

HYDROGENOLYSIS OF METHYL OLEATE OVER OXIDE CATALYST DERIVED FROM HYDROGEN STORAGE ALLOY

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A mixed oxide catalyst was prepared from a binary hydrogen storage alloy, Mg_2Cu , and its activity and selectivity were compared with those of conventional $CuCrO$ catalyst. The catalyst's activity was stable for the synthesis of C_{18} alcohol by gas-phase hydrogenolysis of methyl oleate in a continuous-flow reactor at 553 K under atmospheric pressure. Considerable amounts of unsaturated alcohol were produced together with saturated alcohol. From a kinetic study the rate equation was formulated for each alcohol. From XRD analysis, active sites are thought to be copper species on MgO support.

Introduction

Long-chain alcohols are important as industrial materials. It is especially desirable to produce long-chain alcohols economically by the hydrogenolysis of naturally occurring fatty acid derivatives^{16,17}. Copper-based catalysts have been noted as outstandingly effective for the hydrogenolysis of fatty acid esters to the corresponding alcohols². Among the copper catalysts, Adkins-type copper chromite catalyst is widely used³. However, the hydrogenolysis of esters on copper chromite requires high hydrogen pressures and high reaction temperatures such as 560 K, 20 MPa¹³. Alternative catalytic systems such as $Cu-Na-SiO_2$ ⁵ and $Cu-Zn-Cd-Al$ ¹⁰ were proposed for better efficiency. But these still required severe reaction conditions.

Moreover, the alcohols produced from unsaturated esters were completely saturated; thus unsaturated alcohols could not be produced. Unsaturated fatty alcohols are especially important as industrial products. But these alcohols are difficult to produce and the production cost is high⁴.

The kinetics of the hydrogenation of fatty acid ester have usually been studied in the liquid phase. In spite of the importance of the kinetics in the gas phase, only a few studies have been done in gas-phase hydrogenation of unsaturated bonds in the fatty acid esters^{8,11,12}. Kinetic studies of hydrogenolysis of fatty acid esters to the corresponding alcohols could not be found in the gas-phase condition.

On the other hand, hydrogen storage alloys have been used for several catalytic systems^{6,7}. The hydrogenolysis of methyl oleate (cis-9-octadecenoic acid methyl ester) to produce C_{18} alcohols (cis- and/or

trans-octadecenol and octadecanol) was investigated using various hydrogen storage alloys as catalyst with a pulse reaction system¹⁴. Among the alloys tested, Mg_2Cu was found to be the most effective catalyst. It had higher activity than the conventional $CuCrO$ catalyst for the hydrogenolysis reaction¹⁴.

It was revealed in further studies that oxidation treatment of Mg_2Cu alloy was effective for the hydrogenolysis of methyl oleate with a gas-phase pulse reactor¹⁵. A catalyst of the same composition prepared by the co-precipitation method only showed instability and lower activity.

In this study, the selective hydrogenolysis of methyl oleate to the unsaturated alcohol was tested under mild conditions. A kinetic study was also made with a gas-phase continuous-flow reactor.

1. Experimental

1.1 Catalysts

A binary hydrogen storage alloy HY-302 (Mg_2Cu denoted as ALLOY) was obtained from Ergenics, a division of MPD Technology Corporation^{6,7,14,15}. The surface area of ALLOY was 2.1×10^3 m²/kg.

In the previous work on the oxidation treatment of Mg_2Cu at various temperatures, it was found that catalytic activity was maximum between 773 K and 973 K¹⁵. In the present study, the alloy was preoxidized overnight in a flow of air at 775 K and sieved into 35–42 mesh (denoted as AL-775). The surface area of AL-775 was 6.1×10^3 m²/kg.

Adkins-type copper chromite catalyst ($CuCrO$) was prepared according to Adkins and Connor¹. The surface area of $CuCrO$ was 90×10^3 m²/kg.

Surface areas of the samples were measured by the BET method. X-ray diffraction (Rigaku Denki) was used for the characterization.

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1.2 Reactor apparatus

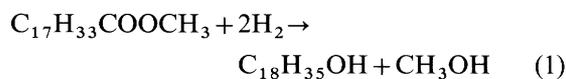
The experimental apparatus for hydrogenolysis is shown in Fig. 1. A Pyrex glass reactor (10 mm i.d.) was used as a continuous-flow reactor. A thermocouple well (4 mm o.d.) was placed at the middle of the reactor. Catalyst (1.0 g) was diluted with glass beads (35 mesh under) to make the total volume 2 ml and was placed in the reactor.

