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Roles of Promoter and Support of Sulfided Mo-based Catalyst in Selective Hydrotreating of Palm Fatty Acid Distillate

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A series of CoMo/Al₂O₃ catalysts with various Co/Mo mole ratios and a series of CoMo/TiO₂-Al₂O₃ catalysts supported on TiO₂ coating Al₂O₃ were prepared. The effects of Co/Mo mole ratio and TiO₂ loadings on Al₂O₃ on hydrodeoxygenation (HDO) and decarboxylation/decarbonylation (DCO) in the hydrotreating of palm fatty acid distillate (PFAD) were investigated. The catalysts were characterized by BET, XRF, pulse NO chemisorption, and H₂-TPR. The maximum yields of *n*-C₁₆ and *n*-C₁₈ was observed at Co/Mo = 0.05 for the CoMo/Al₂O₃ series, and the yield of *n*-C₁₅ and *n*-C₁₇ was increased at Co/Mo > 0.05. CoMoS phase apparently has both HDO and DCO activities. CoMo(0.05)/Ti(20)-Al showed the maximum yields of *n*-C₁₆ and *n*-C₁₈ due to the formation of TiMoS in all catalysts. TiMoS phase may be formed by adding TiO₂ on Al₂O₃ and promotes the HDO reaction, but not isomerization or cracking.

Keywords

Hydrodeoxygenation, Titania alumina support, Cobalt molybdenum catalyst, Palm fatty acid distillate, Metal support interaction, Phase change material

1. Introduction

Latent heat storage systems using Phase Change Material (PCM) are an effective method for storing thermal energy, such as solar energy which practically inexhaustible so will be significant in building a sustainable society^{1),2)}. Paraffins (*n*-C₁₆ and *n*-C₁₈) are considered one of the best primary raw materials for PCMs because of the non-hazardous, easy to handle, and stable characteristics³⁾. In addition, *n*-C₁₆ and *n*-C₁₈ have higher latent heat than *n*-C₁₅ and *n*-C₁₇ in the optimum temperature range for humans⁴⁾. However, sustainable energy generation requires that paraffin should be made from vegetable oils, not petroleum. The desirable PCM components can be produced through hydrodeoxygenation (HDO) of vegetable oil^{4)~9)}. A previous study produced 66.4 % of *n*-C₁₆ and *n*-C₁₈ from palm fatty acid distillate (PFAD) using PtSn/ALPO-11. However, the HDO selectivity was still insufficient for industrialization.

Transition metal sulfide (TMS) catalysts are the most critical industrial catalysts used in hydrotreating processes such as hydrosulfurization and hydrodenitro-

genation. NiMo and CoMo are well known to exhibit higher activity than single metal catalysts due to their “synergy effect”¹¹⁾; the “ensemble effect” caused by specific geometry, and the “ligand effect” due to the electronic interaction. Modifications of the mole ratio of Co/(Co + Mo) by changing the loading amount of Mo for HDO of 4-methylphenol showed the conversion of 4-methyl phenol over all catalysts was close to 100 %, and the selectivity for toluene was 87.9 % over CoMo/ZrO₂ (0.30)¹²⁾. However, the effect of the mole ratio on selective hydrotreating of vegetable oil has not been fully investigated using Co/Mo ratios lower than 0.35. In addition, the effect of the loading amount of Co is still unclear.

The deoxygenation mechanisms occurring on TMS catalysts are mainly HDO and decarboxylation/decarbonylation (DCO). Therefore, the deoxygenation activity of the catalyst involves the support as well. For example, γ -Al₂O₃ has considerable activity in deoxygenation reactions due to its Lewis acid sites¹³⁾. However, Al₂O₃ only has considerable activity due to its strong metal-support interaction¹⁴⁾. Therefore, we previously applied TiO₂ to overcome the disadvantages of Al₂O₃ and improve the common catalytic activity¹⁵⁾. The carboxylic group of a fatty acid ester may adsorb on the surface of TiO₂^{17),18)}. CoMo catalysts supported on TiO₂ among the CoMo catalysts supported on TiO₂,

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ZrO₂, Al₂O₃, MCM-41, and MgO exhibited the highest $Cn/C(n-1)$ selectivity, *i.e.* inherent HDO selectivity¹⁸⁾. However, the problem with TiO₂ is the lower activity than Al₂O₃ due to its low specific surface area (140 m²/g)¹⁸⁾. To solve this problem, TiO₂ coating supports have been applied such as TiO₂-Al₂O₃. TiO₂ enhanced the reduction, formation, and stacking of CoMoS active slabs^{15),16)}. TiO₂ coated Mo-based sulfided catalyst showed increased of CoMoS and TiMoS formation. However, the effect of TiMoS active slab is still unclear.

