Reaction Pathway and Selective Hydrogenation on Catalyst Derived from Oxidation Treatment of Mg_2Cu Alloy

Nobuyasu CHIKAMATSU, Tomohiko TAGAWA, and Shigeo GOTO*
Department of Chemical Engineering, Nagoya University, Chikusa, Nagoya 464-01
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A catalyst derived from oxidation treatment of Mg_2Cu alloy was studied in a gas-phase continuous-flow reactor under atmospheric pressure to investigate the specific selectivity for hydrogenation. In order to propose the reaction pathways for hydrogenation of long chain unsaturated ester, reactivities of characteristic functional groups were tested.

The reactions of ester and aldehyde groups showed higher selectivity to alcohols than to paraffins. We concluded from competitive reactions of two reactants that hydrogenation of unsaturated bond group was inhibited by the adsorption of ester or aldehyde group.

The effect of partial pressure on each reaction rate was summarized into the Langmuir equation. The main route to unsaturated alcohol and reasons for the increased selectivity to alcohol are discussed.

Selective hydrogenation is important for organic compounds which contain more than two specific functional groups, such as unsaturated bond groups and ester groups. Among the copper catalysts, Adkins-type copper-chromite catalyst is widely used for hydrogenolysis of fatty acid esters to alcohols.[1] However, it requires high reaction temperature and high hydrogen pressure such as 560 K and 20 MPa.[2] Although unsaturated long chain alcohols are especially important as the industrial intermediates, alcohols produced from unsaturated esters were completely saturated under these conditions.

The selective synthesis of unsaturated alcohols has been examined by using several catalysts such as zinc aluminium catalyst at 523—623 K and 10 MPa hydrogen pressure,[3,4] iron oxide–zinc catalyst at 523—623 K and 15—30 MPa[5] and ruthenium–tin catalyst.[6,7] Ruthenium–tin catalyst was reported to convert methyl oleate to oleyl alcohol with a high efficiency at 543 K and 4.4 MPa in the liquid-phase with a batch reactor.

In our previous papers, copper–magnesium oxide catalyst derived from Mg_2Cu alloy was studied for hydrogenolysis of methyl oleate[8,9] and methyl linoleate[10] to produce alcohols in a gas-phase continuous-flow reactor. This oxide catalyst showed hydrogenolysis activity under mild reaction conditions such as atmospheric pressure of hydrogen at 513 K. Considerable amounts of unsaturated alcohol were obtained from these unsaturated esters. The catalyst had higher selectivity to alcohols than the conventional Adkins-type catalyst at the similar conversion.[9]

For the design of selective hydrogenation catalyst, reaction mechanisms and pathways should be investigated. The relationship between characterization and activity test will be discussed elsewhere.

In this study, reactivities of ester, aldehyde and unsaturated bond groups were compared in detail. Long chain compounds were tested according to our previous study. The reaction pathways for hydrogenation of ester are proposed. The cause of high selectivity to unsaturated product is discussed, based on a viewpoint of kinetic studies.

Reaction Pathways

The possible pathways for hydrogenation of unsaturated ester are shown in Fig. 1. Starting with unsaturated ester, six compounds may be produced. As for reaction pathways, hydrogenolysis of ester to produce alcohol (paths 1 and 7) and aldehyde (paths 2 and 8), hydrogenation of aldehyde to alcohol (paths 5 and 9) can be considered for both saturated and unsaturated compounds. As a side reaction, the production of paraffins (path 10) is considered. Saturation of an intermediate is also possible (paths 3, 4, and 6). The reverse reactions are negligible under the reaction conditions of this study.

Experimental

Reactants. The following organic compounds with characteristic functional groups were used as reactants. Long chain compounds were selected as reactants in accordance with our previous studies.[8—10] Each elementary step of Fig. 1 was examined by these reactants. Each reactant was purchased and used without further purification: methyl oleate ($C_{17}H_{33}COOCH_3$), oleyl alcohol ($C_{18}H_{35}OH$), methyl laurate ($C_{11}H_{23}COOCH_3$), lauryl al-