Pretreatment of the catalyst was carried out in a flow of hydrogen under various conditions. Methyl oleate was fed by a microfeeder at a rate of 1.1×10^{-7} kg/s and was vaporized at 553 K in a glass tube (4 mm i.d., 180 mm long) filled with quartz particles. This vaporizer was directly connected to the reactor by a glass joint. The methyl oleate vapor was charged into the catalyst bed together with the flow of hydrogen (2.0×10^{-6} m³/s at 273 K, 1.0×10^5 Pa) at 553 K. The effluent was cooled to room temperature and the liquid portion was trapped.

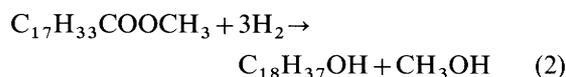
1.3 Analysis

In the hydrogenolysis of methyl oleate, several reactions may take place as follows.

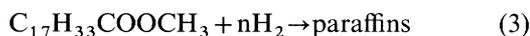
1. production of unsaturated alcohol



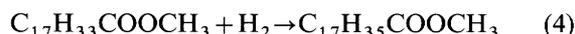
2. production of saturated alcohol



3. formation of paraffins

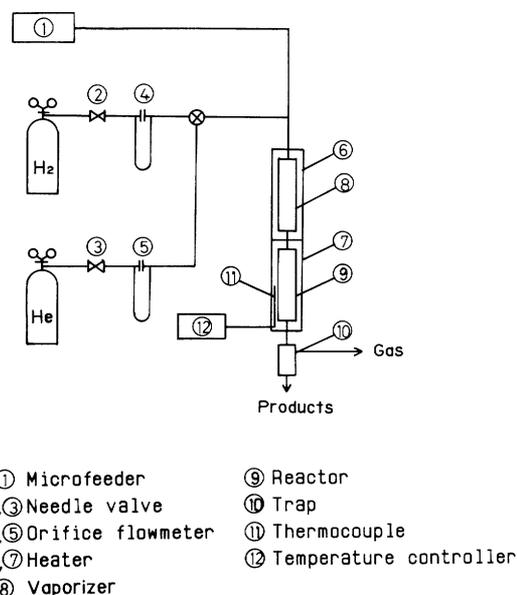


4. saturation of reactant



All the above products and unreacted methyl oleate were identified and analyzed by a gas chromatograph. The sampling liquid was dissolved in acetone, and then dibenzyl ether was added as an internal standard. The gas chromatograph was equipped with 3 m of PEG column at 483 K. Methanol could not be analyzed because the peak was masked by the large peak of solvent (acetone).

In the following calculations, the saturated ester produced according to Eq. (4) was regarded as part of the reactant because it retained the ester group. Several peaks were observed in the chromatogram at the retention of paraffinic compounds, but they were represented by octadecane. The conversion, X , is defined as moles of total C₁₈ products in moles of total C₁₈ effluents. The selectivity of a specified product, S_i , is defined as moles of a specified product in moles of total C₁₈ products. The yield of a specified product, Y_i , is defined as moles of a specified product



① Microfeeder
②,③ Needle valve
④,⑤ Orifice flowmeter
⑥,⑦ Heater
⑧ Vaporizer
⑨ Reactor
⑩ Trap
⑪ Thermocouple
⑫ Temperature controller

Fig. 1. Experimental apparatuses for hydrogenation

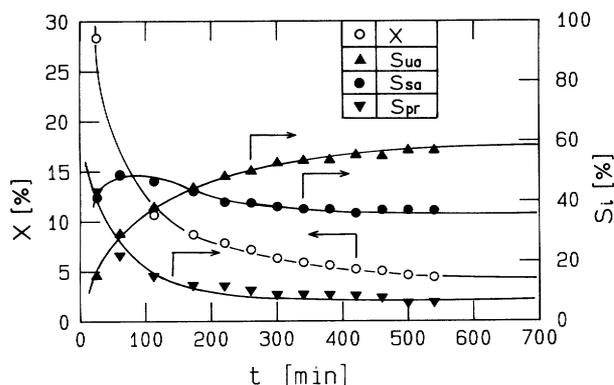


Fig. 2. Change of activity and selectivities with time on stream

in moles of total C₁₈ effluents. Then the following relation holds.

