Influence of Catalyst Structure on Direct Ethoxylation of Fatty Methyl Esters over Al–Mg Composite Oxide Catalyst

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ABSTRACT: During direct ethoxylation of fatty methyl ester over Al–Mg composite oxide catalyst, the activity was nearly proportional to the total number of active Al acidic sites on the catalyst surface per unit weight of catalyst. Lower active Al acidic site densities resulted in a narrower ethylene oxide (EO) adduct distribution of obtained ethoxylate. We developed a new catalyst with a large surface area on which many acidic sites are distributed uniformly by partially poisoning the Al acid sites of high-Al content Al–Mg composite oxide with alkali. This catalyst was used for direct ethoxylation of fatty methyl esters to obtain ethoxylated fatty methyl esters with narrow EO adduct distribution efficiently.

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KEY WORDS: Adduct distribution, Al–Mg composite oxide catalyst, direct ethoxylation, ethoxylated fatty methyl ester, ethoxylation, ethylene oxide, fatty methyl ester, solid catalyst.

Ethoxylated fatty methyl ester (EFME) is readily synthesized from the corresponded fatty methyl ester by direct ethoxylation over a novel Al–Mg composite oxide catalyst (1). EFME have excellent surface-active properties and are useful as nonionic surfactants (1–4). On the surface of an Al–Mg composite oxide catalyst, the bifunctional effect of acid-base active sites results in dissociative chemisorption of fatty methyl ester that leads to direct insertion of ethylene oxide (EO), which involves coordination anionic polymerization as shown in Scheme 1 (5). In the presence of EO, the following reaction can then take place:

$$RCOOCH_3 + n\mathrm{EO} \rightarrow RCO(\mathrm{EO})_nOCH_3 = \mathrm{EFME} \qquad [1]$$

In this paper, the effect of calcination temperature during preparation of the Al–Mg composite oxide and the Al content in the catalyst on the activity and EO adduct distribution is determined, and the catalyst with high activity and narrow EO adduct distribution is examined further.

EXPERIMENTAL PROCEDURES

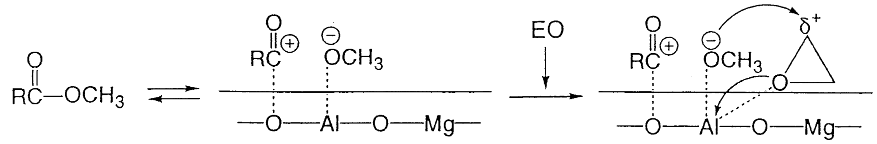
Preparation of catalyst. Magnesium oxide (Kyowa Chemical Industry, Tokyo, Japan) was dispersed in pure water, a prescribed amount of an aqueous aluminum nitrate solution (Junsei Chemical, Tokyo, Japan) was added to deposit Al ions on the surface of the magnesium oxide. After filtration, rinsing and drying, the powder was calcined to obtain Al–Mg composite oxide catalyst (6). The preparation conditions of various catalysts are shown in Table 1.

Method for synthesis. Methyl laurate (Paster M12; Lion Corp., Tokyo, Japan) and a catalyst were placed in an autoclave, and air in the autoclave was substituted with nitrogen

TABLE 1
Catalyst Preparation Conditions at a Calcination Time of 1 h in N_2 Atmosphere

Catalyst number	Al content[a] (%)	Calcination temperature[b] (°C)
C-1	0.8	600
C-2	1.0	600
C-3	1.2	400
C-4	1.2	500
C-5	1.2	600
C-6	1.2	700
C-7	1.2	800
C-8	1.2	950
C-9	1.5	600
C-10	3.0	600

[a]Average Al concentration in entire calcined material.
[b]Programmed temperature rising rate 30°C/min.



SCHEME 1

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with stirring. Then, the mixture was heated, and a prescribed amount of EO (Mitsubishi Chemical, Tokyo, Japan) was introduced into the autoclave while keeping the temperature at 180°C and the pressure at 3 atm. After aging and cooling, the reaction mixture was filtered to remove catalyst to yield EFME.