Therefore, CoMo catalysts are good candidates for producing the PCM components (n -C₁₆ and n -C₁₈) through hydrodeoxygenation of vegetable oil. However, more active catalysts for reaction at low temperatures are necessary. The effects of metal promoters on the hydrotreating reaction selectivity have been well investigated, but the effect of the active metal species Co and Mo ratio on the active metal species is unclear. In addition, the effects of Co and Mo on desulfurization reactions are well studied, but the mechanisms and effects on the selectivity and reaction rates of HDO and DCO reactions in vegetable oils are still unknown. The effect of TiO₂ coated supports on the hydrogenation pathway of vegetable oils is also unclear. Therefore, we prepared catalysts supported on Al₂O₃ support with several ratios of Co and Mo for optimizing the Co/Mo mole ratio. Then, catalysts supported on TiO₂ coated Al₂O₃ support with specific amounts of Co and Mo were prepared. Palm fatty acid distillate (PFAD) was chosen as a feedstock, because PFAD is the byproduct of the crude palm oil refinery process and is inexpensive. Also, PFAD has high durability to oxidation because of the low content of linolenic acid (18 : 3) and a high level of vitamin E, which acts as an antioxidant^{2),25)}. The effect of Co/Mo mole ratio and TiO₂ coating on Al₂O₃ on the deoxygenation activity, HDO yield (n -C₁₆ + n -C₁₈), and DCO yield (n -C₁₅ + n -C₁₇) of the catalyst were investigated.

2. Experimental

2.1. Materials

PFAD, a byproduct of the palm oil refining process, was used as the feedstock to evaluate the catalytic activity. Physical properties (density, dynamic viscosity, acid value, and cloud point), fatty acid composition, and element analysis (C, H, O, S) were determined previously²⁾. The density, dynamic viscosity, acid value, and cloud point are 0.86 g/cm³, 14.1 mPa s/50 °C, 195 mg KOH/g and 45 °C, respectively. PFAD consists of 88.9 % fatty acids and 11.1 % triglycerides. Palmitic acid (C16 : 0) and oleic acid (C18 : 1) are the major fatty acids in PFAD, at 45.5 wt% and 38.8 wt%, respectively. In addition, PFAD contains 3.9 % of stearic acid, 9 % of oleic acid, and trace amounts of other fatty acids.

2.2. Catalyst Preparation

Co and Mo supported catalysts were prepared by the conventional incipient wetness impregnation method²⁰⁾. Commercial γ -Al₂O₃ (NK31925, Nippon Ketjen Co., Ltd.) was used as the support for the following impregnation. The catalysts were prepared using successive addition of aqueous solutions of Co(NO₃)₂ and (NH₄)₆Mo₇O₂₄. After impregnation, the samples were dried at 120 °C for 2 h in air and then calcined at 450 °C for 10 h in air. The loading amount of MoO₃ was fixed at 20 wt% and catalysts with several Co/Mo ratios CoMo(X)/Al₂O₃ (X = 0.02, 0.05, 0.1, 0.35) were prepared.

TiO₂ coated Al₂O₃ support was synthesized as previously reported¹⁵⁾. Titanium ethoxide (Sigma-Aldrich Co.) was used as the titania source. First, Al₂O₃ support, titanium ethoxide, and anhydrous ethanol with various amounts of TiO₂ 10, 15, 20 wt% were added into an eggplant flask so that the air inside was replaced by nitrogen. Next, the eggplant flask was connected with the evaporator and slowly stirred for about 5 h at 85 °C in a water bath until the anhydrous ethanol was fully vaporized. Then, the flask was filled with distilled water and stirred at 40 °C overnight to hydrolyze the titanium ethoxide. Finally, the formed solid was separated by suction filtration and calcinated at 600 °C for 4 h. The prepared support samples are denoted as Ti(X)-Al (Ti: added TiO₂, X : weight percentage). The loading amounts of CoO and MoO₃ are the same as those of the CoMo/Al₂O₃ catalysts, which showed the highest yield of n -C₁₆ + n -C₁₈.

2.3. Characterization of Catalysts

Physical properties were measured by established methods. Specific surface areas and pore sizes of catalysts were calculated by using nitrogen physisorption at -196 °C with a Belsorp-mini II automated sorption system (MicrotracBEL Corp.). Specific surface area was calculated using the Brunauer-Emmett-Teller method²¹⁾ at a relative partial pressure of 0.05-0.3. Prior to the measurement, the sample was degassed under a vacuum ($p < 10^{-2}$ kPa) at 400 °C for 1 h. The total pore volume and pore size distribution were measured by a desorption curve using the Barret-Joyner-Halenda model²²⁾ at a relative partial pressure of 0.95.

The loading amounts of CoO, MoO₃, and TiO₂ were determined by X-ray fluorescence (XRF) measurement using a Rayny EDX13 700/800XRF analyzer (Shimadzu Corp.). Catalyst samples 200 mg were crushed, then compression molded into a shape disk before analyzing²³⁾.

The dispersion of active metals was measured by the pulse NO chemisorption method¹⁵⁾ using a ChemBET Pulsar temperature-programmed reduction/temperature-programmed desorption (TPR/TPD) (Quantachrome Instruments Co.). Prior to adsorption, the desired amount of the calcined catalyst (200 mg) was sulfided

with 5 % H₂S in H₂ at 100 °C for 1 h, 200 °C for 1 h, 300 °C for 1 h, and 400 °C for 3 h, and then pretreated in a highly pure helium flow at the same temperature for 2 h to remove impurities, followed by cooling to 40 °C. 10 % NO/He gas pulses were gradually introduced into the catalyst loop through a calibrated injection valve (250 µL NO pulse⁻¹) at intervals of 10 min until the signal of the introduced NO pulse became constant.

H₂-TPR measurements were carried out using the same instrument for NO pulse chemisorption and conventional measurements²⁾. The samples were first pretreated in a highly pure helium flow at 500 °C for 3 h to remove the adsorbed impurities and then were cooled down to 30 °C, followed by changing the gas to 5 vol% H₂ in an argon gas mixture (15 mL/min). H₂-TPR was performed by linearly increasing the temperature to 1000 °C with a heating rate of 5 °C/min. Thermal conductivity detectors (TCD) were used to monitor hydrogen consumption.

