

HYDROGENOLYSIS OF METHYL LINOLEATE OVER OXIDE CATALYST DERIVED FROM Mg_2Cu ALLOY

NOBUYASU CHIKAMATSU, TOMOHIKO TAGAWA
AND SIGEO GOTO

*Department of Chemical Engineering, Nagoya University,
Nagoya 464-01*

Key Words: Chemical Reaction, Hydrogenolysis, Methyl Linoleate, Kinetics, Catalyst, Unsaturated Alcohol

Introduction

Recently, naturally occurring fatty acid esters have become noted as a source of long-chain alcohols because of their biodegradability and uniform molecular weight. Catalytic systems to produce unsaturated alcohols under milder conditions are now especially needed.

In a previous paper²⁾ we proposed a new hydrogenolysis catalyst prepared by the oxidation treatment of hydrogen storage alloy. Copper-magnesium oxide catalyst derived from Mg_2Cu alloy was examined as a catalyst^{1,2)} for the hydrogenolysis of methyl oleate (with one double bond) to produce C_{18} alcohols (cis- and/or trans-9-octadecenol and octadecanol). Considerable amounts of C_{18} alcohols were obtained, and this oxide catalyst had higher selectivity than the conventional Adkins-type catalyst in a gas-phase reactor at 553 K and atmospheric pressure.

In this study, the selective hydrogenolysis of methyl

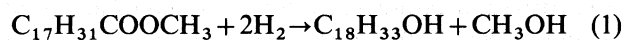
linoleate (with two double bounds) to produce unsaturated alcohols was investigated with this catalyst.

1. Experimental

The hydrogen storage alloy Mg_2Cu was preoxidized at 775 K overnight in a flow of air.

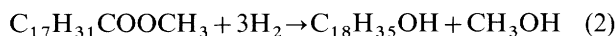
The hydrogenolysis was performed in a continuous-flow reactor. Details of the reactor were described in the previous paper¹⁾. Pretreatment of the catalyst was carried out in a flow of hydrogen at 553 K for 2 h. The reaction was mainly carried out under the following conditions: methyl linoleate, 1.1×10^{-7} kg/s vaporized at 553 K; hydrogen, 2.0×10^{-6} m³/s at 273 K and 1.0×10^5 Pa; W/F , 5.2×10^2 (kg·s)/m³; reaction temperature: 513 K. The following products are expected in the hydrogenolysis of methyl linoleate (methyl-cis-9, cis-12-octadecadienoate).

1. production of alcohol with two double bonds (linoleyl alcohol)

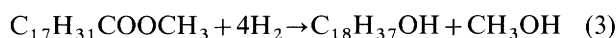


* Received May 27, 1992. Correspondence concerning this article should be addressed to S. Goto.

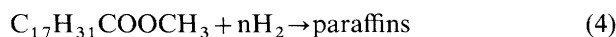
2. production of alcohol with one double bond (oleyl alcohol)



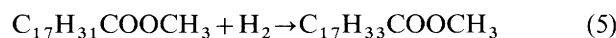
3. production of saturated alcohol (stearyl alcohol)



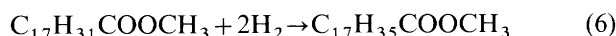
4. formation of paraffins



5. saturation of reactant ester (methyl oleate)



(methyl stearate)



Methyl oleate produced by Eq. (5) may be further hydrogenated by several reactions shown in the previous paper¹⁾.

2. Results and Discussions

2.1 Reactivity of unsaturated esters

Reactivities of methyl oleate and methyl linoleate were compared at 513 K. **Figure 1** shows the changes in the conversions and selectivities to C_{18} alcohol with time with both reactants. The conversions decreased with time, but stabilized at 500 min. The selectivities to C_{18} alcohol increased and reached more than 90% after 500 min. Methyl linoleate always exhibits higher reactivity than methyl oleate. Thus, the catalytic activity could be affected by the number of double bonds in the reactant ester.