Method of analysis. EO adduct distributions were measured by liquid chromatography (LC-6A; Shimadzu, Kyoto, Japan) under the following conditions: column, Zorbax C8, 4.6 mm × 250 mm (DuPont, Boston, MA); moving phase, acetonitrile/water = 60:40; ultraviolet detector (SPD-10A; Shimadzu), 220 nm.

The surface area of the catalysts was measured by the B.E.T. (Brunauer, Emmett, and Teller) method (7) (SA-1000; Sibata Scientific Technology, Tokyo, Japan).

Acidity and alkalinity of the catalysts were measured by a temperature-programmed desorption method (ATD700; Ohku-ra Riken, Tokyo, Japan) under the following conditions:

Acidity: Pretreatment temperature, 500°C; adsorption conditions, NH_3, 100°C, 10 min, 10 torr; programmed temperature increase, 10°C/min.

Alkalinity: Pretreatment temperature, 500°C; adsorption conditions, CO_2, 100°C, 10 min, 10 torr; programmed temperature increase, 10°C/min.

The Al concentration near the surface of the catalyst (about 30 Å) was measured by X-ray photoelectron spectroscopy.

RESULTS AND DISCUSSION

With catalysts prepared at different calcination temperatures, 6 moles of EO were added on average to methyl laurate. The activities in these reactions and the EO adduct distributions (peak top percentage: weight percentage of EO adduct having the major weight percentage) of the obtained EFME are shown in Table 2.

As shown in Figure 1, the activity increases with an increase of catalyst calcination temperature and reaches a maximum around 700°C. This increase likely can be attributed to dehydration of the catalyst precursor with increasing calcination temperature to give strong alkalinity around 600 to 700°C. Further increase of calcination temperature results in reduced activity. The reduced activity is attributed to sintering of the catalyst surface due to high calcination temperature. EO adduct distribution of the obtained individual EFME is shown in Figure 2, which shows broad EO adduct distributions for higher calcination temperatures.

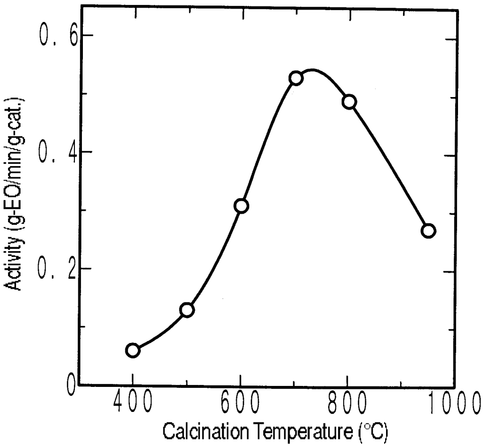

FIG. 1. Activity of catalysts (cat.) prepared at different calcination temperatures; EO, ethylene oxide.

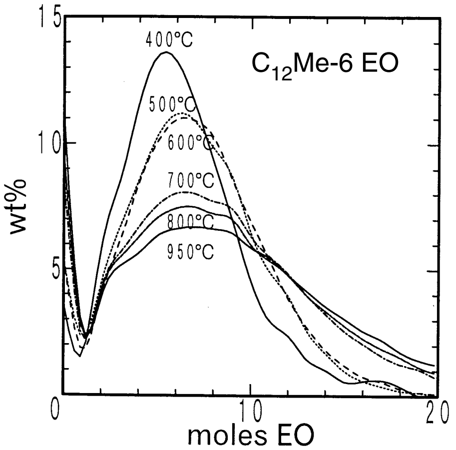

FIG. 2. EO adduct distribution of ethoxylated fatty methyl esters synthesized with various catalysts that were prepared at different calcination temperatures (1.2% Al–MgO). See Figure 1 for abbreviation.