2. 4. Activity Test of Catalysts

Details of our experimental reactor were reported earlier²⁴⁾. PFAD was chosen for the feedstock. Bis-(1,1,3,3-tetramethylbutyl)-pentasulfide CS-40 (DIC Corp.), which decomposes during the reaction to generate hydrogen sulfide, was mixed in PFAD at 0.1 wt% to prevent deactivation of the catalyst. The molecular structure and physical properties of CS-40 are shown in the Appendix (Fig. A-1 and Table A-1). Catalysts (9 cm³) were mixed with quartz (21 cm³, Kishida Chemical Co., Ltd.) and charged into the isothermal region of the reactor. Before each test, diluted catalysts were sulfided according to the previous procedure²⁵⁾. Diluted catalysts were sulfided with 5 % H₂S in H₂ at 100 °C for 1 h, 200 °C for 1 h, 300 °C for 1 h, and 400 °C for 3 h. After activation of catalysts was finished, PFAD was pumped into the reactor. The pump instrument and piping were heated during the activity test with ribbon heaters due to the high melting point of the reactant. The reaction was conducted under 3 MPa hydrogen pressure, with a liquid hourly space velocity (LHSV) of 1 h⁻¹, H₂/feedstock ratio of 1000 (mL/mL), and a temperature range of 300-350 °C. The catalytic activity was measured after stabilization at approximately 3.5 h. Gas and liquid samples were taken and analyzed by GC. The last three samples which showed stable GC data were collected, and the average of the results was taken. During the activity test, at least three samples were obtained at every reaction temperature, and the analysis was conducted in triplicate. All data were the average of three samples.

Product identification was performed using a gas chromatograph-mass spectrometer (GC-MS-QP5050A, Shimadzu Corp.) equipped with the same capillary column. Another gas chromatograph with a TCD and a Unibeads C column (GL Sciences Inc., 3 m × 3 mm

i.d.) was used to measure the other components, such as CO and CO₂, in the gaseous products. The conversion, selectivity, and yield were calculated using the following equations:

$$\text{Conversion [C \%]} = \left(1 - \frac{\text{Carbon atoms of unreacted in feedstock [C mol]}}{\text{Carbon atoms in feedstock [C mol]}}\right) \times 100$$

$$\text{Selectivity of component i [C \%]} = \frac{\text{Carbon atoms in component i [C mol]}}{\text{Carbon atoms in all components [C mol]}} \times 100$$

$$\text{Yield of component i [C \%]} = \frac{\text{Conversion [C \%]} \times \text{Liquid selectivity of component i [C \%]}}{100}$$

3. Results

3. 1. Catalyst Characterization

3. 1. 1. Physical Properties of Catalysts

The physical properties of the catalysts are shown in **Table 1**. The surface area of the CoMo catalysts decreased with higher Co/Mo mole ratio, with 224 m²/g for CoMo(0.02)/Al₂O₃, and 197 m²/g for CoMo(0.35)/Al₂O₃. All catalysts had a lower total pore volume and pore size distribution than Al₂O₃. TiO₂ coated Al₂O₃ supports had lower surface area than Al₂O₃, and the surface area decreased with higher TiO₂ coating amount. Comparing CoMo(0.05)/Al₂O₃ and CoMo(0.05)/Ti-Al catalysts, the surface area decreased in the order of CoMo(0.05)/Al₂O₃ (220 m²/g) > CoMo(0.05)/Ti(10)-Al (191 m²/g) > CoMo(0.05)/Ti(15)-Al (173 m²/g) > CoMo(0.05)/Ti(20)-Al (163 m²/g). Therefore, the specific surface area of the supports decreased with higher loading of TiO₂ onto Al₂O₃. The XRF results confirmed that all catalysts were prepared at the target Co/Mo ratio.

3. 1. 2. NO Chemisorption

Pulse NO chemisorption showed that the adsorption amount of NO increased from 3.4 to 8.4 µmol/g with higher Co/Mo mole ratio from 0.02 to 0.35, due to the increase in the amount of CoMoS phase with higher Co content^{32),33)}. Pulse NO chemisorption also showed no difference in NO adsorption on CoMo(0.05)/Al₂O₃ and CoMo(0.05)/Ti(10)-Al. In contrast, NO adsorption amount increased from 5.3 to 8.0 µmol/g with the increase in amount of TiO₂ coating from 10 to 15 % and 20 %.