$$Y_i = S_i X \quad (5)$$

2. Experimental Results

The catalytic activity was tested in a continuous-flow reactor at 553 K under atmospheric pressure. Figure 2 shows the changes in conversions and selectivities with time. The conversion, X , decreased with time, but stabilized at 500 min. Paraffinic compounds were observed at the initial stage but decreased with time. The selectivity of C₁₈ unsaturated alcohol, S_{ua} , increased and reached 57% after 500 min. On the other hand, the selectivity of C₁₈ saturated alcohol, S_{sa} , decreased to reach 37% after 500 min. The ratio of unsaturated to saturated alcohol was kept at about 1.5 at steady state. The selectivity of paraffins, S_{pr} , was only 6% at steady state. Thus these kinetic studies were conducted with steady-state activity.

2.1 Effect of pretreatment with hydrogen

Figure 3 shows the influence of pretreatment conditions. Several hydrogen treatments of the fresh catalyst were carried out in a reactor before the reaction. The reduction temperature and the reduction period were changed from 553 to 623 K and from 0.2 to 14 h, respectively. The initial activities were varied with pretreatment conditions. But these conditions did not affect the conversion at steady state. The selectivities at steady state were also unaffected by pretreatment conditions. Thus the pretreatment with hydrogen in the following experiment was fixed at 553 K and 14 h.

2.2 Catalyst activity test

Activities of three catalysts were compared at the same W/F (=about 5×10^2 (kg·s)/m³). For each experiment, the activity of the fresh catalyst initially decreased with time and then stabilized after several hours. Table 1 shows the activities at steady state. The original alloy HY-302 (ALLOY) indicated low activity ($X=1.4\%$), but the selectivities to alcohols were similar to those of AL-775. Adkins-type copper chromite catalyst (CuCrO) showed higher activity ($X=11.3\%$) than that of AL-775 ($X=4.8\%$), but the selectivities to alcohols were lower because paraffinic compounds were major products. To compare the selectivities of AL-775 with Adkins catalyst, another experiment was conducted. It was carried out with an increased W/F to make the conversion of AL-775 higher than that of CuCrO. The selectivities to alcohols were still higher than that of CuCrO.

2.3 Effect of W/F

The effect of W/F on the yields is illustrated in Fig. 4. Total flow rate was changed from 2.3×10^{-5} to 16.9×10^{-5} mol/s. It is seen from Fig. 4 that yields of paraffins and saturated alcohol increase with W/F . But the yield of unsaturated alcohol does not change significantly with W/F . The selectivity of each alcohol was not extrapolated to either 0 or 100% at $W/F=0$. These results suggest that each alcohol was produced in a parallel reaction at the initial stage. The saturation of unsaturated bond proceeded with increased contact time. Paraffins may be mainly produced by the consecutive reaction.

2.4 Effect of partial pressure of reactants

The effect of partial pressure of hydrogen on the initial rate of alcohol production is illustrated in Fig. 5. Hydrogen pressure was changed from 0.3×10^5 to 1.0×10^5 Pa with helium balance. The reaction rate was determined as a differential reactor condition because conversions were within 5%. As shown in Fig. 5, the reaction rates are nearly first-order with respect to hydrogen pressure for each alcohol.

The effect of partial pressure of methyl oleate on the initial rate of alcohol production is shown in Fig. 6. Ester pressure was changed from 0.3×10^3 to

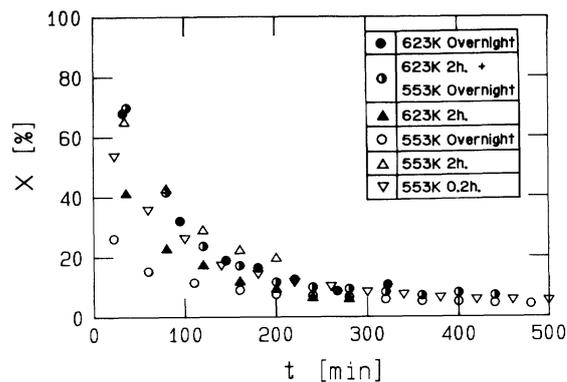


Fig. 3. Effect of pretreatment

Table 1. Activities with catalysts. $T=553$ K

Catalyst $W/F \times 10^{-2}$ [(kg·s)/m ³]	ALLOY 5.2	AL-775 5.3	CuCrO 4.6	AL-775 15.8
X [%]	1.4	4.8	11.3	17.6
S_{pr} [%]	3	6	50	14
S_{sa} [%]	29	37	30	43
S_{ua} [%]	67	57	20	43

