Fatty Methyl Ester Hydrogenation to Fatty Alcohol
Part II: Process Issues

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ABSTRACT: Fatty alcohols are produced by hydrogenating fatty methyl esters in slurry phase in the presence of copper chromite catalyst at temperatures of 250–300°C and hydrogen pressures of 2000–3000 psi. The fatty methyl ester, catalyst, and hydrogen are fed to the reactor cocurrently. The product slurry is passed through gas–liquid separators and then through a continuous filtration system for removal of the catalyst. A portion of the used catalyst in crude alcohol is recycled to the hydrogenator. The overall efficiency of the process depends upon the intrinsic activity, life, and filterability of the catalyst. The fatty alcohol producer therefore requires a catalyst with high activity, long life, and good separation properties. The main goal of the present laboratory investigation was to develop a superior copper chromite catalyst for the slurry-phase process. Two copper chromite catalysts, prepared by different procedures, were tested for methyl ester hydrogenolysis activity, reusability, and filtration characteristics. The reaction was carried out in a batch autoclave at 280°C and 2000–3000 psi hydrogen pressure. The reaction rates were calculated by assuming a kinetic mechanism that was first-order in methyl ester concentration. The catalyst with the narrower particle size distribution was 30% more active, filtered faster, and maintained activity for several more uses than the catalyst with the broader particle size distribution. X-ray photoelectron spectroscopy data showed higher surface copper concentrations for the former catalyst.

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KEY WORDS: Copper chromite, fatty alcohol, fatty-fatty ester, filtration, hydrogenolysis, methyl ester, particle size distribution, slurry hydrogenation, wax ester.

Commercially, fatty alcohols are produced by methanolysis of triglyceride or fatty acid feed stock, followed by catalytic hydrogenolysis of the methyl ester (1). In the slurry process, the overall alcohol production rate per kilogram of catalyst depends upon the intrinsic activity, deactivation rate, and filtration characteristics of the catalyst. Conversion levels are maintained by continuously adding a small amount of fresh catalyst in the recycle stream, and withdrawing spent catalyst (2). The fresh catalyst in the oxide form is activated *in situ* (reduction of the cupric ions) under reaction conditions. The *in situ* reduction creates the active sites required for hydrogenolysis. The fatty alcohol producer therefore requires a catalyst with high activity, long life, and good separation properties. Therefore, research was undertaken to develop a catalyst with higher hydrogenation activity and selectivity.

Catalyst samples were prepared by using procedures described in the literature (3). CuCr-I was prepared by a simultaneous precipitation technique, which involves injecting two streams, a metal-bearing (Cu and Cr) solution and ammonia, into a tank at rates that maintain a constant pH. CuCr-II was prepared by a sequential method in which ammonium chromate solution was added to copper nitrate solution. Catalytic activity measurements were conducted in a batch autoclave as described earlier (4).

RESULTS AND DISCUSSION

Alcohol generation data as a function of time for the two catalysts are presented in Figure 1. This comparison shows that the equilibrium conversion values are reached within

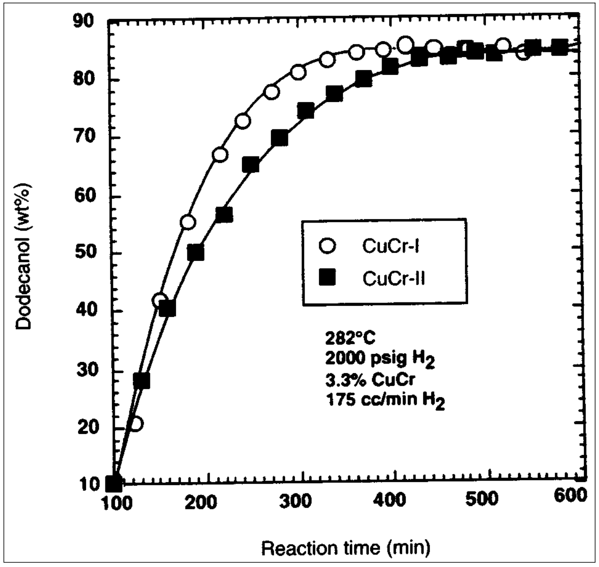

FIG. 1. Dodecanol generation as a function of reaction time.

