil, WCO1; reaction temperature, 350 °C; hydrogen pressure, 7 MPa; reaction time, 3 h.

Table 5
Hydrodeoxygenation of various low-grade oils.

	Samples			
	WCO1	SWCO	LTG	STG
HDO (%)	99.9	99.5	99.8	99.3
n-Paraffin	91.4	96.0	96.0	94.8
Isoparaffin	7.5	2.4	2.6	3.4
Olefin	1.0	1.1	1.2	1.1
Alcohol	0	0	0	0
Free fatty acid	0	0	0	0
Long chain ester	0	0	0	0
C15 + C16 n-Paraffin	7.7	9.3	8.5	18.2
C17 + C18 n-Paraffin	79.4	83.4	83.6	68.4

Catalyst, $NiMo/B_2O_3–Al_2O_3$; reaction temperature, 350 °C; hydrogen pressure, 7 MPa; reaction time, 3 h.

ity of hydrodeoxygenation was not influenced by the species of fatty acid component.

3.2. *Hydrodeoxygenation of low-grade oil in a fixed-bed flow reactor*

Fig. 1 shows the effect of reaction temperature on the composition of product oil in the hydrodeoxygenation of waste cooking oil (WCO2) over NiW/Al_2O_3 catalyst. At 300 °C, hydrodeoxygenation well proceeded until 30 h. However, the hydrodeoxygenation activity of the catalyst decreased after 30 h and the formation of long chain esters formed by esterification of alcohol and free fatty acid was observed. Catalyst deactivation was not observed at 350 °C.

Fig. 2 shows the relationship between reaction time and the composition of product oil in the hydrodeoxygenation of WCO2. The compositions of product were almost constant using $NiMo/B_2O_3–Al_2O_3$ (Fig. 2(A)) and NiW/Al_2O_3 (Fig. 2(C)) as catalysts. Waste cooking oil (WCO2) contains large amount of unsaturated fatty acid (25.1% of oleic acid (C18:1), 50.9% of linoleic acid (C18:2) and 5.8% of linolenic acid (C18:3)). To obtain paraffin rich product, both deoxygenation activity for removing oxygenated functional group and hydrogenation activity for olefin saturation are needed. These catalysts kept the activities of hydrodeoxygenation of oxygenated compounds and hydrogenation of olefin under the reaction condition. However, n-paraffin decreased and olefin increased with the elapse of reaction time using $CoMo/B_2O_3–Al_2O_3$ (Fig. 2(B)) as a catalyst. This result suggested that active sites of CoMo catalyst for hydrogenation of olefin were immediately poisoned. NiMo and NiW are more suitable for hydrodeoxygenation catalyst. Hydrodeoxygenation of 10 wt% solidified waste cooking oil/waste cooking oil mixture over NiW/Al_2O_3 catalyst is shown in Fig. 2(D). The reaction profile of the mixture was almost similar to waste cooking oil. 12-Hydroxystearic acid is usually used as a commercial solidified reagent. From the HDO result, this reagent did not influence on hydrodeoxygenation and was converted into hydrocarbons.

According to the proposed reaction pathway [5,6,9], C*n* (*n* = carbon number) fatty acids give C*n* hydrocarbons by hydrogenation and dehydration. C*n* fatty acids also give C*n* − 1 hydrocarbons by decarboxylation or decarbonylation. To investigate the selectivity of decarboxylation/decarbonylation to hydrogenation–dehydration, the ratio of heptadecane (n-C17, decarboxylation/decarbonylation product) in total amount of heptadecane and octadecane (n-C18, hydrogenation–dehydration product) was calculated. As shown in Fig. 3, the ratio of n-C17 dramatically decreased at initial stage and then showed almost constant. The ratio of n-C17 in the hydrodeoxygenation over CoMo was similar to that over NiMo catalyst, while the ratio of n-C17 in the hydrodeoxygenation over NiW catalyst was much higher than those over Mo based catalysts. It is noted that tungsten based catalyst accelerates decarboxylation/decarbonylation routes in the hydrotreating of waste cooking oil.