3. 1. 3. H₂-TPR

The H₂-TPR patterns of various catalysts are shown in **Fig. 1**. The observed reduction peaks occurred mainly in two ranges from 150 to 400 °C, and 400 to 600 °C. The peak in the lower temperature range from 150 to 400 °C represents the consumption of H₂, which reacts with the weak H-S bond on the surface of the

Table 1 Chemical Composition and Physical Properties of Catalysts

Catalyst	Chemical composition ^{a)} [wt%]				Parameter			
	CoO	MoO ₃	TiO ₂	Co/Mo ratio [-]	S_{BET} ^{b)} [m ² /g]	V_{total} ^{c)} [cm ³ /g]	d_{avg} ^{c)} [nm]	NO uptake ^{d)} [μmol/g]
Al ₂ O ₃	-	-	-	-	260	0.726	11.3	-
Ti(10)-Al	-	-	8.46	-	228	0.689	12.1	-
Ti(15)-Al	-	-	14.1	-	209	0.624	11.8	-
Ti(20)-Al	-	-	17.5	-	199	0.656	10.6	-
Mo/Al ₂ O ₃	-	21.7	-	-	220	0.512	9.25	-
CoMo(0.02)/Al ₂ O ₃	0.247	20.3	-	0.0233	224	0.524	9.36	3.4
CoMo(0.05)/Al ₂ O ₃	0.521	20.5	-	0.0487	220	0.479	10.6	5.4
CoMo(0.1)/Al ₂ O ₃	1.08	19.3	-	0.108	218	0.518	9.29	7.3
CoMo(0.35)/Al ₂ O ₃	3.68	18.8	-	0.378	197	0.619	10.9	8.4
CoMo(0.05)/Ti(10)-Al	0.541	19.9	-	0.0516	191	0.538	16.0	5.3
CoMo(0.05)/Ti(15)-Al	0.542	20.1	-	0.0512	173	0.536	13.9	6.5
CoMo(0.05)/Ti(20)-Al	0.504	19.5	-	0.0490	163	0.451	8.06	8.0

a) Chemical composition was measured by XRF.

b) Specific surface area calculated by the BET method.

c) Total pore volume and pore size distribution calculated by the BJH model.

d) Amount of adsorbed NO measured by pulse chemisorption at 40 °C.

Fig. 1 H₂-TPR Patterns of Various Catalysts; (a) Mo/Al₂O₃, (b) CoMo(0.02)/Al₂O₃, (c) CoMo(0.05)/Al₂O₃, (d) CoMo(0.1)/Al₂O₃, (e) CoMo(0.35)/Al₂O₃, (f) CoMo(0.05)/Ti(10)-Al, (g) CoMo(0.05)/Ti(15)-Al, and (h) CoMo(0.05)/Ti(20)-Al

catalyst in the recombination of H₂S¹⁵⁾. The peak in the higher temperature range from 400 to 600 °C was assigned to the consumption of H₂ in the reduction of CoMoS and MoS₂, or CoMoS, TiMoS, and MoS₂ to form an active site (sulfur vacancy) in the case of TiO₂-free and TiO₂-coated catalysts, respectively¹⁵⁾. For catalysts with Co/Mo mole ratio up to 0.05, the reduction temperature in the higher temperature range decreased, and for catalysts with higher mole ratios, the reduction temperature in the higher temperature range increased. The reduction temperature in the higher temperature range increased more for CoMo(0.05)/Ti(15)-Al than for TiO₂-free catalysts, but the reduction temperature decreased for CoMo(0.05)/Ti(10)-Al and

CoMo(0.05)/Ti(20)-Al catalysts.

3. 2. HDO of Palm Fatty Acid Distillate

3. 2. 1. Hydrotreating Reaction on Mo/Al₂O₃ and CoMo(0.35)/Al₂O₃

The detailed results of the activity tests over Mo/Al₂O₃ and CoMo(0.35)/Al₂O₃ catalysts are shown in Tables A-2 and A-6. The composition of the product was similar for all HDO reactions. CO, CO₂ and C₃H₈ were produced, at 0.49, 1.43 and 0.22 %, respectively, and C1, C2 and C4 hydrocarbons were produced in trace amounts over Mo/Al₂O₃ at 350 °C. Mo/Al₂O₃ and CoMo(0.35)/Al₂O₃ formed similar products. Liquid products formed clear and colorless oil and water phases at reaction temperatures higher than 325 °C. In contrast, the liquid products became cloudy and contained a suspension of white crystals at reaction temperatures lower than 325 °C, indicating that as the catalysts were inactive, the liquid products became cloudy and contained the white crystals. The oil phase, considered to contain liquid hydrocarbon products, was separated and analyzed using the GC-MS. The gas chromatograph with hydrogen-flame ionization detector (GC-FID) analysis showed that the liquid hydrocarbon products were a simple mixture containing mainly *n*-paraffins of C15-18 (86.6 %). The liquid hydrocarbon products also contained alkanes of C4-14 (2.74 %) and isomers of C15-18 (2.39 %), with trace amounts of olefin of C15-18 (1.26 %). Some oxygenates (*e.g.*, fatty acid, fatty alcohol, monoglycerides, diglycerides and long-chain ester) were also contained in the C18 + fraction. Mo/Al₂O₃ and CoMo(0.35)/Al₂O₃ showed similarly high PFAD conversion of more than 99 % at all reaction temperatures. Selectivity for oxygenated compounds decreased from 2.9 to 1.0 % at 300 °C and from 2.6 to 1.1 % at 325 °C over CoMo(0.35)/Al₂O₃ compared to Mo/Al₂O₃, showing the highest deoxygen-

ation activity. Selectivity for oxygenated compounds was 4.32 % at 275 °C for CoMo(0.35)/Al₂O₃ (Table A-6), which is higher than 2.61 % at 300 °C for the Mo/Al₂O₃ (Table A-2), indicating that the reaction temperature should be above 300 °C, consistent with the results of the previous study. Sulfided CoMo catalysts showed poor performance in comparison with the sulfided Mo catalyst at reaction temperature 280 °C²⁸. This is because the higher synergy between Co and Mo can be expected at reaction temperatures higher than 280 °C. In addition, all catalysts showed low cracking reactant selectivity of less than 3 % at all reaction temperatures. The selectivity for *n*-C₁₆ + *n*-C₁₈ was 77.9 % at 300 °C (Table A-6) for CoMo(0.35)/Al₂O₃, which is higher than the selectivity at 275 °C, indicating that the reaction temperature of 300 °C is desirable. In addition, formation of olefins was suppressed by the loading of Co as a promoter. However, the promoter (Co) had no effect on the cracking reaction. Selectivity for the isomerization reaction was high at 13.0 % over CoMo(0.35)/Al₂O₃ at a reaction temperature of 275 °C (Table A-6), but the same low value as that of Mo/Al₂O₃ was observed at reaction temperatures of