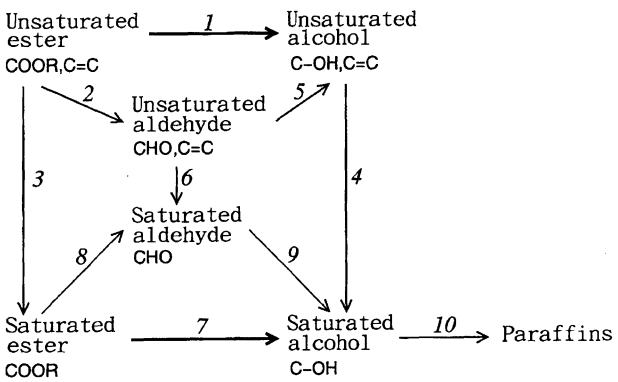

Fig. 1. Reaction pathways for hydrogenation of unsaturated ester.

dehyde ($C_{11}H_{23}CHO$), 1-tetradecene ($C_{14}H_{28}$).

Procedure. A binary hydrogen storage alloy HY-302 (Mg_2Cu alloy) was obtained from Ergenics, a division of MPD Technology Corporation.[8—11] The alloy was preoxidized overnight in a flow of air at 775 K and sieved into 35—42 mesh. The catalyst consisted of a mixture of copper oxide and magnesium oxide. Details of the catalyst preparation were reported elsewhere.[8]

Hydrogenation was performed in a gas-phase continuous-flow reactor under atmospheric pressure. The details of reaction apparatus were described in the previous paper.[9] The pretreatment of the catalyst was carried out for 2 h in a flow of hydrogen at 553 K.

The reactant was made to flow by a micro feeder and was vaporized at 553 K. The vapor was charged into the catalyst bed together with the flow of hydrogen. The reaction temperature (T) was 513 K. The weight of catalyst (W) was 1.0 g and the total feed gas flow rate (F) was 8.8×10^{-5} mol s^{-1} as the standard condition. The effluent was cooled to the room temperature and the liquid portion was trapped for analysis. All products were analyzed by a FID Gas Chromatograph.

Results and Discussion

Reactants and Pathways. The possible reaction pathways shown in Fig. 1 were tested as follows. The path-numbers were imposed from the reaction pathways in Fig. 1.

1) Unsaturated Ester; Methyl Oleate. This compound is the primary reactant of this study.[9] All paths in Fig. 1 may be followed.

2) Unsaturated Alcohol; Oleyl Alcohol. This compound is the primary product of the study.[9]
(a) Production of saturated alcohol (stearyl alcohol) by hydrogenation of C=C group without hydrogenolysis of OH group, path 4.

$$C_{18}H_{35}OH + H_2 \longrightarrow C_{18}H_{37}OH. \quad (1)$$

(b) Formation of paraffins by complete hydrogenation, paths 4 and 10.

$$C_{18}H_{35}OH + nH_2 \longrightarrow \text{paraffins}. \quad (2)$$

3) Saturated Ester; Methyl Laurate. This compound is a model of a long chain ester without C=C group.
(a) Production of alcohol (lauryl alcohol) by hydrogenation of COOR group, path 7.

$$C_{11}H_{23}COOCH_3 + 2H_2 \longrightarrow C_{12}H_{25}OH + CH_3OH. \quad (3)$$

(b) Formation of saturated aldehyde (lauryl aldehyde) by hydrogenation of COOR group, path 8.

$$C_{11}H_{23}COOCH_3 + H_2 \longrightarrow C_{11}H_{23}CHO + CH_3OH. \quad (4)$$

(c) Formation of paraffins by complete hydrogenation, path 7—10.

$$C_{11}H_{23}COOH_3 + nH_2 \longrightarrow \text{paraffins}. \quad (5)$$

4) Saturated Aldehyde; Lauryl Aldehyde. This compound is used for the comparison with COOR group.
(a) Production of alcohol (lauryl alcohol) by hydrogenation of CHO group, path 9.

$$C_{11}H_{23}CHO + H_2 \longrightarrow C_{12}H_{25}OH. \quad (6)$$

(b) Formation of paraffins by complete hydrogenation, path 9 and 10.

$$C_{11}H_{23}CHO + nH_2 \longrightarrow \text{paraffins}. \quad (7)$$

5) Olefin; 1-Tetradecene. This compound is a model of a hydrocarbon with a C=C group.
Formation of paraffin (tetradecane) by hydrogenation of C=C group, as a model of paths 3, 4, and 6.