When the metal sulfide catalyst is used as a hydrodeoxygenation catalyst, contamination of sulfur into product oil should be considered. Fig. 4 shows the sulfur concentration in product oil. Until 24 h, sulfur eliminated from sulfided catalyst and dissolved

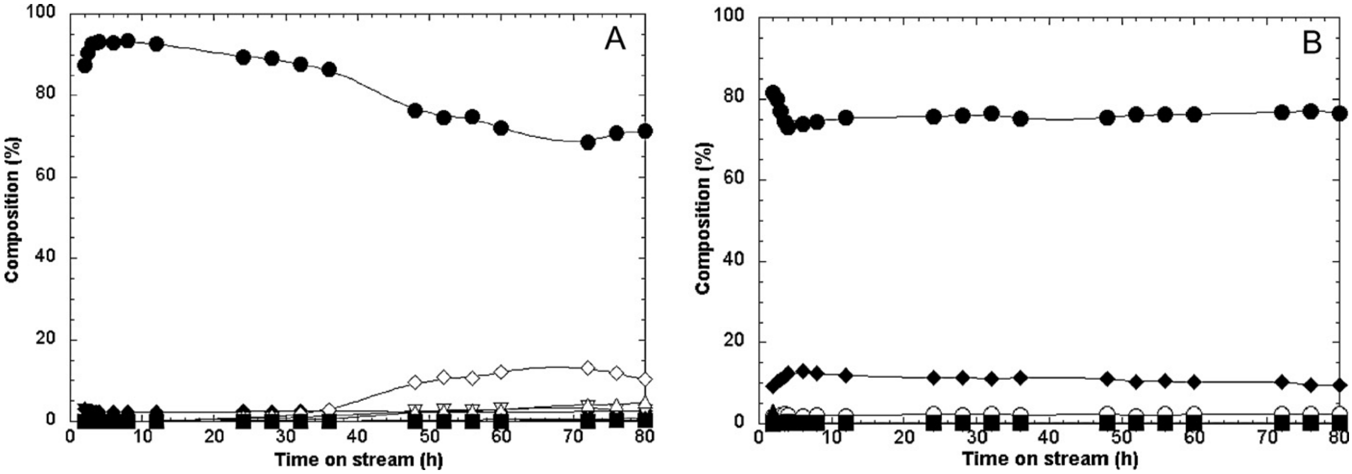

Fig. 1. Hydrodeoxygenation of waste cooking oil over $NiMO/B_2O_3–Al_2O_3$ catalyst: (●) n-paraffin; (♦) isoparaffin; (○) olefin; (▽) alcohol; (△) free fatty acid; (◊) long chain ester; (■) monoglyceride; (▲) diglyceride; (▼) triglyceride. Reaction temperature: (A) 300 °C and (B) 350 °C.

