The Development of Nonchromium Catalyst for Fatty Alcohol Production

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ABSTRACT: Fatty alcohols are obtained by hydrogenation of fatty acid methyl esters derived from coconut oil and palm kernel oil. Cu-Cr has been widely used as a hydrogenation catalyst. We have developed a new environment-friendly catalyst that could substitute for the conventional Cu-Cr catalyst, preventing the release of toxic hexavalent Cr. Here we report the development of Cr-free, Cu-Fe-Al oxide catalyst. We found that iron has a strong promoting effect nearly equivalent to that of Cr and that the addition of Al significantly improved the reuse property (durability) through a study of trivalent metal addition to Cu. Powder X-ray diffraction analysis of the used catalyst revealed that the Al addition suppressed the transformation of the $CuFe_2O_4$ component (Cu-Fe spinel) to α-Fe. It was concluded that the stabilization of $CuFe_2O_4$ during reduction improved the catalyst durability. A plant-scale experiment confirmed that the Cu-Fe-Al oxide catalyst performs as well as the conventional Cu-Cr catalyst.

Paper no. J9579 in *JAOCS 77,* 1283–1287 (December 2000).

KEY WORDS: Cu-Cr, Cu-Fe-Al oxide catalyst, fatty acid methyl ester, fatty alcohol, non-Cr hydrogenation catalyst, slurry-bed process, spinel.

Fatty alcohols are mainly derived from vegetable oils such as palm kernel oil and coconut oil and serve as raw materials for various household products and surfactants. Fatty alcohols are produced by continuous hydrogenation of fatty acids or fatty acid methyl esters under high temperature (250–300°C) and high hydrogen pressure (25–35 MPa) in a liquid-phase slurry-bed process. The catalyst used in this process consists mainly of copper-chromite (Cu-Cr) oxide as a basic structure (1–3). Although many modifications have been made for practical use, basic composition has not changed from the original. Safety is a major concern in using Cu-Cr catalyst since hexavalent Cr is discharged in catalyst manufacturing.

Fatty alcohol producers and catalyst manufacturers have attempted to develop non-Cr catalysts for many years; however, non-Cr catalysts with equivalent performance to the Cu-Cr catalyst have not been developed to date. Catalysts must have high activity, selectivity, and durability (catalyst life). A catalyst used in a slurry-bed system should have filtration, sedimentation, and agglomeration properties for stable operation.

We have developed an environment-friendly Cu-based Cr-free catalyst, and the results are presented here.

EXPERIMENTAL PROCEDURES

Fatty acid methyl ester was used as raw material for the hydrogenation reaction. It was obtained by transesterification of coconut oil or palm kernel oil with methanol. Transesterification was carried out at 80°C for 3 h with 0.5 wt% of NaOH as a catalyst. Methyl ester was washed and dried before reaction to remove glycerin formed as a by-product.

Cu-metal oxide catalysts were prepared by a coprecipitation method. Aqueous solutions of Cu sulfate (Meltex Inc., Tokyo, Japan) and various metal sulfates were stirred at 90°C, and 22% Na_2CO_3 solutions were added to pH 9.0 and kept for 1 h at 95°C. After washing and filtering, catalyst cakes were dried at 110°C for 24 h and calcined at 450°C for 2 h in air. Metal composition of calcined catalyst was CuO/M_2O_3 = 70:30 in weight ratio.

$CuO-Fe_2O_3-Al_2O_3$ catalysts were prepared by coprecipitation with $CuSO_4$, $FeSO_4$, and $Al_2(SO_4)_3$. Preparation conditions were the same as described above. The catalyst composition was Cu/Fe/Al = 1:1.1:0–1.2 in molar ratio.

A Cu-Cr catalyst for comparison was supplied by Nikki Chemicals Co. Ltd. (Tokyo Japan) and used as it was (CuO/Cr_2O_3 = 1:1 by wt, mean particle size 8 μm).

Hydrogenation activities of catalysts were evaluated with 0.5-L autoclaves. Experimental runs were carried out at 250–275°C under H_2 pressure of 12–25 MPa with 5 wt% of catalyst vs. methyl ester. In the case of durability evaluation, catalysts were filtered out after reaction and used repeatedly.