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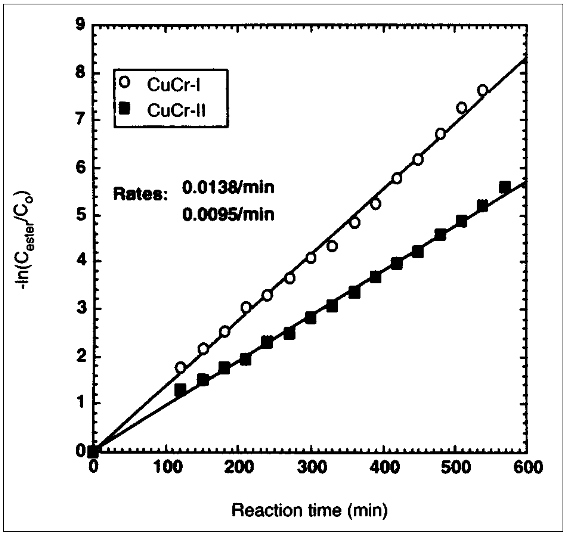

FIG. 2. First-order rate constant plots.

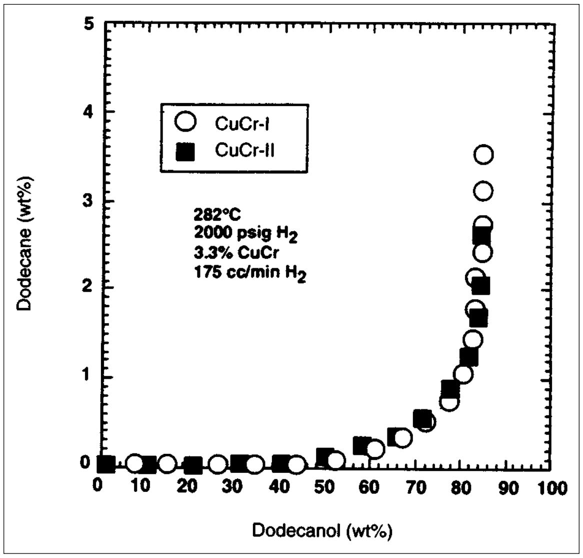

FIG. 4. Dodecane generation as a function of conversion.

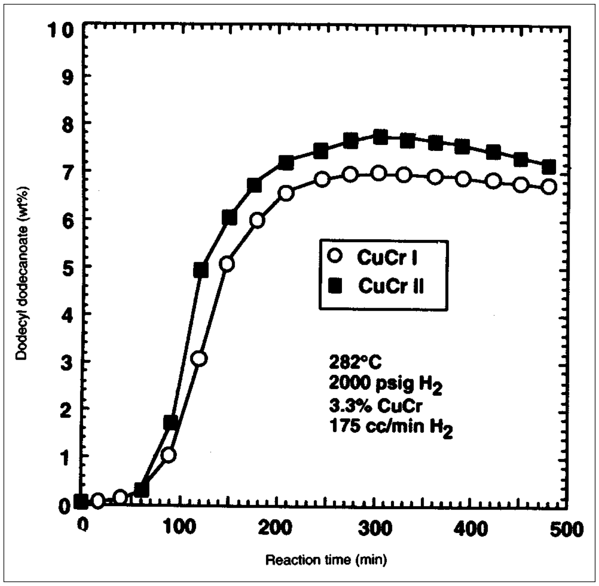

FIG. 3. Dodecyl dodecanoate generation as a function of reaction time.

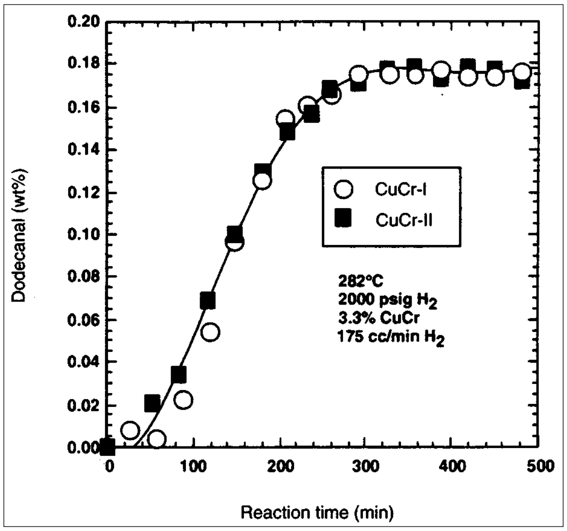

FIG. 5. Dodecanal generation as a function of reaction time.

300–350 min for CuCr-I and 450–500 min for CuCr-II, indicating that the former is more active than the latter. The first-order rate equation plots, shown in Figure 2, clearly show that the hydrogenolysis rate is about 40% faster with CuCr-I than with CuCr-II.