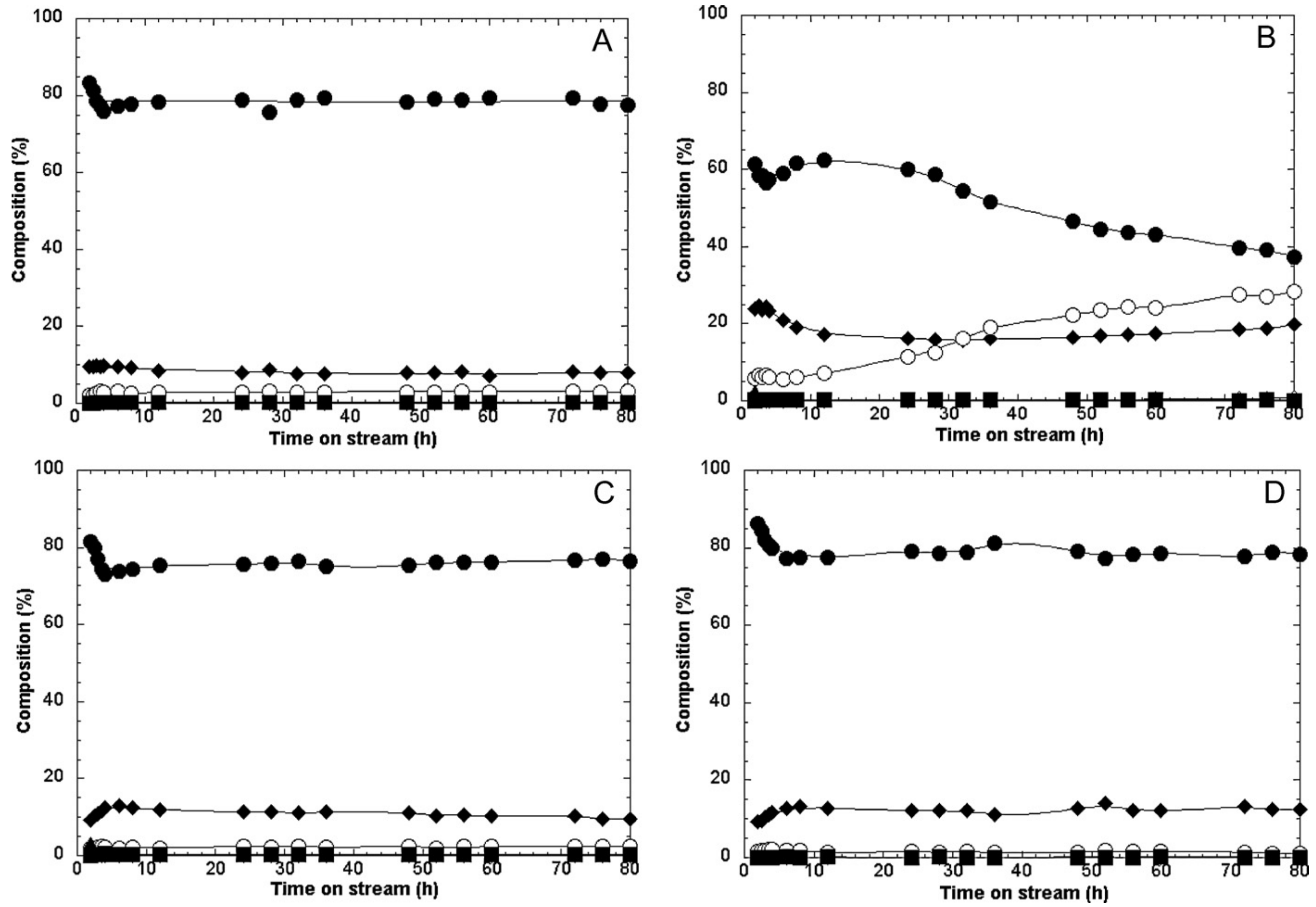

Fig. 2. Effect of catalyst species on hydrodeoxygenation of waste cooking oil (A–C) and solidified waste cooking oil (D): (●) n-paraffin; (♦) isoparaffin; (○) olefin; (▽) alcohol; (△) free fatty acid; (◊) long chain ester; (■) monoglyceride; (▲) diglyceride; (▼) triglyceride; (A) NiMo/B_2O_3–Al_2O_3, (B) CoMo/B_2O_3–Al_2O_3, (C) NiW/Al_2O_3, and (D) NiW/Al_2O_3; reaction temperature, 350 °C.

into product. Sulfur content of the product was 0.5–131 ppm. After 24 h, Sulfur contents of the product were low and similar to waste cooking oil (S = 1.1 ppm) used as a feedstock. Sulfur content of the product hydrotreated by CoMo/B_2O_3–Al_2O_3 increased with the passage of reaction time because the deactivation of hydrogenation active sites occurred. In the hydrodeoxygenation of fatty acids using a batch reactor, sulfur contents of product oils obtained from stearic acid, oleic acid and linoleic acid are 26 ppm, 1204 ppm and 1629 ppm, respectively. Thee results indicate that unsaturated fatty acids gave sulfur compounds formed by addition of hydrogen sulfide to olefin. This means that active sites on the CoMo catalyst are not stable under this reaction condition and high hydrogenation activity is needed to prevent formation of sulfur added compounds.