Fig. 2 Yields of *n*-C₁₆ + *n*-C₁₈ (solid symbols) and Deoxygenation Rate (open symbols) over Mo/Al₂O₃ (triangles) and CoMo(0.35)/Al₂O₃ (circles)

300 °C and 325 °C. The yields of *n*-C₁₆ + *n*-C₁₈, which are produced through the HDO reaction, and deoxygenation rates of Mo/Al₂O₃ and CoMo(0.35)/Al₂O₃ are compared in Fig. 2. Mo/Al₂O₃ showed higher yield of *n*-C₁₆ + *n*-C₁₈, whereas CoMo(0.35)/Al₂O₃ showed higher deoxygenation rate, indicating that the addition of Co improves the activity but reduces the yield of *n*-C₁₆ + *n*-C₁₈.

3. 2. 2. Hydrotreating Reaction over CoMo/Al₂O₃ Catalysts with Different Co/Mo Ratios

The activity test results of all CoMo/Al₂O₃ catalysts at reaction temperatures 300 °C and 325 °C are shown in Table 2. Detailed results are shown in Tables A-2 to A-6. For all CoMo/Al₂O₃ catalysts, the isomerization yield was significantly low at reaction temperatures above 300 °C and was below approximately 3 % in all tests. Conversion over Mo/Al₂O₃ and CoMo/Al₂O₃ catalysts was more than 99 % at all reaction temperatures. In addition, CoMo(0.05)/Al₂O₃ and CoMo(0.35)/Al₂O₃ showed lower oxygenated yield than Mo/Al₂O₃. CoMo(0.05)/Al₂O₃ gave a slightly higher yield of *n*-C₁₆ and *n*-C₁₈ than Mo/Al₂O₃ at 300 °C (87.1 %). Basically, the yield over the Co-containing catalysts showed no significant change compared to the Mo/Al₂O₃ catalysts. However, CoMo(0.35)/Al₂O₃ formed higher yields of *n*-C₁₅ and *n*-C₁₇, and lower yields of *n*-C₁₆ and *n*-C₁₈ than Mo/Al₂O₃ at all reaction temperatures. Selectivity for CO and CO₂ over CoMo/Al₂O₃ catalysts was about twice as high as Mo/Al₂O₃, and the selectivity increased with higher reaction temperature, but remained lower than 4 % at all reaction temperatures.

3. 2. 3. Hydrotreating Reaction over CoMo/Ti-Al Catalysts

To elucidate the influence of TiO₂-Al₂O₃, HDO reactions of PFAD over various sulfided CoMo/Ti-Al catalysts with different TiO₂ coating amounts were carried out under the following reaction conditions: *T* = 275–325 °C, WHSV = 1 h⁻¹, *P* = 3 MPa, and H₂/feed = 1000 mL/mL, as shown in Table 3. The yields of oxygenates compounds show that TiO₂ coating did not

Table 2 Conversion and Several Yields over Sulfided Mo-based Catalysts for Hydrotreating of PFAD

	Mo/Al ₂ O ₃		CoMo(0.02)/Al ₂ O ₃		CoMo(0.05)/Al ₂ O ₃		CoMo(0.1)/Al ₂ O ₃		CoMo(0.35)/Al ₂ O ₃	
	300 ^{a)}	325 ^{a)}	300 ^{a)}	325 ^{a)}	300 ^{a)}	325 ^{a)}	300 ^{a)}	325 ^{a)}	300 ^{a)}	325 ^{a)}
Conversion	99.5	99.5	99.4	99.5	99.5	99.5	99.3	99.5	100	100
Yields [%]										
< C ₁₄	1.7	2.0	2.0	2.4	1.7	1.9	1.9	2.3	2.4	2.6
<i>i</i> -C ₁₅₋₁₈	1.4	1.5	1.6	2.0	0.9	1.2	1.3	1.6	0.6	0.6
olefin-C ₁₅₋₁₈	3.0	1.4	1.9	0.8	0.7	0.8	1.8	0.5	0.8	0.6
<i>n</i> -C ₁₅ + <i>n</i> -C ₁₇	4.6	7.9	4.8	9.1	5.3	8.8	7.7	11.5	15.3	17.8
<i>n</i> -C ₁₆ + <i>n</i> -C ₁₈	85.9	84.1	85.8	82.5	87.1	84.4	83.1	81.1	79.9	77.2
Oxygenates ^{b)}	3.0	2.6	3.4	2.6	1.9	2.4	3.4	2.4	1.1	1.2

a) Reaction temperature (°C).

b) Oxygenates represent the total selectivity for alcohol, aldehyde, and ester.