Reaction products were identified by gas chromatography (GC). Crystallographic analysis of catalyst components was performed with powder X-ray diffraction analysis (XRD).

RESULTS AND DISCUSSION

Reaction kinetics. The hydrogenation of fatty acid methyl

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*To whom correspondence should be addressed at Kao Corporation, Materials Development Research Laboratories, Minato 1334, Wakayama, 640-8580 Japan. E-mail: 127698@kastanet.kao.co.jp ester consists of the following three elementary steps:

$$\mathrm{RCOOCH_3 + 2H_2 \rightarrow RCH_2OH + CH_3OH} \quad [1]$$

$$\mathrm{RCOOCH_3 + RCH_2OH \rightarrow RCOOCH_2R + CH_3OH} \quad [2]$$

$$\mathrm{RCOOCH_2R + 2H_2 \rightarrow 2RCH_2OH} \quad [3]$$

where R represents alkyl chains of any length.

Reaction analysis revealed that Reactions 1 and 2 are predominant at the early stage of the reaction, and they can be regarded as zero-order for saponification value (*SV*). The zero-order rate constant k_0 is defined as:

$$k_0 = \frac{(SV_0 - SV_t)}{t} \quad [4]$$

where t is reaction time (min), SV_0 is saponification value of raw material, and SV_t is saponification value at t minutes.

On the other hand, Reaction 3 is predominant at the final stage and is regarded as the first-order reaction. The first-order reaction rate constant k_1 is defined as:

$$k_1 = \frac{1}{t} \cdot \ln\left(\frac{SV_0 - SV_{\mathrm{eq}}}{SV_t - SV_{\mathrm{eq}}}\right) \quad [5]$$

where SV_{eq} is the equilibrium SV at a given temperature and pressure calculated according to Muttzal and van den Berg (4).

Side reactions. Hydrocarbons, aldehydes, and ethers were found as by-products in the reaction product. Figure 1 shows predicted reaction pathways for these chemical species. Even chain hydrocarbons and ethers were the predominant by-products. These species can be used as an indicator of selectivity.

Screening for ingredients promoting Cu oxide (co-catalyst). Metallic copper particles are considered as active species in copper-containing catalysts. If high dispersion is kept throughout the operation, high activity would be maintained. However, Cu readily deactivates due to sintering. The high durability of Cu-Cr catalyst suggests stabilization of Cu particles in the structure of Cu-Cr spinel ($\mathrm{CuCr_2O_4}$).

We focused on the promoting effect of trivalent metals as supplemental catalyst ingredients alternative to Cu, because Cu and trivalent metals form spinel structures. Figure 2 shows hydrogenation activity of each catalyst represented by k_0. Fe and Al exhibited promoter effects as high as chromium.

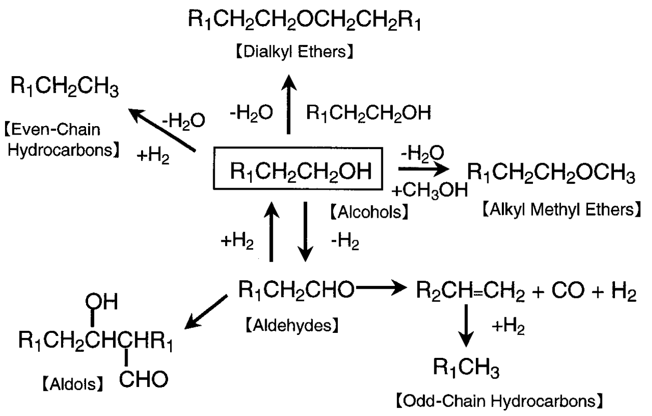

FIG. 1. Side reactions on the catalytic hydrogenation process from fatty acid methyl esters to fatty alcohols.