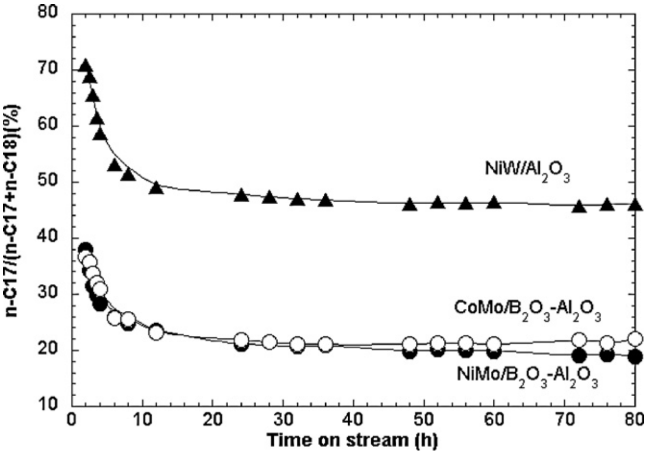

Fig. 3. The ratio of heptadecane/(heptadecane + octadecane) in HDO product oil: (●) NiMo/B_2O_3–Al_2O_3; (○) CoMo/B_2O_3–Al_2O_3; (▲) NiW/Al_2O_3; (▽) alcohol; (△) free fatty acid; (◊) long chain ester; (■) monoglyceride; reaction temperature, 350 °C.

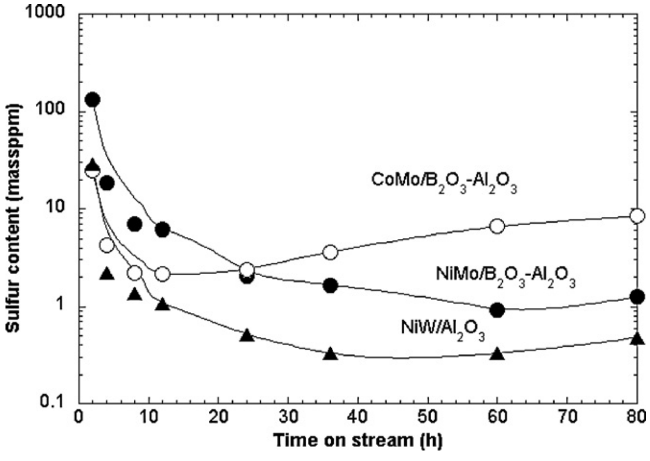

Fig. 4. The sulfur content in HDO product oil: (●) NiMo/B_2O_3–Al_2O_3; (○) CoMo/B_2O_3–Al_2O_3; (▲) NiW/Al_2O_3; (▽) alcohol; (△) free fatty acid; (◊) long chain ester; (■) monoglyceride; reaction temperature, 350 °C.

4. Conclusions

Low-grade waste oils such as waste cooking oil and trap grease were completely converted into hydrocarbons more than 300 °C. From the viewpoint of the stability of catalytic activity, 350 °C is preferable for hydrodeoxygenation. NiMo and NiW catalysts are more suitable for hydrodeoxygenation of low-grade waste oils than CoMo catalyst to prevent the formation of olefin. The solid acid support such as B_2O_3–Al_2O_3 accelerates the formation of isoparaffin and is suitable for the production of oil with good cold flow property. Tungsten based catalyst accelerates deoxygenation by decarboxylation or decarbonylation routes in the hydrotreating of waste cooking oil. Sulfur eliminated from sulfided catalyst and dissolved into product at initial stage of the reaction, while sulfur content of the product was low when catalytic activity showed constant.

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