$$C_{14}H_{28} + H_2 \longrightarrow C_{14}H_{30}. \quad (8)$$

Reactivities of Functional Groups for Hydrogenation. The reactivities of functional groups for hydrogenation were tested under atmospheric pressure of hydrogen at 513 K. Figures 2 and 3 show the results of the single reactant runs. Changes in the conversions of reactants with time on stream under the similar reaction conditions are compared. Tested reactants in Fig. 2 were methyl laurate, lauryl aldehyde, and 1-tetradecene. The initial conversion of methyl laurate was 28% and decreased with time but stabilized to 14% at 500 min. The product was mainly lauryl alcohol. On the other hand, lauryl aldehyde exhibited high and stable conversion of 87%. The product was mainly lauryl alcohol. 1-Tetradecene also indicated very high and stable conversion of 98% to tetradecane.

Tested reactants in Fig. 3 were methyl oleate and oleyl alcohol. The initial conversion of methyl oleate was 35%; this decreased with time but stabilized at 10% after 500 min. The main products were both oleyl alcohol and stearyl alcohol. On the other hand, the

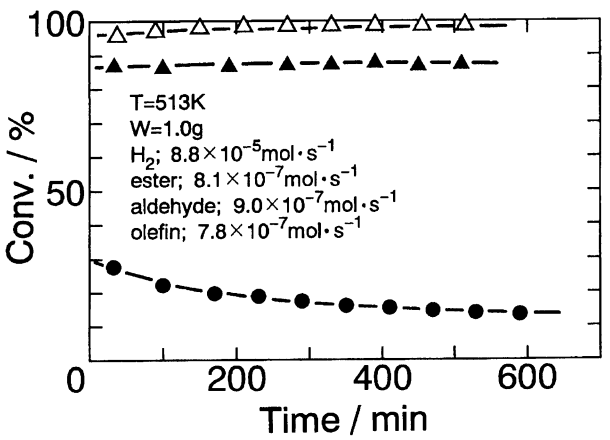

Fig. 2. Changes in conversions of ester, aldehyde, and olefin: (●) ester (methyl laurate); (▲) aldehyde (lauryl aldehyde); (△) olefin (1-tetradecene).

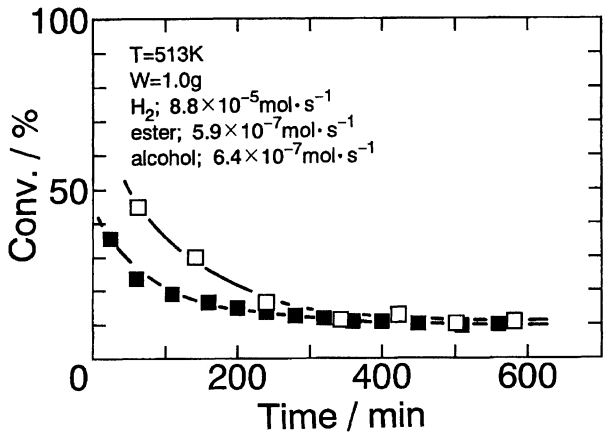

Fig. 3. Changes in conversions of unsaturated ester and unsaturated alcohol: (■) ester (methyl oleate); (□) alcohol (oleyl alcohol).

initial conversion of oleyl alcohol was 31%; it also decreased with time but stabilized at 10% after 350 min. The product was mainly stearyl alcohol. Little hydrogenation of alcohol to paraffins occurred.

Catalytic Activity for Competitive Reactions. In this section, two reactants were mixed prior to the reaction. The time factor, W/F was adjusted to that in Fig. 2.

(i) Competitive Reactions between Ester and Olefin: In order to discuss the selectivity to unsaturated alcohol in hydrogenolysis of unsaturated ester, competitive reactions were attempted between hydrogenation of ester group and unsaturated bond group. A mixture of methyl laurate and 1-tetradecene was examined for the reaction. Figure 4 shows the changes in the conversions of reactants with time on stream. The conversion of methyl laurate was similar to that of the reaction of a single reactant shown in Fig. 2, but that of 1-tetradecene was much lower than the case of the single reactant.

The feed of methyl laurate was stopped at 300 min to check the change in the conversion of 1-tetradecene. When the feed was changed from the mixture to the single reactant (1-tetradecene), the conversion increased gradually and reached over 90% after 10 h, which was almost the same as that of 1-tetradecene itself. It is seen from these results that hydrogenation of an unsaturated bond group is inhibited by the adsorption of an ester group.