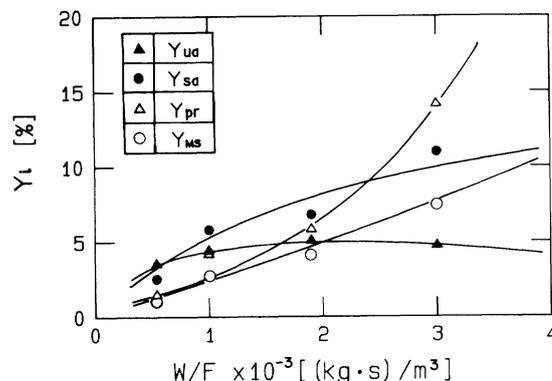


Fig. 4. Dependence of W/F

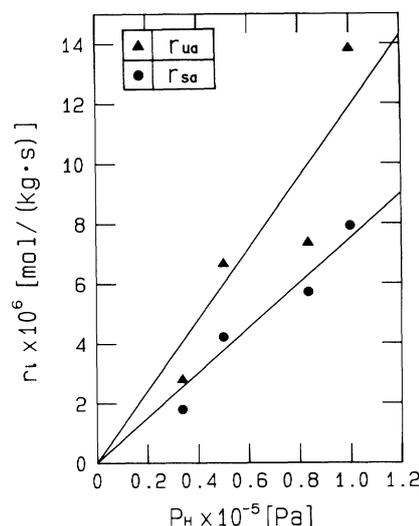


Fig. 5. Effect of partial pressure of hydrogen on alcohol synthesis. $T=553$ K; $P_{MO}=0.6 \times 10^3$ Pa

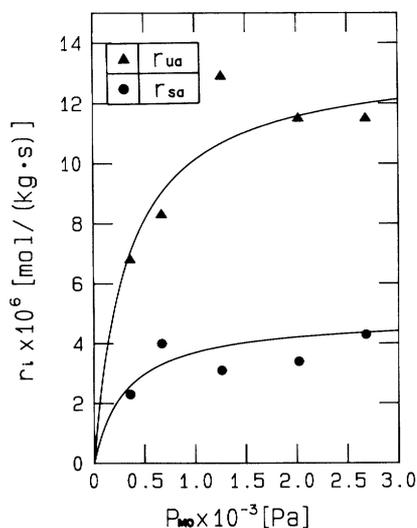


Fig. 6. Effect of partial pressure of methyl oleate for alcohol synthesis. $T = 553 \text{ K}$; $P_H = 1.0 \times 10^5 \text{ Pa}$

$2.7 \times 10^3 \text{ Pa}$. The effect of partial pressure of the ester is well expressed by the following empirical equation for each alcohol.

The initial reaction rates can be written as follows for both unsaturated and saturated alcohols:

$$r_i = k_i \frac{K_i \cdot P_{MO}}{1 + K_i \cdot P_{MO}} P_H \quad (6)$$

In the liquid-phase hydrogenolysis of fatty acid esters, the rate equation was derived on the assumption that the reaction rate was determined by the surface reaction of adsorbed species¹³. In this study, a Langmuir-type mechanism can be applied. Assuming that the adsorption of hydrogen is low at elevated temperatures, a rate equation identical to Eq. (6) can be obtained. The values of kinetic parameters are presented in **Table 2**. The solid lines of Figs. 5 and 6 are results calculated by Eq. (6). K_i of all the alcohols was almost the same, so that the adsorption of methyl oleate was an important factor in the reaction. The details of the relation between the assumed mechanism and the rate equation will be discussed in a future paper.

2.5 Effect of reaction temperature

The effect of reaction temperature on the initial rate of alcohol production is illustrated as an Arrhenius plot in **Fig. 7**. The reaction temperature was changed from 503 to 553 K. The activation energies for unsaturated alcohol and saturated alcohol were determined from the slopes of lines as $E_{ua} = 0.9 \times 10^5 \text{ J/mol}$ and $E_{sa} = 1.1 \times 10^5 \text{ J/mol}$ respectively. The two activation energies are similar to each other.