TABLE 2
Effect of Catalyst Calcination Temperature (1.2% Al–MgO)

Catalyst number	Calcination temperature[a] (°C)	Activity[b] (g-EO·min^{-1}·g-cat.$^{-1}$)	EO adduct distribution peak top %[c] (wt%)
C-3	400	0.06	13.4
C-4	500	0.13	11.1
C-5	600	0.31	11.0
C-6	700	0.53	8.0
C-7	800	0.49	7.5
C-8	950	0.27	6.7

[a] Same as Table 1.
[b] Ethylene oxide (EO) weight consumed per unit weight of catalyst in 1 min.
[c] Weight percentage of EO adduct having the major weight percentage (C_{12}Me-ester + 6 EO).

TABLE 3
Effect of Al Content of Catalysts (calcination temp. 600°C)

Catalyst number	Al content[a] (wt%)	Activity[b] (g-EO·min^{-1}·g-cat.$^{-1}$)	EO adduct distribution peak top %[c] (wt%)
C-1	0.8	0.17	12.1
C-2	1.0	0.25	11.1
C-5	1.2	0.31	11.0
C-9	1.5	0.39	9.4
C-10	3.0	0.60	8.3

[a]Same as Table 1. [b]Same as Table 2. [c]Same as Table 2.

Next, catalysts with different Al content were calcined at 600°C, 6 moles of EO on average were added to methyl laurate in the same manner as described above. Reactivity and peak top percentage of obtained EFME are listed in Table 3.

The activity increases with increasing Al content (Fig. 3). A smaller Al content gives a narrower EO adduct distribution (Fig. 4).

Factors that influence activity and adduct distribution. Factors that influence activity and EO adduct distribution have been determined on the basis of the experimental results shown in Tables 2 and 3.

Regarding activity, it is essential that acidic and basic active sites are formed consistently on the surface of the catalyst, because direct ethoxylation of fatty methyl ester occurs catalytically on Al–Mg composite oxide catalyst with the aid of bifunctional acidic and basic active sites on the surface of the catalyst. The peak activity at a calcination temperature of around 700°C (Fig. 1) is also attributed to the same reason. We can also predict that the condition of the Al acidic active sites with strong affinity to EO serves as adsorption sites of EO and influences its activity (EO consumption rate), based on Scheme 1. To understand the condition of Al acidic active sites near the surface of the catalyst, surface areas and surface Al concentrations were measured. The results are given in Table 4. In the table, the TA value (total amount of Al acidic sites on the surface per unit weight of catalyst) is the product of surface area and surface Al concentration, and is an index of the total amount of Al acidic sites on the surface per unit

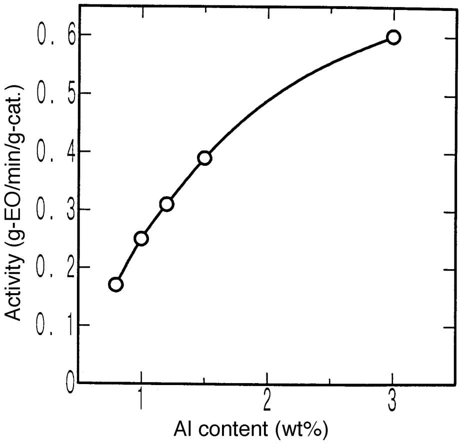

FIG. 3. Activity of catalyst (cat.) with different Al contents (calcination temp. 600°C). See Figure 1 for abbreviation.

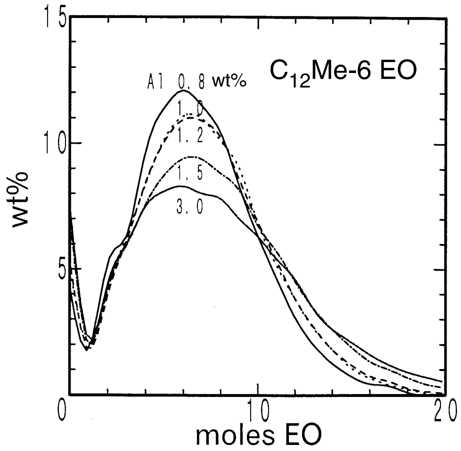

FIG. 4. EO adduct distribution of ethoxylated fatty methyl esters synthesized with catalysts with different Al contents. See Figure 1 for abbreviation.