The reaction of methyl linoleate was carried out at 513 K. **Figure 2** shows the changes in selectivity of each alcohol with time. The catalyst exhibited high selectivity to alcohol. The main products were stearyl alcohol and oleyl alcohol. The selectivities to linoleyl alcohol and paraffins were rather small. The hydrogenation of one of the double bonds in methyl linoleate (Eq. (5)) occurred to produce methyl oleate. Further saturation of double bond (Eq. (6)) to produce methyl stearate was small.

2.2 Effect of partial pressure of reactants

Kinetic studies were carried out with steady-state activity. The initial reaction rate was determined in a differential reactor condition. The effects of film resistance and pore diffusion resistance were estimated by the same method as was used in the previous paper¹⁾. These resistances were revealed to be negligible.

The effect of partial pressure of hydrogen at 513 K on the initial rate of alcohol production is illustrated in **Fig. 3**. The reaction rates are first-order with respect to hydrogen pressure for both stearyl alcohol and oleyl alcohol. The reaction rate of linoleyl alcohol was too

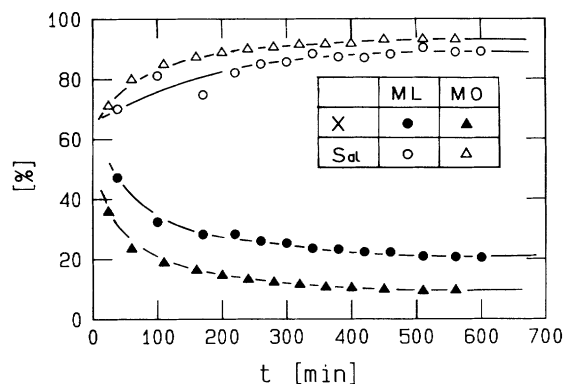


Fig. 1. Reactions of methyl oleate and methyl linoleate. $T = 513\text{ K}$

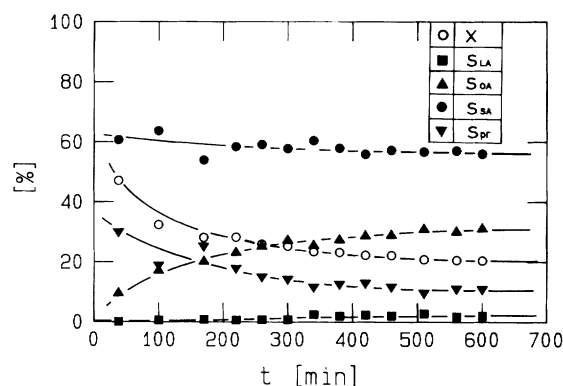


Fig. 2. Change of conversion and selectivities with time on stream. $T = 513\text{ K}$

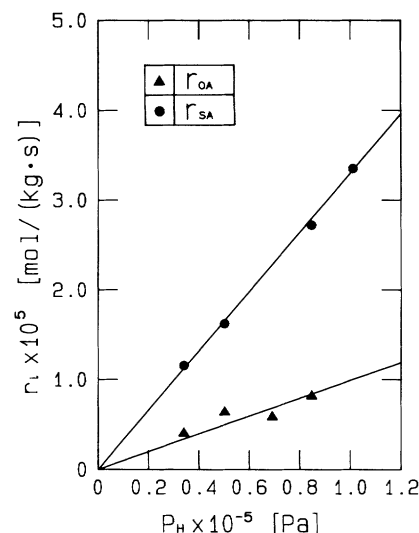


Fig. 3. Effect of partial pressure with respect to hydrogen for alcohol synthesis. $T = 513\text{ K}$; $P_{ML} = 0.7 \times 10^3\text{ Pa}$

low to determine. These first-order kinetics are similar to the reaction of methyl oleate at 553 K¹⁾.

The effect of partial pressure of methyl linoleate at 513 K on the initial rate of alcohol production is shown in **Fig. 4**. The initial reaction rates at 513 K have peaks with respect to partial pressure of methyl linoleate.