(ii) Competitive Reactions between Aldehyde and Olefin: Other competitive reactions were conducted between hydrogenation of aldehyde group and that of unsaturated bond group. A mixture of lauryl aldehyde and 1-tetradecene was used as the reactant. Figure 5 shows the changes in the conversions of reactants with time on stream. The conversion of lauryl aldehyde was similar to that of the reaction of the single reactant shown in Fig. 2, but that of 1-tetradecene was much lower than the case of the single reactant.

The feed of lauryl aldehyde was also stopped at 300 min. When feed was changed from the mixture to the single reactant (1-tetradecene), the conversion increased gradually and reached over 90% at 20 h. These results also suggest that hydrogenation of unsaturated bond group is inhibited by the adsorption of aldehyde group.

Effect of W/F. Hydrogenation of methyl laurate with various time factors, W/F, was examined. These results are shown in Fig. 6. The value of W/F was changed from 6.3 to 45.6 kg s mol^{-1}. The yields (Y_i) of alcohol, aldehyde, and paraffins increased with W/F owing to Eqs. 3, 4, and 5, respectively. The selectivities to alcohol and aldehyde are independent of the change of the conversions. Accordingly the reactions of Eqs. 3 and 4 take place in parallel manners. The reaction indicates higher selectivity to alcohol than to paraffins in all cases.

Effect of Partial Pressure of Reactant. Hydrogenations of ester, aldehyde, and unsaturated bond

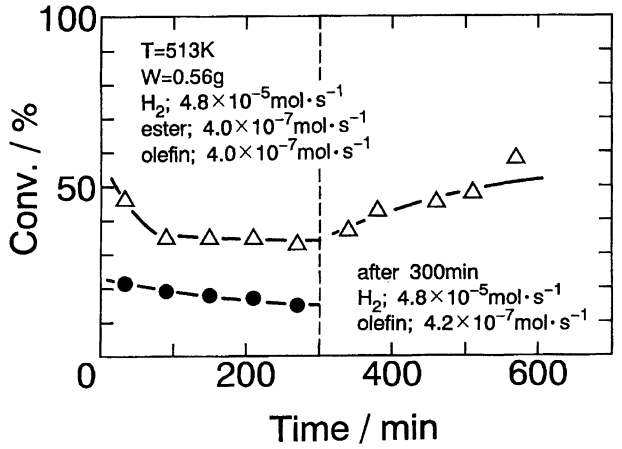

Fig. 4. Changes in conversions of competitive reactions between ester and olefin: (●) ester (methyl laurate); (△) olefin (1-tetradecene).

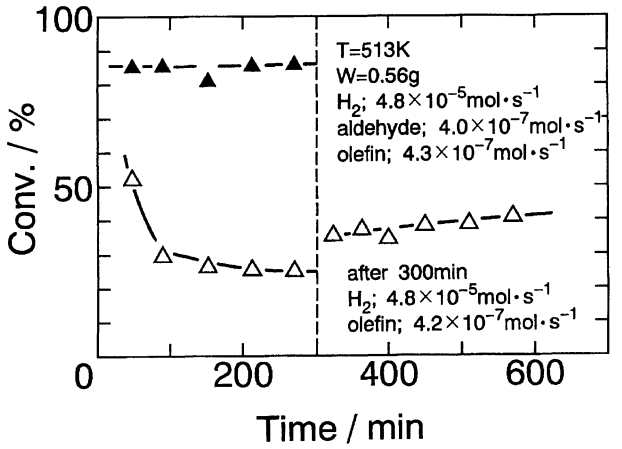

Fig. 5. Changes in conversions of competitive reactions between aldehyde and olefin: (▲) aldehyde (lauryl aldehyde); (△) olefin (1-tetradecene).