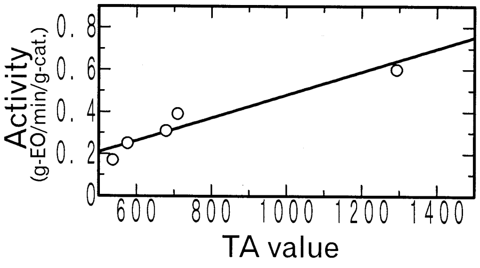

FIG. 5. Relationship between total amount of Al acidic sites on the surface per unit weight of catalyst (TA value) and activity. See Figure 1 for other abbreviations.

TABLE 4
Surface Area and Surface Al Concentration of Catalysts with Different Al Contents

Catalyst number	Surface area: *S* (m^2/g)	Surface Al concentration: *C* (wt%)	TA value (*S*·*C*)	Activity[a] (g-EO·min^{-1}·g-cat.$^{-1}$)	EO adduct distribution peak top %[b] (wt%)
C-1	78	6.9	538	0.17	12.1
C-2	78	7.4	577	0.25	11.1
C-5	79	8.6	679	0.31	11.0
C-9	78	9.1	710	0.39	9.4
C-10	101	12.8	1293	0.60	8.3

[a]Same as Table 2; TA, total amount of Al acidic sites on the surface per unit weight of catalyst. [b]Same as Table 2.

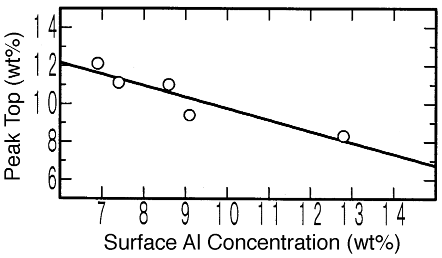

FIG. 6. Relationship between surface Al concentration and peak top value.

weight of catalyst. Based on Tables 3 and 4, the relationship between TA value and activity is shown in Figure 5. It is obvious that the activity is proportional to the total amount of Al acidic sites on the surface of the catalyst for the same calcination temperature and the same structure of catalyst and active sites. As to EO adduct distribution, a smaller Al content gives a narrower distribution, as shown in Figure 4.

The relationship between surface Al concentration and peak top percentage value is shown in Figure 6. A higher surface Al concentration gives a lower peak top value. A lower Al acidic site density on the surface, which means better dispersion of Al acidic sites, gives a narrower EO adduct distribution of EFME.

It is obvious from Figure 2 that a lower calcination temperature also gives a narrower EO adduct distribution of EFME. Surface areas and surface Al concentrations of the catalysts used in this experiment were measured and are shown in Table 5.

For catalysts that were calcined at different temperatures, the relationship between surface Al concentration and EO adduct distribution cannot be quantified because the structure and properties of the active sites of the catalysts vary depending on calcination temperature. However, considering that Al acidic sites on the surface of the catalysts (C-3, and C-4) calcined at low temperature are still covered with hydroxyl groups, the true Al surface concentration is lower than shown in Table 5. Similarly, a lower active Al acidic site density on the catalyst surface gives a narrower EO adduct distribution.

Examination of highly active/highly selective catalyst. To obtain a catalyst that has high activity and gives a narrow EO adduct distribution requires that many Al acidic sites are dispersed widely and homogeneously on the catalyst surface, resulting in a lower density of Al sites. However, it is impossible to deposit a large amount of Al ions by the method described above. To solve this problem, we selected a calcined hydrotalcite ($Mg_6Al_2O_9$, Al content of 15.6 wt%: referred to as CHT hereinafter) and a calcined aluminum–magnesium hydroxide ($Mg_{2.5}Al_2O_{5.5}$, Al content of 26.6 wt%: referred to as CMAG hereinafter) as catalyst precursors. They have high Al contents and large surface areas. By adopting a method of partial poisoning of Al acidic sites of the precursor with alkali, we were able to prepare a catalyst in which many Al acidic sites were apparently dispersed uniformly on the large catalyst surface.