Muttzall *et al.*¹³ reported the kinetics of hydrogenolysis of C_{18} saturated ester to C_{18} alcohol in the liquid phase. The activation energy at 30 MPa was determined as $0.72 \times 10^5 \text{ J/mol}$. The reported activa-

Table 2. Values of kinetic parameters. $T = 553 \text{ K}$

C_{18} Alcohol	$k_i \times 10^6$ [mol/(kg·s)]	$K_i \times 10^3$ [1/Pa]	$E_i \times 10^{-5}$ [J/mol]
Unsaturated	11.5	3.0	0.9
Saturated	4.9	3.1	1.1

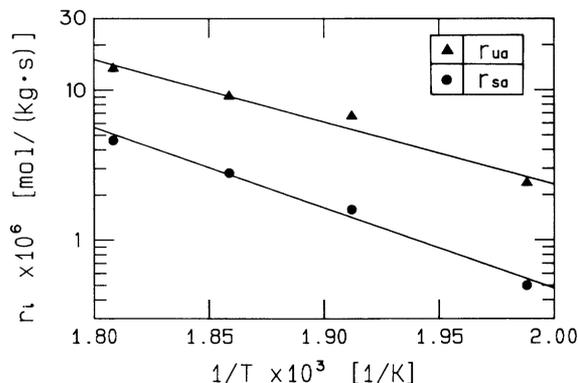


Fig. 7. Effect of reaction temperature

tion energy is similar to our results in the gas phase at atmospheric pressure.

2.6 Influence of diffusion limitations

The influence of diffusion limitations on both film resistance and pore diffusion resistance was considered. For film resistance, the drop of partial pressure of ester was calculated as

$$\frac{\Delta P}{P} = \frac{-r}{k_G \cdot S_p \cdot P} \quad (7)$$

Hence the mass transfer coefficient k_G was given by the j_D factor. Therefore, the drop in partial pressure became

$$\frac{\Delta P}{P} = 4.4 \times 10^{-4} \quad (8)$$

The drop was so small that the influence of film resistance could be negligible.

For pore diffusion resistance the catalytic effectiveness factor was given by the Weisz modulus:

$$W_s = \frac{V_p}{S_p} (n+1) \frac{-r}{2D_e \cdot C_s} \quad (9)$$

Hence it was assumed that the reaction was first-order with spherical catalyst. Therefore, the Weisz modulus became

$$W_s = 3.7 \times 10^{-5} \quad (10)$$

From this number, it was found that the catalytic effectiveness factor was almost one. Thus the influence of pore diffusion resistance could be negligible. Both calculated results were confirmed by the experimental results.

2.7 Characterization

It was found in the previous study¹⁵⁾ that AL-775 consisted of a mixture of copper oxide and magnesium oxide, while ALLOY showed typical XRD peaks of Mg₂Cu alloy. AL-775 showed no such peaks like those of the alloy itself, metallic copper, Cu₂O and Cu–Mg compounds.

In this study, changes in the structure of catalyst by pretreatment and reaction were studied by XRD analysis. **Figure 8** shows the XRD spectra of AL-775 with various treatments. AL-775 before treatment (Fig. 8(a)) consisted of copper oxide (○) and magnesium oxide (△). It didn't show any peaks characteristic to Mg₂Cu. After hydrogen pretreatment at 775 K and 14 h. (Fig. 8(b)) the peaks characteristic of CuO disappeared. After the hydrogenolysis reaction (Fig. 8(c)), AL-775 showed the same diffraction patterns as those obtained with hydrogen pretreatment (Fig. 8(b)). There were only peaks identical to those of MgO.

The catalyst used was treated by air at 775 K and 14 h as described in section 1.1. The XRD spectra are also shown in Fig. 8(d). The peaks of CuO again appeared. The resulting peaks indicated peaks similar to those of fresh AL-775 (Fig. 8(a)). Thus copper species might be reduced to well-dispersed state during hydrogen pretreatment. This state was unchanged during the reaction. The species were reoxidized to CuO by oxidation treatment.

These findings suggest that the copper species can interchange between well-dispersed reduced state and CuO during reduction-oxidation treatment. In contrast, MgO is stable during these treatments.