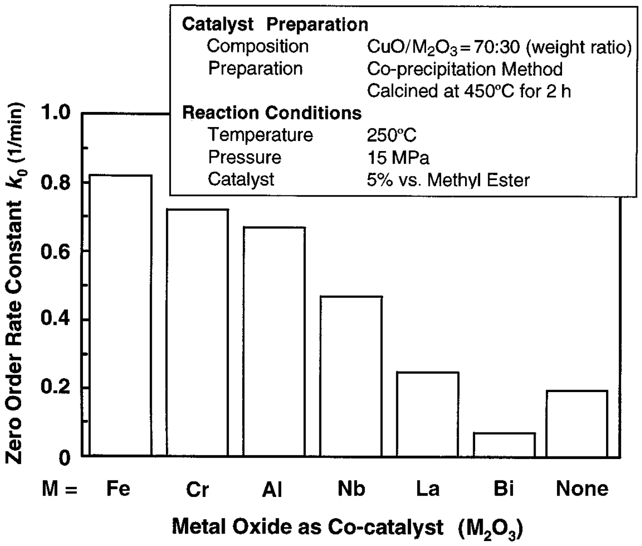

FIG. 2. Hydrogenation activity of binary oxide catalyst ($\mathrm{CuO\text{-}M_2O_3}$).

RESULTS AND DISCUSSION

Then we conducted catalyst reuse tests for Cu-Cr and Cu-Fe catalysts to compare durability. Results are shown in Figure 3. For both catalysts, k_0 increased at the second reaction run. It seems that Cu oxide is not fully activated at the beginning of the first run. After the second run, k_0 decreased as run cycles increased. Cu-Fe catalyst lost activity quicker than Cu-Cr. For comparison, we defined catalyst deactivation factor (D) as follows:

$$D = \frac{k_0(2) - k_0(n)}{k_0(2)} \times \frac{100}{n-2} (\%) \quad [6]$$

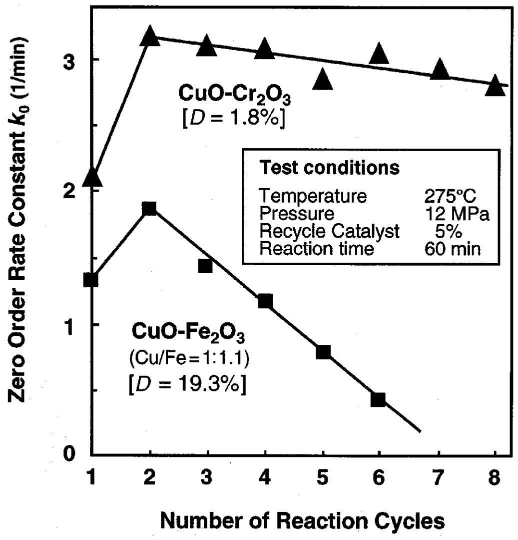

FIG. 3. Hydrogenation catalyst recycle test. *D*, catalyst deactivation factor.

where n is number of reaction cycles, $k_0(2)$ is k_0 at the second run, and $k_0(n)$ is k_0 at nth run. Catalyst deactivation factors for Cu-Cr and Cu-Fe catalyst were 1.8 and 19.3%, respectively.

Figure 4 shows the results of XRD analysis of the Cu-Fe catalyst before and after the reaction. Unreacted catalyst consisted of CuO and $CuFe_2O_4$ spinel, but CuO was reduced to Cu metal and α-Fe appeared after the reaction. Destruction of $CuFe_2O_4$ spinel would generate α-Fe, and this change would lead sintering of copper particles and catalyst deactivation.

Effect of Al_2O_3 addition. For maintaining the spinel structure ($CuFe_2O_4$), we investigated additives as a third component to the Cu-Fe catalyst. As shown in Figure 2, Al also exhibited a promoting effect to Cu, and this result suggests that Al also generates spinel structure and maintains the dispersion of Cu particles. Therefore, we carried out hydrogenation reaction for a series of Cu-Fe-Al catalysts and examined XRD analysis after each reaction. The results are shown in Figure 5. As the atomic ratio of Al to Cu increases from 0 to 1.2, the peak of α-Fe decreases and spinel structure is maintained. Cu particle size calculated from the peak width of the XRD pattern also indicates that aluminum addition prevents sintering of copper particles.