Six moles of EO on average were added to methyl laurate with the CHT and CMAG catalysts, and CHT and CMAG treated with a small amount of KOH. The results are shown in Table 6. We found that activity is reduced by KOH treat-

TABLE 5
Surface Area and Surface Al Concentration of Catalysts Prepared at Different Calcination Temperatures

Catalyst number	Calcination temperature[a] (°C)	Surface area: *S* (m^2/g)	Surface Al concentration: *C* (wt%)	EO adduct distribution peak top %[b] (wt%)
C-3	400	174	8.6	13.4
C-4	500	117	8.6	11.1
C-5	600	79	8.6	11.0
C-6	700	52	8.6	8.0
C-7	800	40	9.7	7.5
C-8	950	26	11.3	6.7

[a] Same as Table 1. [b] Same as Table 2.

TABLE 6
Modification of High-Al Content Al–Mg Composite Oxide Catalyst by KOH Treatment

				EO adduct distribution	
Catalyst	Al content[a] (wt%)	Calcination temperature[b] (°C)	Surface area: *S* (m^2/g)	Activity[c] (g-EO·min^{-1}·$cat.^{-1}$)	Peak top %[d] (wt%)
CHT	15.6	500	217	5.5	6.8
CMAG	26.6	500	351	11.3	6.0
CHT-KOH[e]	—	—	—	1.5	12.4
CMAG-KOH[f]	—	—	—	2.9	15.6

[a] Same as Table 1. [b] Same as Table 1. [c] Same as Table 2. [d] Same as Table 2. [e] Treatment of 1 g of calcined hydrotalcite (CHT) with 7×10^{-4} mol of KOH. [f] Treatment of 1 g of calcined aluminum–magnesium hydroxide (CMAG) with 7×10^{-4} mol of KOH.