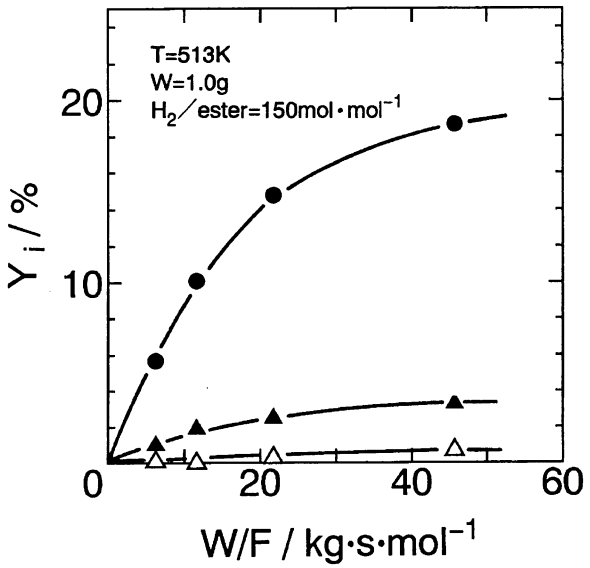

Fig. 6. Dependence of W/F for hydrogenation of ester (methyl laurate): (●) lauryl alcohol; (▲) lauryl aldehyde; (△) paraffins.

group were examined from the viewpoint of reaction rates. Each initial rate was determined in a differential reactor condition. Figure 7 shows the effect of partial pressure of hydrogen (P_{H2}) at 513 K on the initial reaction rate (r_i) or each main product from methyl laurate (Eq. 3), lauryl aldehyde (Eq. 6), and 1-tetradecene (Eq. 8), respectively. Hydrogen pressure was changed from 20 to 100 kPa with helium used as the balance. As shown in Fig. 7, each reaction rate was expressed by the first-order with respect to hydrogen pressure. The initial rate of the by-product was too low to determine.

Figure 8 shows the effect of partial pressure of the reactant at 513 K on the initial reaction rate of each main product from methyl laurate, lauryl aldehyde, and 1-tetradecene, respectively. The partial pressure of reactant (P_A) was changed from 0.3 to 6.5 kPa. The effect of partial pressure on each reaction rate can be summarized into the following Langmuir equations. The initial rate r of product i may be written as follows for each reactant, A:

$$r_i = k_i \frac{K_i \cdot P_A}{1 + K_i \cdot P_A} P_{H2}. \quad (9)$$

The values of kinetic parameters, reaction rate constant (k_i) and adsorption equilibrium constant (K_i) are summarized in Table 1. Table 1 shows that the adsorption equilibrium constant of 1-tetradecene is lower than those of the others, while the rate constant of methyl laurate is lower than those of the others. The results can explain the behaviors of competitive reactions in the previous section. The solid lines in Figs. 7 and 8 represent the calculation of Eq. 8.

Reaction Pathways for Selective Hydrogenation. In general, hydrogenation of pi-bonds (C=C, C=O) is easier than the reductive cleavage of C–O bond. This tendency can be observed in the differences in reaction rate constants in Table 1 and explains the difficulty of hydrogenation from alcohol to paraffin, as shown in Fig. 3.

From the viewpoint of catalyst components, our

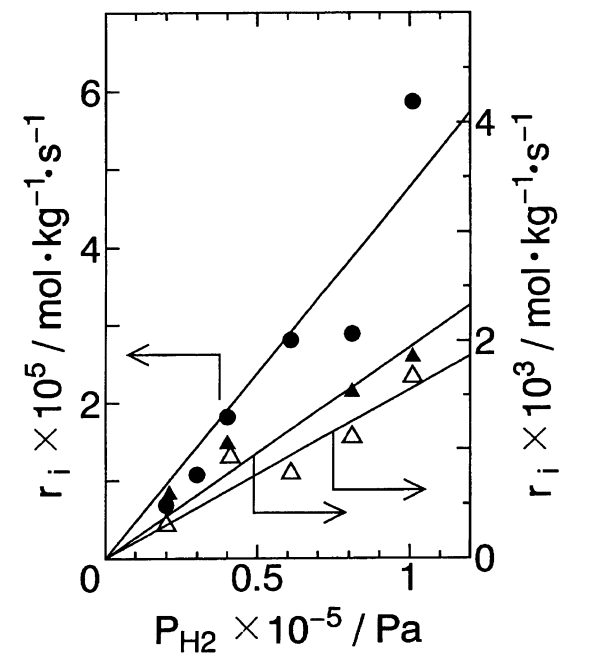

Fig. 7. Effect of partial pressure with respect to hydrogen for hydrogenation: T=513 K; (●) ester (methyl laurate); (▲) aldehyde (lauryl aldehyde); (△) olefin (1-tetradecene).