Table 3 Conversion and Several Yields over TiO₂ Coated Sulfided Catalysts for Hydrotreating of PFAD

	CoMo(0.05)/Ti(10)-Al			CoMo(0.05)/Ti(15)-Al			CoMo(0.05)/Ti(20)-Al		
	275 ^{a)}	300 ^{a)}	325 ^{a)}	275 ^{a)}	300 ^{a)}	325 ^{a)}	275 ^{a)}	300 ^{a)}	325 ^{a)}
Conversion	97.8	99.2	99.7	96.8	99.1	99.7	97.6	99.7	99.7
Selectivity [%]									
< C ₁₄	2.3	2.7	3.0	2.0	2.4	2.3	2.2	2.2	2.3
<i>i</i> -C ₁₅₋₁₈	1.6	1.8	2.4	1.3	1.2	1.7	1.7	1.6	2.2
olefin-C ₁₅₋₁₈	6.4	4.0	0.4	8.5	1.4	1.3	5.1	1.2	1.3
<i>n</i> -C ₁₅ + <i>n</i> -C ₁₇	1.8	3.9	7.1	1.9	4.1	7.3	2.0	3.5	6.1
<i>n</i> -C ₁₆ + <i>n</i> -C ₁₈	60.7	81.5	83.6	68.4	86.9	84.3	72.1	88.0	84.9
Oxygenates ^{b)}	25.0	5.3	3.2	14.6	3.3	2.8	14.7	3.6	3.1

a) Reaction temperature (°C).

b) Oxygenates represent the total selectivity for alcohol, aldehyde, and ester.

change the catalytic activity but decreased the deoxygenation activity at all reaction temperatures. Especially at 275 °C in the low-temperature range, all CoMo/Ti-Al catalysts achieved high olefin yield with oxygenates yield of more than 5 %. Comparing CoMo(0.05)/Ti(10)-Al with CoMo(0.05)/Ti(15)-Al and CoMo(0.05)/Ti(20)-Al, CoMo(0.05)/Ti(10)-Al showed higher yield for oxygenates compounds at all reaction temperatures, which implies lower deoxygenation activity. The yield of *n*-C₁₆ and *n*-C₁₈ increased with higher amount of TiO₂ coating from 10 to 20 % for all reaction temperatures. In addition, CoMo(0.05)/Ti(20)-Al showed slightly higher yield 88.0 % than CoMo(0.05)/Al₂O₃ catalyst at 300 °C. The three TiO₂ coated catalysts showed low cracking yield of less than 5 % at all reaction temperatures. Comparing CoMo(0.05)/Al₂O₃ with the three TiO₂-coated catalysts, CoMo(0.05)/Ti(20)-Al showed *n*-C₁₅ + *n*-C₁₇ yields of 3.5 % and 6.1 % whereas CoMo(0.05)/Al₂O₃ showed 5.3 % and 8.8 % at reaction temperatures of 300 °C and 325 °C, respectively, which indicates that DCO yield was suppressed by coating of TiO₂. All TiO₂ coated catalysts showed low isomerization yield of less than 2 % at all reaction temperatures, except for CoMo(0.05)/Ti(10)-Al at 325 °C (2.4 %) and CoMo(0.05)/Ti(20)-Al at 325 °C (2.2 %).

4. Discussion

4.1. Hydrotreating of PFAD over Sulfided CoMo Catalysts

Based on the activity test results, the hydrogenation of PFAD mainly produced two types of liquid products, oxygenate compounds such as aldehydes, alcohols, and esters, and hydrocarbons, including normal hydrocarbons, isomers, and cracking products (light hydrocarbons) as found by previous studies of reduced Pt-Sn catalyst²⁾. TiO₂ free and TiO₂ coated CoMo catalysts produced oxygenate compounds such as aldehydes, alcohols, and ester, in excellent agreement with the previous study²⁾. Among the liquid hydrocarbons, *n*-C₁₅ ~ *n*-C₁₈ were the main components with high yields. For

all catalysts with high deoxygenation activity, the yields of *n*-C₁₆ and *n*-C₁₈ decreased and the yields of *n*-C₁₅ and *n*-C₁₇ increased with higher reaction temperature. As with PtSn catalysts, fatty acids were transformed into 1-hexadecanol and 1-octadecanol *via* HDO and *n*-C₁₅ and *n*-C₁₇ hydrocarbons *via* decarboxylation/decarbonylation. Then, 1-hexadecanol and octadecyl alcohol were converted to *n*-C₁₆ and *n*-C₁₈ as the HDO reaction progressed further. In addition, the isomerization yield also increased slightly with higher reaction temperature. However, the Mo/Al₂O₃ based catalysts caused little isomerization and cracking products because the catalyst surface has almost non-existent Brønsted acid sites³⁰⁾. Consequently, Mo/Al₂O₃ based catalysts showed higher yield of *n*-C₁₆ and *n*-C₁₈ than PtSn catalysts, consistent with the results of previous studies^{2),7)}.