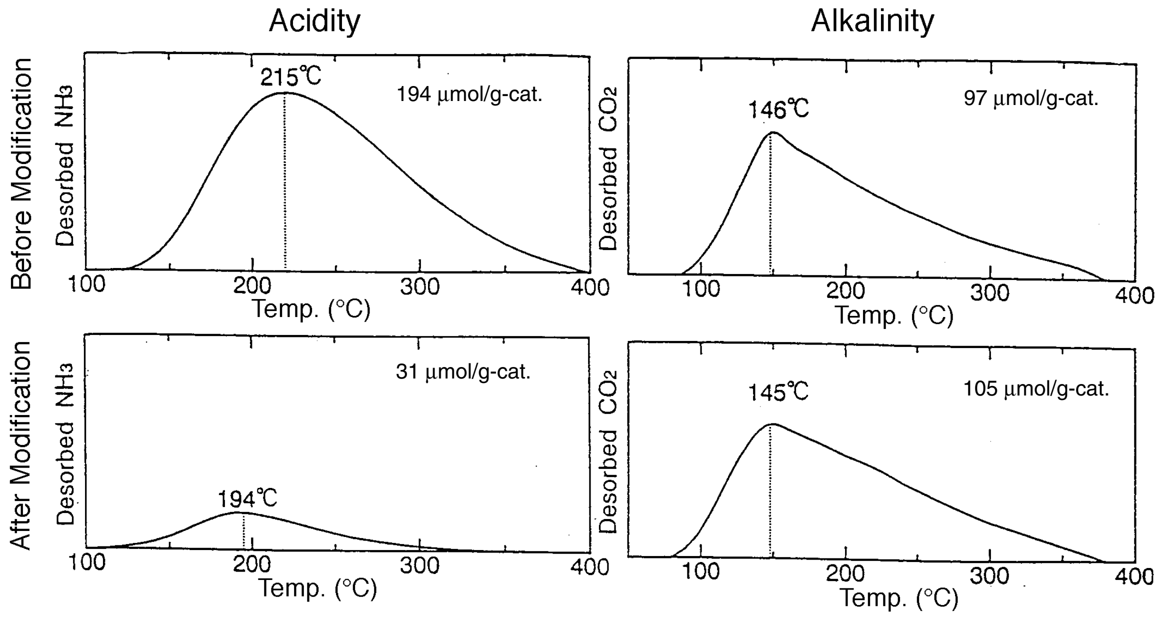

FIG. 7. Temperature-programmed desorption (TPD) spectrum of calcined aluminum–magnesium hydroxide catalyst before and after KOH modification.

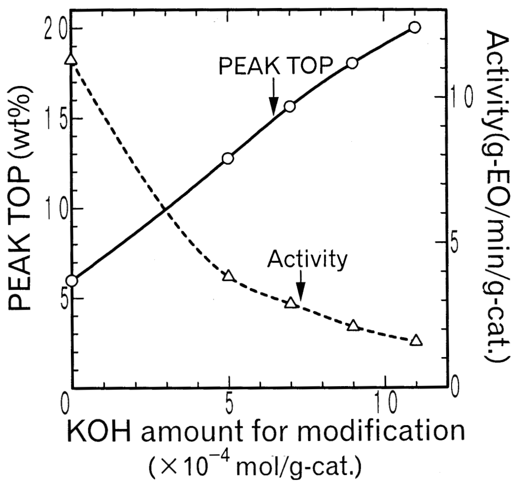

FIG. 8. Modification of calcined aluminum–magnesium hydroxide catalyst (cat.) by KOH treatment. See Figure 1 for abbreviation.

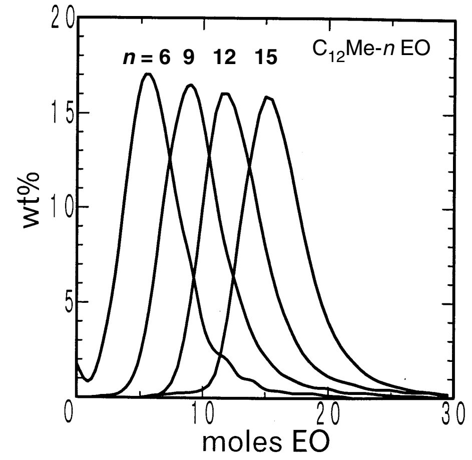

FIG. 9. EO adduct distribution of ethoxylated methyl laurate synthesized with modified calcined aluminum–magnesium hydroxide catalyst. See Figure 1 for abbreviation.

ment, but the modified catalysts maintain considerably high activity in comparison with catalysts listed in Table 3, which give narrow EO adduct distributions.

Figure 7 presents a temperature-programmed desorption spectrum that shows acidity and alkalinity of a CMAG catalyst before and after KOH modification. The alkalinity of the catalyst does not change significantly before and after modification. However, the acidity changes significantly. The amount of acidic sites and their acidic strength both decrease. This suggests that KOH used for modification is adsorbed preferentially on strong acidic sites of the catalyst to poison partially acidic sites.

As shown in Figure 8, the increased KOH-modified CMAG catalyst gives a lowered activity but a narrow EO adduct distribution. The EO adduct distribution of ethoxylated methyl laurate, synthesized with modified CMAG catalyst, is shown in Figure 9. All ethoxylates obtained had narrow oligomer distributions and a reduced amount of residual unreacted ester.

This research leads to three conclusions: (i) Activity is nearly proportional to the total number of active Al acidic sites on the catalyst surface; (ii) the EO distribution of the obtained ethoxylate becomes narrower with decreasing density of active Al acidic sites on the catalyst surface; (iii) the new catalyst, prepared by KOH modification of Al–Mg composite oxide with high Al content, gives EFME with narrow EO adduct distribution at high activity.

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