Figure 6 shows the durability improvement due to the addition of Al to the Cu-Fe catalyst. D was 19.3% for Cu-Fe catalyst without Al addition; however, D decreased as Al/Cu increased, and in the case of Al/Cu = 1.2, D of Cu-Fe-Al catalyst was comparable to conventional Cu-Cr catalyst (D = 1.8%). It was confirmed that Al addition to Cu-Fe catalyst maintained spinel structure and improved durability.

Performance of Cu-Fe-Al catalyst. We mention here other catalytic performances, i.e., final stage activity and selectivity. Results are listed in Table 1. At the final stage, first-order rate constant k_1 increased as Al content increased and the catalyst of Cu/Fe/Al = 1:1.1:1.2 had comparable activity to the Cu-Cr catalyst. Hydrocarbon production was as high as 20.5% without Al addition to Cu-Fe catalyst. However, it decreased with Al addition, and the catalyst of Cu/Fe/Al = 1:1.1:1.2 had comparable selectivity to the Cu-Cr catalyst. Considering XRD analysis, it is suggested that improvement of selectivity comes from suppression of α-Fe formation, which acts as a dehydration catalyst. It was confirmed that Al addition plays an important role not only for durability but also for final-stage activity and selectivity.

Physical properties of Cu-Fe-Al oxide catalyst. By optimizing the Cu/Fe/Al ratio, we found the Cu-Fe-Al catalyst, which was applicable to actual plant operation. The physical properties of the newly developed Cr-free Cu-Fe-Al oxide catalyst are a composition of Cu/Fe/Al = 1:0.75:1.7 (atomic ratio); a specific surface area of 30 m^2/g; an average particle size of 12.1 μm; total pore volume of 0.19 mL/g with a pore radius >3 nm; and a true density of 5.3 g/mL. Specific surface area of Cu-Fe-Al catalyst is 30 m^2/g and is comparable to the Cu-Cr catalyst available on the market. Mean particle diameter was approximately 12 μm and is appropriate for a slurry-

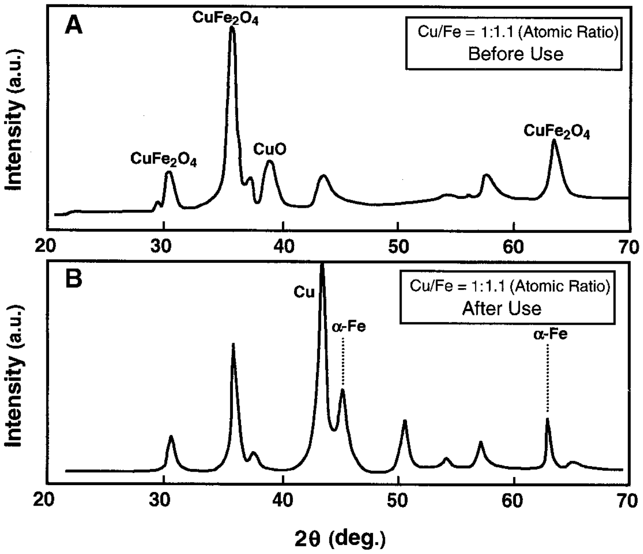

FIG. 4. Powder X-ray diffraction (XRD) pattern of $CuO-Fe_2O_3$ catalyst before (A) and after (B) use.