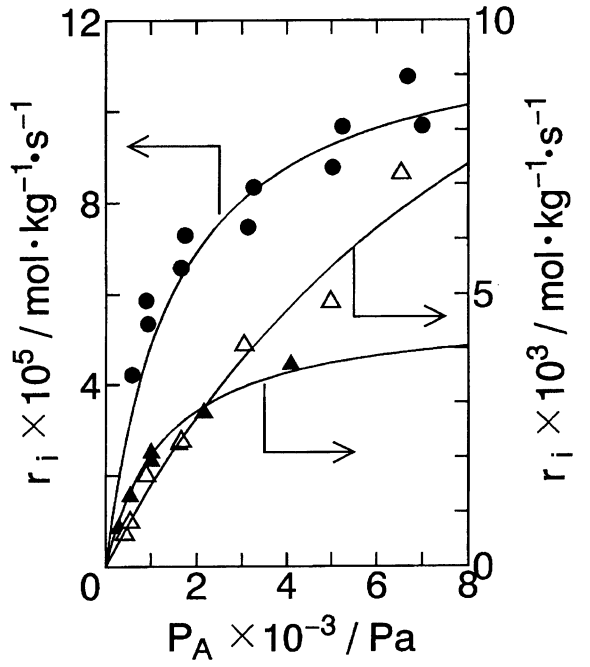

Fig. 8. Effect of partial pressure with respect to reactant for hydrogenation: T=513 K; (●) ester (methyl laurate); (▲) aldehyde (lauryl aldehyde); (△) olefin (1-tetradecene).

Table 1. Values of Kinetic Parameters $T=513$ K

Reactant	Product	k_i	K_i
		mol kg^{-1} s^{-1} Pa^{-1}	Pa^{-1}
Methyl laurate	Lauryl alcohol	1.2×10^{-9}	6.8×10^{-4}
Lauryl aldehyde	Lauryl alcohol	4.7×10^{-7}	7.7×10^{-4}
1-Tetradecene	Tetradecane	1.7×10^{-7}	9.6×10^{-5}

screening test revealed that a copper component was needed for an adequate hydrogenation activity.[11] Results also suggested that the second component of the copper-based-catalyst played an important role. Magnesia, one of the strong base material, could increase the basicity of the catalyst. This may make the catalyst to interact more easily with acidic functional groups than the neutral groups, that is,

$$C{=}O > C{-}OH > C{=}C.$$

This agrees with the differences in adsorption equilibrium constants in Table 1, the inhibition of adsorption by oxygen containing groups observed in competitive reactions, and the difficulty of hydrogenation of C=C group when OH group exists in the same molecule, as shown in Fig. 3.

In order to discuss the high selectivity to unsaturated alcohol from unsaturated ester, the reaction pathways are examined with the mechanism postulated in Fig. 1. The effect of W/F shown in Fig. 6 suggested that the main route was the direct pathway from saturated ester to saturated alcohol. Therefore, path 7 was proposed along with the aldehyde route, paths 8 and 9. The difficulty of breakage of C–O bonds would make paths 7, 8, and 10 slow. These can be applied in the case of unsaturated esters. Therefore, paths 1, 2, and 10 would be slow and path 1 might be the main route from unsaturated ester to unsaturated alcohol.

The results of competitive reactions in Figs. 3 and 4 suggest that hydrogenation of C=C bonds (paths 3, 4, and 6) can be suppressed when oxygen-containing groups such as ester, aldehyde, and alcohol exist together. Therefore, they are the reasons of the increased selectivity for hydrogenation of unsaturated ester to unsaturated alcohol via the main route, path 1.

Conclusion

The catalyst derived from oxidation treatment of Mg_2Cu alloy was examined for selective hydrogenation of characteristic functional groups. The steady-state activity was obtained for each reactant in the gas-phase under atmospheric pressure. The reaction pathways for hydrogenation of unsaturated ester were considered. The main route to alcohol from ester was the direct pathway, paths 1 and 7.

Hydrogenation of unsaturated bond group was inhibited by the adsorption of ester or aldehyde group. Magnesia would make the catalyst activate the acidic functional groups. Therefore, magnesia could be the origin for the high selectivity to unsaturated alcohol from unsaturated ester.

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