4.2. Addition Effect of Co

Co was added to Mo/Al₂O₃ as a promoter and activity tests were carried out to investigate the effect of Co addition. Mo/Al₂O₃ showed high deoxygenation activity with the yield of oxygenates below 5 % at all reaction temperatures, whereas Co loaded Mo/Al₂O₃ showed slightly improved deoxygenation. Addition of Co promoter to the MoS₂ phase clearly affects the mechanism and kinetics of reconstruction of the active phases^{30),35)~37)}. Co prefers the sulfur edge and forms Co-S-Mo phases with high activity^{29),33),36)}. CoMo(0.35)/Al₂O₃ showed higher deoxygenation activity, but lower yield of *n*-C₁₆ + *n*-C₁₈ and higher yield of *n*-C₁₅ + *n*-C₁₇ than Mo/Al₂O₃. This is because MoS₂ has a sulfur vacancy, which promotes the HDO reaction²⁹⁾. Then, a series of CoMo/Al₂O₃ catalysts with different Co to Mo ratios were prepared to confirm the effect of the Co/Mo ratio. The changes in yield of *n*-C₁₆ + *n*-C₁₈ and *n*-C₁₅ + *n*-C₁₇ with Co/Mo ratio are shown in Fig. 3. The maximum yields of *n*-C₁₆ and *n*-C₁₈ were observed at Co/Mo = 0.05 (87.1 %) for the CoMo/Al₂O₃ series, and the yield of *n*-C₁₅ and *n*-C₁₇ increased with Co/Mo > 0.05. The reason for this tendency is the presence of CoMoS. The adsorbed amount of NO increased because CoMoS was increased with the higher loading of Co as shown

Reaction conditions: $P = 3$ MPa, $\text{LHSV} = 1 \text{ h}^{-1}$, $\text{H}_2/\text{feed} = 1000$ (v/v). Reaction temperature: 300 °C (circles), 325 °C (triangles), 350 °C (squares).

Fig. 3 Effect of Co/Mo Ratio on Yields of $n\text{-C}_{16} + n\text{-C}_{18}$ (open symbols) and $n\text{-C}_{15} + n\text{-C}_{17}$ (solid symbols)

in **Table 1**. As the mole ratio of Co/Mo increased from 0.02 to 0.35, the amount of NO adsorbed increased from 3.4 to 8.4 mmol/g, indicating higher CoMoS phase content. Co promotes the activity of the hydrosulfurization (HDS) reaction remarkably²⁷. On the other hand, the CoMoS phase has two different adsorption phases for the hydrotreating of PFAD. CoMoS catalyst has HDO activity due to its sulfur vacancy structure, and saturated edge site under hydrogenation conditions, which enabled C-C hydrogenolysis³⁴. The DCO route involves hydrogenation of the hydroxyl group and hydrogenolysis of the C-C bond adjacent to the carbonyl group (C-C(=O)) to yield hydrocarbons with one fewer carbon and CO. Cleavage of the C-C bond can occur through a basic attack on the hydrogen atom in the β -position because the carbon atom carries a positive charge of the cationic intermediate over the Co-promoted catalysts and the final product should be CO. The basic site could be a sulfur anion (S^{2-}) species adjacent to the sulfur vacancy³⁵. Moreover, Co can increase the electron density of sulfur atoms³⁶, which would explain the promotion effect of Co on the DCO route. Therefore, the CoMoS phase has both HDO and DCO activity. Therefore, the amount of Co loading should be controlled to improve the catalyst activity but inhibit the DCO reaction, and the Co/Mo mole ratio of 0.05 is the optimum for this reaction. The reaction pathways over the sulfided CoMo/Al₂O₃ are presented in **Scheme 1**.

4. 3. Coating Effect of TiO₂

CoMo supported on TiO₂ coated Al₂O₃ (10-20 wt%) was prepared for evaluating the effect of TiO₂ coating. The metal loading ratio was set to 0.05, which showed high activity at low temperature (300 °C) and high HDO yield ($n\text{-C}_{16} + n\text{-C}_{18}$). The yields of $n\text{-C}_{16} +$

Scheme 1 Proposed Mechanism of Hydrogenation of PFAD over CoMo/Al₂O₃ Catalysts (R: C₁₅H₃₁ and C₁₇H₃₅).

Reaction conditions: $P = 3$ MPa, $\text{LHSV} = 1 \text{ h}^{-1}$, $\text{H}_2/\text{feed} = 1000$ (v/v). Reaction temperature: 275 °C (squares), 300 °C (circles), 325 °C (triangles).

Fig. 4 Effect of TiO₂ Coating on Yield of $n\text{-C}_{16} + n\text{-C}_{18}$ (open symbols) and $n\text{-C}_{15} + n\text{-C}_{17}$ (solid symbols)

$n\text{-C}_{18}$ and $n\text{-C}_{15} + n\text{-C}_{17}$ over CoMo(0.05)/Al₂O₃ and TiO₂ coated catalysts are shown in **Fig. 4**. The TiO₂-coated catalyst at 275 °C (**Table 3**) showed no increase in activity due to the high yield for oxygenated compounds. On the other hand, the yield of $n\text{-C}_{16} + n\text{-C}_{18}$ increased with higher amount of TiO₂ coating. CoMo(0.05)/Ti(20)-Al showed the highest yield of $n\text{-C}_{16} + n\text{-C}_{18}$ (88.0 %) among the catalysts with CoMo supported on TiO₂ coated Al₂O₃. All TiO₂-coating catalysts showed lower DCO yields than CoMo(0.05)/Al₂O₃, and CoMo(0.05)/Ti(20)-Al showed the lowest DCO yield (3.5 %) at 300 °C. H₂-TPR (**Fig. 1**) showed that the increase in the amount of TiO₂ coating increased the reduction temperature to a higher range. Comparing CoMo(0.05)/Al₂O₃ and CoMo(0.05)/Ti(15)-Al, the latter peak of CoMo(0.05)/Ti(15)-Al₂O₃ was about 80 °C higher, which hinders the reduction of Mo-based active phases. On the other hand, comparing