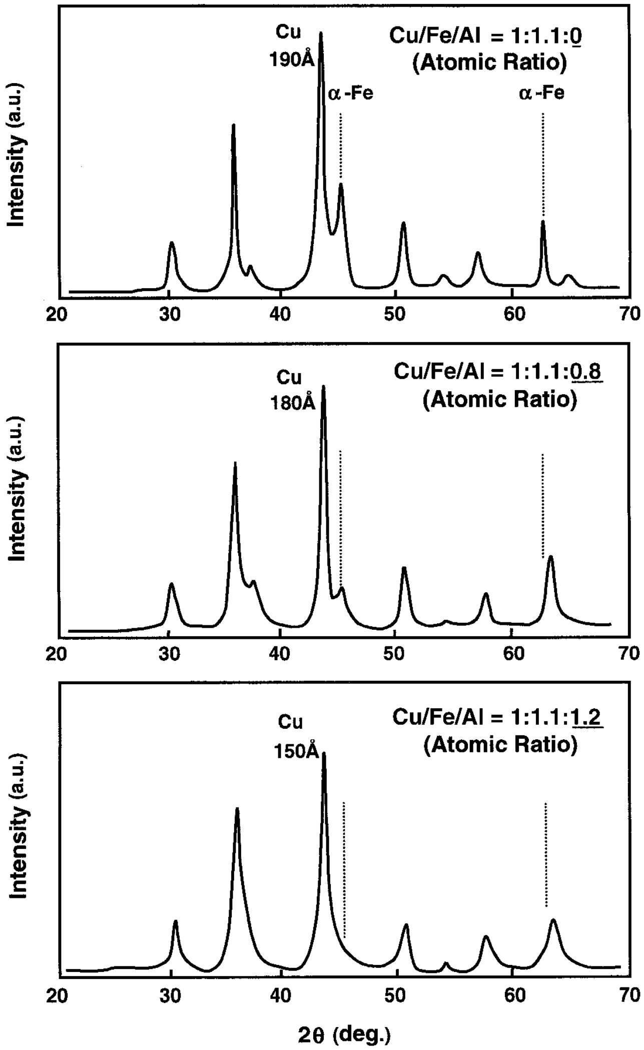

FIG. 5. XRD patterns after use of Cu-Fe catalysts with various Al contents. Cu crystal size (Å) is calculated using Scheerer equation. See Fig-

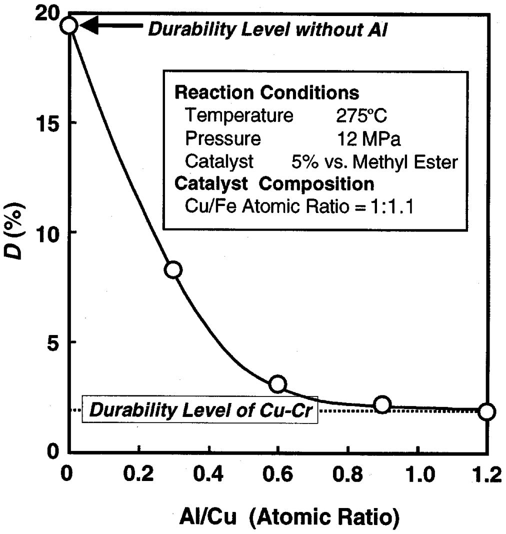

FIG. 6. Durability improvement of CuO-Fe_2O_3 catalyst by addition of Al_2O_3. See Equation 6 for catalyst deactivation factor (*D*).

bed reactor system.

Figure 7 shows a scanning electron micrograph of the catalyst. Good filtration property is expected from the uniformity of particle size. Figure 8 shows the comparison of filtration rate between the Cu-Cr and the Cu-Fe-Al catalysts after reaction. This result suggests that the Cu-Cr catalyst can be replaced with the newly developed Cu-Fe-Al catalyst without plant modification.

Performance test in actual plant. The performance evaluation of the newly developed Cu-Fe-Al oxide catalyst was conducted in an actual plant, which has an annual capacity of 35,000 tons of fatty alcohol. As shown in Figure 9, the operation was continued for 20 d at a reaction temperature of 275°C and a reaction pressure of 25 MPa. The reaction product consisted of 97.4% alcohol, 0.5% unreacted fatty acid methyl ester, 1.3% wax, 0.35% even-chain hydrocarbon, and 0.4% other components. This product distribution was almost the same as the Cu-Cr catalyst. Activity and selectivity were maintained through the test period. The high performance of the Cu-Fe-Al catalyst was confirmed in the actual plant test.

The Cu-Fe-Al catalyst is applicable not only for hydro-

TABLE 1
Final Stage Activity (k_1) and Selectivity Improvement of CuO-Fe_2O_3 Catalyst by Addition of Al

Al/Cu ratio[a]	0	0.3	0.8	1.2	Cu-Cr
k_1[b] (min^{-1})	—	0.049	0.072	0.093	0.092
HC[c] (wt%)	20.5	—	4.5	0.5	0.6

[a] Catalyst composition: Cu/Fe = 1:1.1 (atomic ratio).