Fatty-fatty ester generation (dodecyl dodecanoate) is demonstrated in Figure 3. Fatty-fatty esters (commonly referred to as wax esters or alkyl alkanoates) are formed *in situ* by transesterification of methyl ester with fatty alcohol or *via* aldehyde reaction over copper chromite catalyst. The residual fatty-fatty ester content of the product is lower with CuCr-I than with CuCr-II, which is consistent with earlier findings that the former catalyst is more active than the latter.

Dodecane generation, at equal conversion levels, is compared for the two catalysts in Figure 4. The alkane is formed by various mechanisms discussed earlier (4). This is usually considered as yield loss. The results of Figure 4 show that alkane formation is similar for both catalysts.

Dodecyl aldehyde and didodecyl ether are formed in small amounts by dehydrogenation and dehydration reactions, respectively. In addition, the ether may be formed *via* an intermediate hemiacetal in the hydrogenation of methyl ester. Results shown in Figure 5 indicate that dodecanal formation is independent of the type of catalyst used, while those shown in Figure 6 suggest that ether formation can be minimized by using CuCr-I catalyst.

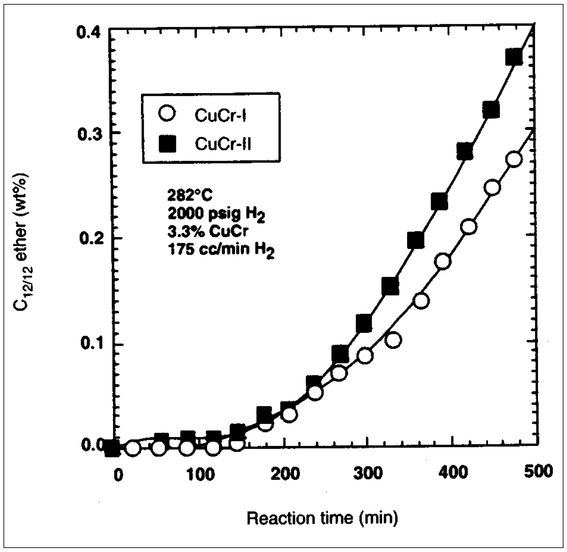

FIG. 6. Didodecyl ether generation as a function of reaction time.

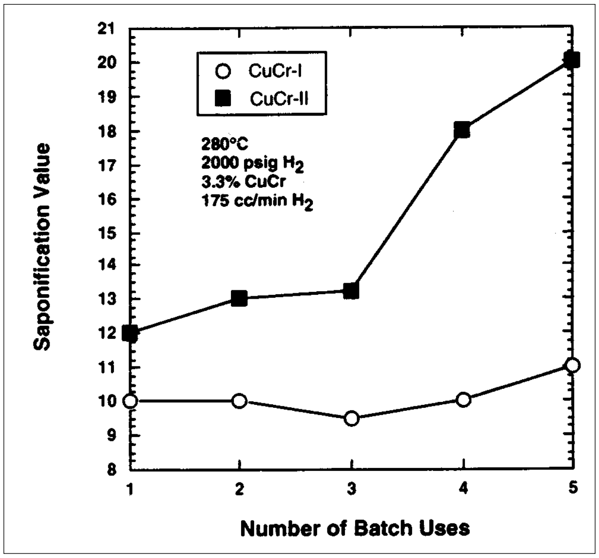

FIG. 7. Catalyst aging characteristics.