Scheme 2 Proposed Mechanism of Hydrogenation of PFAD over CoMo/Ti-Al₂O₃ Catalysts (R: C₁₅H₃₁ and C₁₇H₃₅)

CoMo(0.05)/Al₂O₃ and CoMo(0.05)/Ti(20)-Al, the latter reduction peak of CoMo(0.05)/Ti(20)-Al was almost the same, which indicates that the active phase is efficiently formed if the TiO₂ loading exceeds a certain percentage. This is because TiO₂ coating enhances reduction of active metals and the formation of the CoMoS active phase¹⁴. In addition, TiO₂ coating formed the new active phase TiMoS. The effect of TiO₂ was reported previously^{41,42}. Addition of TiO₂ facilitated the reduction from Mo⁶⁺ to Mo⁴⁺ and enhanced formation of the CoMoS active slab. In addition, the concentration of Ti³⁺ species which forms the TiMoS phase increased with higher amount of TiO₂ from 10 to 20 wt%. TiMoS is formed by coating TiO₂ on Al₂O₃^{15,16,40}. The previous research also showed that coated TiO₂ increased the dispersion of Mo. Consequently, CoMoS and TiMoS were formed effectively¹⁵. Under a H₂ atmosphere, the reduction of TiS₂ accelerated to the formation of anion vacancies that be measured by the ESR method and acted as an electronic promoter of the molybdenum sulfide phase³⁷. NO chemisorption (Table 1) showed that the adsorbed amount of NO was increased with higher amount of TiO₂ coating. These results suggested that the CoMoS phase and some TiMoS phase were formed effectively with TiO₂ coating onto Al₂O₃. Therefore, the HDO yield was increased, and DCO yield decreased with higher TiO₂ coating amount. Focusing on the yield of oxygenates compounds, TiMoS had no deoxygenation activity because the yield did not change at 300 °C and 325 °C even with increased amount of TiO₂ coating. No significant change in isomerization and cracking yield was observed with higher amounts of TiO₂ coating. Therefore, TiMoS does not have isomerization and cracking activity. The suggested reaction mechanism over the sulfided CoMo/Ti-Al is presented in Scheme 2.

5. Conclusions

Based on the HDO results for Mo/Al₂O₃ and CoMo(0.35)/Al₂O₃, addition of Co increased both deoxygenation activity but promoted the DCO reaction. We suggested that MoS₂ has HDO activity, Co₉S₈ has DCO activity, and the CoMoS phase has both HDO and DCO activity. CoMo(0.05)/Al₂O₃ showed the best yield of *n*-C₁₆ and *n*-C₁₈ (87.1 %) among the CoMo catalysts due to the optimum amount of CoMoS phase on the Al₂O₃ support. On the other hand, CoMo(0.35)/Al₂O₃ with the highest amount of Co added showed the lowest HDO yield and the highest DCO yield among the CoMo catalysts. Co addition could improve the HDO activity, but excess addition of Co resulted in decarbonylation and/or DCO because of the presence of excess amount of CoMoS phase. The optimum mole ratio of Co/Mo was 0.05. Based on the activity comparison of TiO₂ coating catalysts, CoMo(0.05)/Ti(20)-Al showed the best yield of *n*-C₁₆ and *n*-C₁₈ (88.0 %). Based on the result of H₂-TPR and pulse NO chemisorption, CoMo(0.05)/Ti(20)-Al contains TiMoS phase, which has HDO activity. However, TiMoS did not have deoxygenation activity, isomerization activity, and cracking activity, but favored formation of *n*-C₁₆ and *n*-C₁₈.

Supporting information

Supplementary data associated with this article can be found in the online version at <https://jstage.jst.go.jp/browse/jpi-char/en> (DOI: doi.org/10.1627/jpi.65.18).

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要 旨

パーム脂肪酸蒸留物の選択的水素化処理硫化 Mo 系触媒における助触媒効果および担体の役割

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異なる Co/Mo モル比を持つ CoMo/Al₂O₃ 触媒および Al₂O₃ に異なる量の TiO₂ をコーティングした担体を用いて, CoMo/TiO₂-Al₂O₃ 触媒を調製した。これらの触媒を用いたパーム脂肪酸蒸留物 (PFAD) の水素化処理反応を行い, Co/Mo モル比と TiO₂ コーティング量の水素化脱酸素反応 (HDO) および脱炭酸/脱カルボニル化反応 (DCO) に及ぼす影響を検討した。触媒解析には, BET, XRF, NO パルス吸着法と H₂-TPR を用いた。Co/Mo モル比が 0.05 では *n*-C₁₆ および *n*-C₁₈ の収率が最

大になったが, それより高い Co/Mo モル比では *n*-C₁₅ および *n*-C₁₇ の収率が上昇した。この結果から触媒上の CoMoS 層が HDO と DCO の両方の活性を持つことが分かった。全ての触媒の中で, CoMo(0.05)/Ti(20)-Al が最も高い *n*-C₁₆ と *n*-C₁₈ の収率を示した。これらの結果から, Al₂O₃ 上に TiO₂ を添加することで形成された TiMoS 相は, HDO 反応を促進するが, 異性化およびクラッキング活性を持たないことが示唆された。