[b] First-order rate constant of final stage (Eq. 5); reaction condition: 275°C, 25 MPa, catalyst = 5%.

[c] Hydrocarbon content, analyzed with gas chromatography after 4 h of reaction.

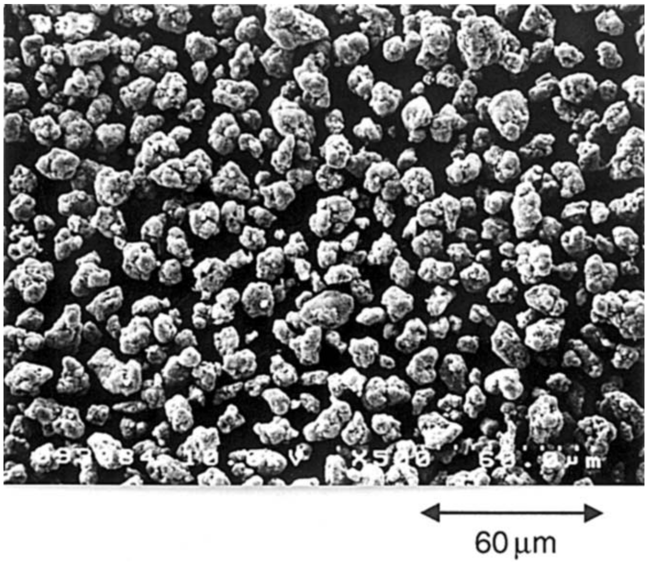

FIG. 7. Scanning electron microscopic analysis of Cu-Fe-Al oxide

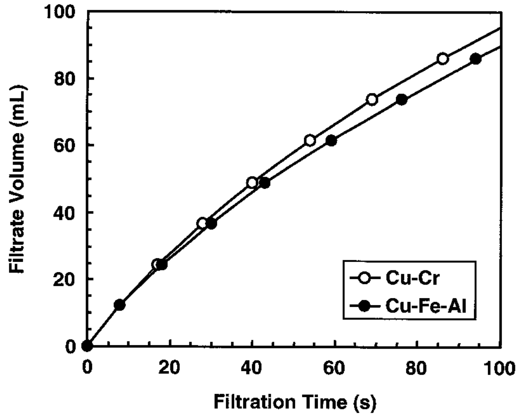

FIG. 8. Filtration data of two types of catalysts (reduced Cu-Fe-Al catalyst and reduced Cu-Cr catalyst).

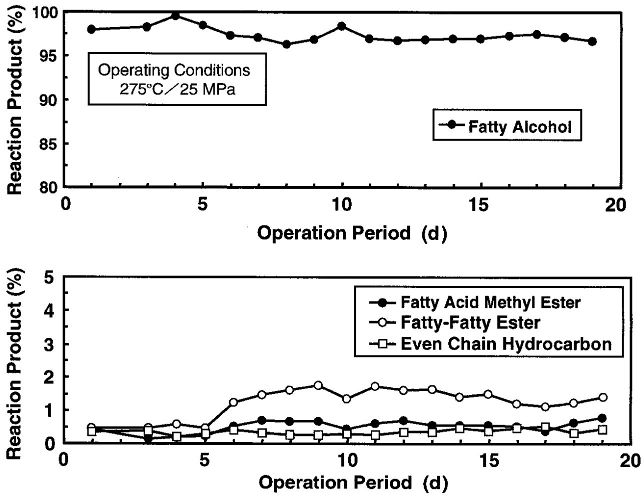

FIG. 9. Reaction data in natural alcohol production plant (alcohol production capacity: 35,000 tons/yr) using Cu-Fe-Al oxide catalyst.

genation of fatty acid methyl esters but also for a variety of reactions in which conventional Cu-Cr catalyst is used. Some examples include dehydrogenation of long-chain fatty alcohol to aldehyde for fragrance, selective hydrogenation of linoleic acid to oleic acid, hydrogenation of nitrobenzene to aniline, and hydrogenation of diesters to diols.

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[Received April 3, 2000; accepted August 18, 2000]