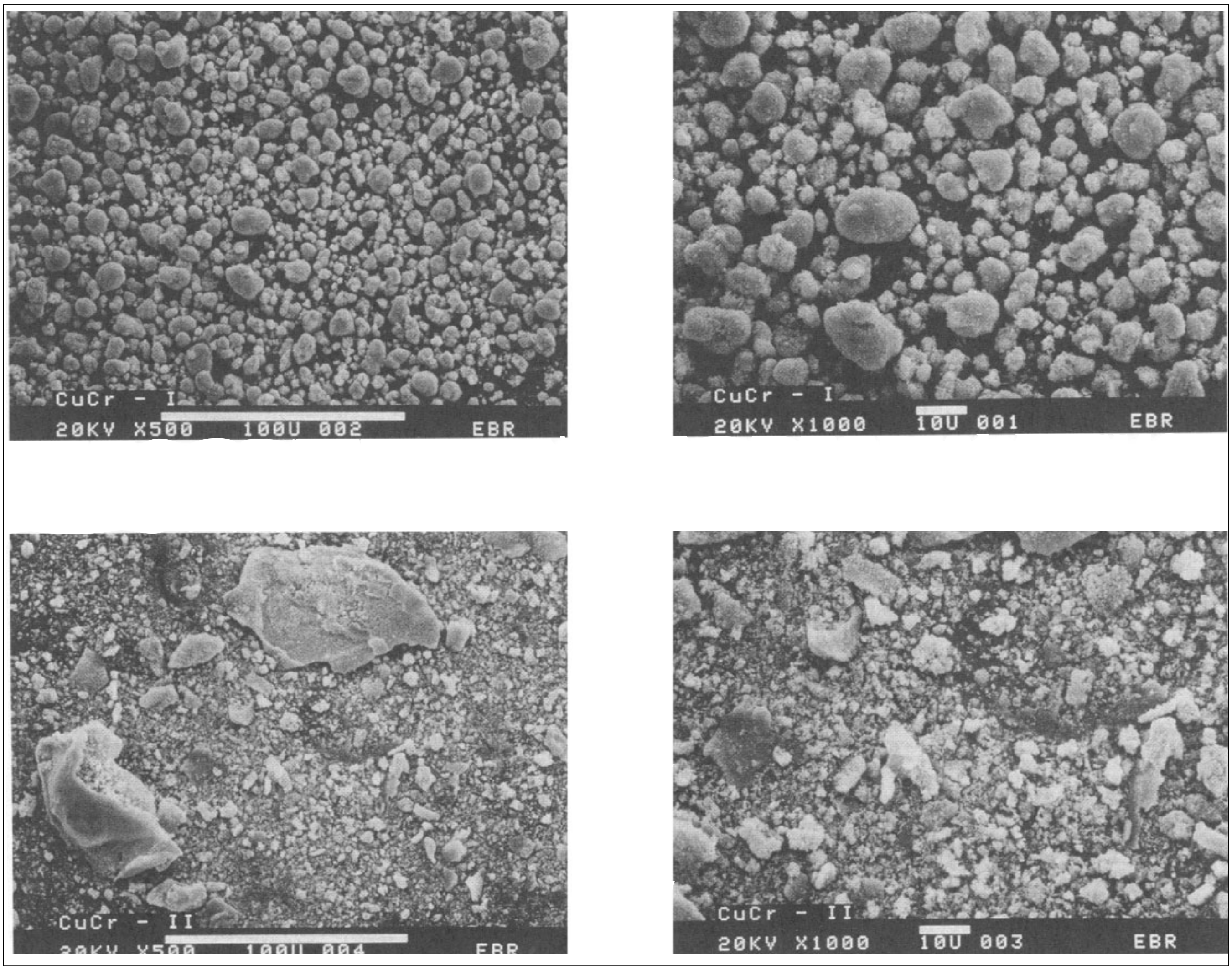

FIG. 8. Scanning electron microscopic analysis of two catalysts.