For methanol synthesis catalyst⁹⁾, XRD spectra of CuZnO catalyst showed the formation of amorphous Cu(I) dispersed in ZnO support by the reduction pretreatment. This species was assigned as an active site of methanol synthesis. The copper species investigated in this study are similar to those in the case of methanol synthesis. Such well-dispersed copper species with reduced valence state might be the cause of steady-state activity, and MgO might play an important role as the support. Thus it was suggested that copper species finely dispersed on MgO support was the active site for hydrogenolysis.

As shown in the previous papers¹⁵⁾, ALLOY showed typical peaks of Mg₂Cu alloy and retained part of the alloy structure even after oxidation in air at 623 K. The same alloy peaks were observed after the hydrogenolysis reaction. Thus copper species were suggested to be strongly combined with magnesium. This may make the activity of ALLOY small.

Conclusion

A new type of catalyst was derived from one of the hydrogen storage alloys, Mg₂Cu, by oxidation

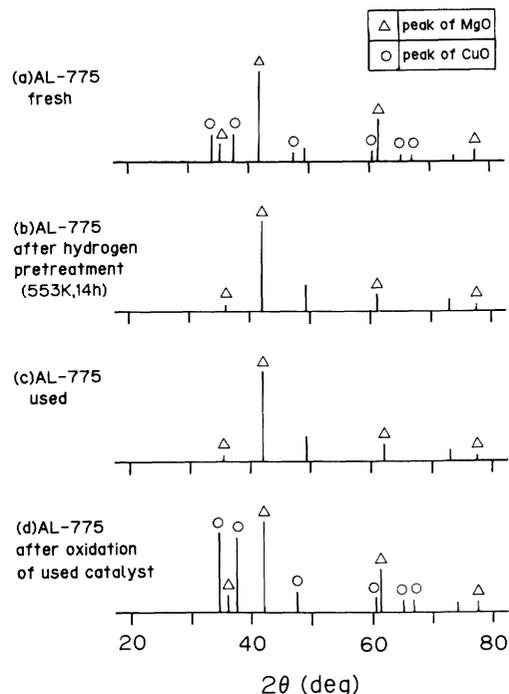


Fig. 8. X-ray diffraction spectra for AL-775

treatment at 775 K. The catalyst was a mixed oxide of CuO and MgO. CuO species were affected by various treatments. The activity and selectivity of the catalyst were tested with a continuous-flow reactor in the gas phase.

The activity was much higher than that of the original alloy. The selectivity to unsaturated alcohol was much higher than that of the conventional CuCrO catalyst. The active site was thought to be copper species on MgO.

The formation of paraffins could lead to the subsequent hydrogenolysis of alcohols. Steady-state activity was obtained after a considerable decrease in the initial activity. It is especially interesting that the synthesis of unsaturated alcohol can be obtained with high selectivity at the steady state.

Acknowledgement

The authors would like to thank Mr. H. Itoh for the design of the reaction system, and Mr. T. Imura and Mr. J. Watanabe for skillful glass blowing.

Nomenclature

C_s	= concentration at catalyst surface	[mol/m ³]
D_e	= effective diffusion coefficient	[m ² /(m·s)]
E_i	= activation energy	[J/mol]
F	= total feed gas flow rate at 273 K, 1.0 × 10 ⁵ Pa	[m ³ /s]
j_D	= j_D factor	[—]
k_G	= mass transfer coefficient	[mol/(s·m ² ·Pa)]
K_i	= adsorption equilibrium constant of component i	[1/Pa]
k_i	= reaction rate constant of component i	[mol/(kg·s·Pa)]
n	= reaction order	[—]

P	= partial pressure	[Pa]
r_i	= reaction rate of component i	[mol/(kg·s)]
S_i	= selectivity of component i	[%]
S_p	= specific surface area	[m ² /kg]
T	= reaction temperature	[K]
t	= time on stream	[min]
V_p	= specific volume of catalyst	[m ³ /kg]
W	= catalyst weight	[kg]
W_s	= Weisz modulus	[—]
X	= conversion	[%]
Y_i	= yield of component i	[%]

<Subscripts>

H	= hydrogen
MO	= methyl oleate
MS	= methyl stearate
pr	= paraffins
sa	= C ₁₈ saturated alcohol
ua	= C ₁₈ unsaturated alcohol

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