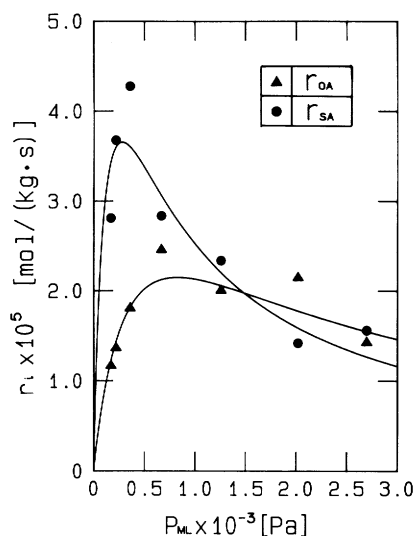


Fig. 4. Effect of partial pressure with respect to methyl linoleate for alcohol synthesis. $T = 513\text{ K}$; $P_H = 1.0 \times 10^5\text{ Pa}$

The effects can be expressed by the following empirical equation for stearyl alcohol and oleyl alcohol;

$$r_i = k_i \frac{K_i P_{ML}}{(1 + K_i P_{ML})^2} P_H \quad (7)$$

In this case, a Langmuir-competitive-type mechanism can be applied. It is suggested that the reactant ester and hydrogen are adsorbed on the same active site of the catalyst. Assuming that the adsorption of hydrogen is low and that $K_H P_H \ll 1$, a rate equation identical to Eq. (7) can be obtained. Ordinary Langmuir-type kinetics was observed in the case of methyl oleate at 553 K ¹⁾. The values of kinetic parameters are presented in Table 1. The solid lines in Figs. 3 and 4 are results calculated by Eq. (7).

Conclusion

A catalyst for hydrogenolysis was derived from the oxidation of Mg_2Cu alloy. Its activity and selectivity with methyl linoleate were tested in a continuous flow reactor in the gas phase at atmospheric pressure.

Steady-state activity was obtained with high selectivity to C_{18} alcohols and synthesis of mono-olefinic

Table 1. Values of kinetic parameters

	$k_i \times 10^{10}$ [mol/(kg·s·Pa)]	$K_i \times 10^3$ [1/Pa]
stearyl alcohol	15.6	3.5
oleyl alcohol	8.6	1.2

alcohol was achieved. The catalytic activity was affected by the number of double bonds. A Langmuir-competitive-type mechanism can be applied for the hydrogenolysis of methyl linoleate.

Nomenclature

F	= total feed gas flow rate at 273 K and $1.0 \times 10^5\text{ Pa}$	[m ³ /s]
K_i	= adsorption equilibrium constant of component, i	[1/Pa]
k_i	= reaction rate constant of component, i	[mol/(kg·s·Pa)]
P	= partial pressure	[Pa]
r_i	= reaction rate of component, i	[mol/(kg·s)]
S_i	= selectivity of component, i , moles of a specified product in moles of C_{18} products	[%]
T	= reaction temperature	[K]
t	= time on stream	[min]
W	= catalyst weight	[kg]
X	= conversion, moles of total C_{18} products in moles of C_{18} effluents	[%]

<Subscripts>

al	= C_{18} alcohol
H	= hydrogen (H_2)
LA	= linoleyl alcohol ($\text{C}_{18}\text{H}_{33}\text{OH}$)
ML	= methyl linoleate ($\text{C}_{17}\text{H}_{31}\text{COOCH}_3$)
MO	= methyl oleate ($\text{C}_{17}\text{H}_{33}\text{COOCH}_3$)
MS	= methyl stearate ($\text{C}_{17}\text{H}_{35}\text{COOCH}_3$)
OA	= oleyl alcohol ($\text{C}_{18}\text{H}_{35}\text{OH}$)
pr	= paraffins
SA	= stearyl alcohol ($\text{C}_{18}\text{H}_{37}\text{OH}$)

Literature Cited

- 1) Chikamatsu, N., T. Tagawa and S. Goto, *J. Chem. Eng. Japan*, **24**, 604 (1991).
- 2) Tagawa, T., N. Chikamatsu, S. Goto and H. Imai, *Appl. Catal.*, **61**, 209 (1990).