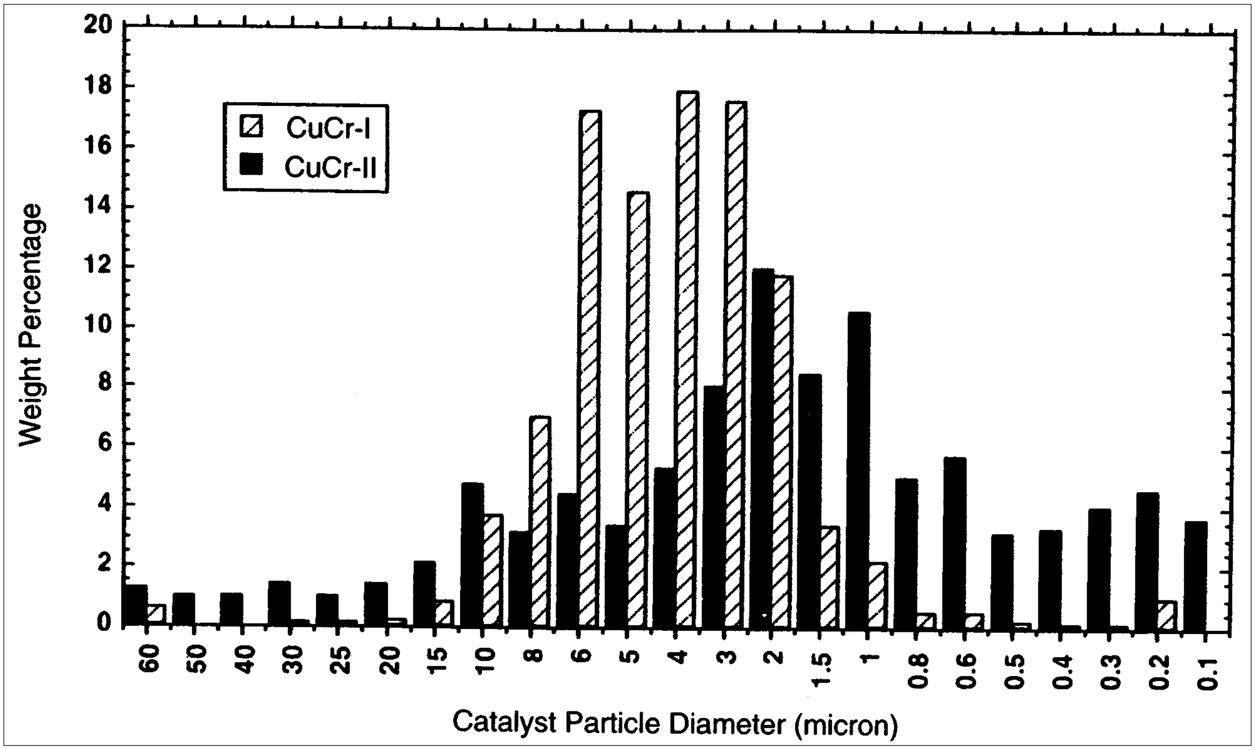

FIG. 9. Particle size distribution of two catalysts.

Catalyst aging data are presented in Figure 7. The catalyst samples were evaluated for five uses in a batch reactor at 280°C and 3000 psig hydrogen pressure. The results clearly demonstrate that CuCr-I retains its activity (as indicated by saponification values around 10) for five uses, while the CuCr-II sample shows high activity (low saponification values) for the first three uses and starts deactivating after the third use, reaching a saponification value of 20 mg KOH/g at the end of the run. This difference in activity is not surprising if one considers the physical properties of the two catalysts as shown in Table 1. CuCr-I has higher pore volume and higher Cu-to-Cr ratio (surface rich in copper). This difference in Cu/Cr atomic ratio accounts for the difference in hydrogenation rates.

Scanning electron microscopic analysis (Fig. 8) reveals the morphology differences between the two catalysts under investigation: CuCr-I has spherical well-defined particles, while the CuCr-II catalyst consists of irregular-shaped particles. Figure 9 shows that the particle size distribution of CuCr-I is narrower than that of CuCr-II. The latter has a significant fraction of particles in the submicron size. The morphology differences and the fraction of small submicron-sized particles lead to differences in filterability of the catalyst, as shown in Figure 10. The filtration rates with CuCr-I are two times faster than the rates with CuCr-II. This property is extremely useful in a continuous operation and improves overall efficiency of the process.

TABLE 1
Physicochemical Properties of Copper Chromite Catalysts

Physicochemical property	CuCr-I	CuCr-II
Surface area (m^2/g)	35	28
Total pore volume (cc/g)	0.19	0.15
Composition (wt%)		
Copper	42.5	40.8
Chromium	32.5	31.8
XPS analysis		
Cu/Cr atomic ratio		
Before reduction	1.2	1.1

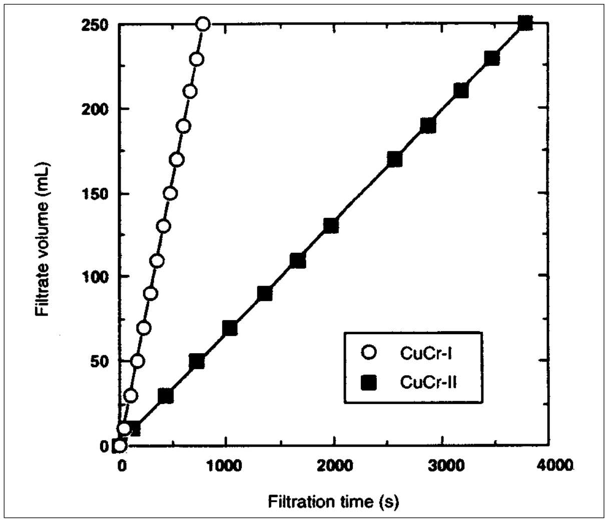

FIG. 10. Filtration data for two catalysts.

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