

Fatty Methyl Ester Hydrogenation to Fatty Alcohol Part I: Correlation Between Catalyst Properties and Activity/Selectivity

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ABSTRACT: Fatty alcohols, derived from natural sources, are commercially produced by hydrogenation of fatty acids or methyl esters in slurry-phase or fixed-bed reactors. One slurry-phase hydrogenation of methyl ester process flows methyl esters and powdered copper chromite catalyst into tubular reactors under high hydrogen pressure and elevated temperature. In the present investigation, slurry-phase hydrogenations of C₁₂ methyl ester were carried out in semi-batch reactions at non-optimal conditions (i.e., low hydrogen pressure and elevated temperature). These conditions were used to accentuate the host of side reactions that occur during the hydrogenation. Some 14 side reaction routes are outlined. As an extension of this study, copper chromite catalyst was produced under a number of varying calcination temperatures. Differences in catalytic activity and selectivity were determined by closely following side reaction products. Both activity and selectivity correlate well with the crystallinity of the copper chromite surface; they increase with decreasing crystallinity. The ability to follow the wide variety of side reactions may well provide an additional tool for the optimized design of hydrogenation catalysts. *JAOCS* 74, 333–339 (1997).

KEY WORDS: Copper chromite, fatty alcohol, fatty-fatty ester, hydrogenation, methyl ester, slurry hydrogenation, wax ester.

Although there are extensive reviews on the hydrogenation of methyl esters with copper chromite as the catalyst (1,2), these studies are limited to discussions of the major reaction, with little evaluation of side reaction products. In addition, reaction mechanisms are usually limited to speculation, due to the lack of substantial side reaction data. It is well known that the major reaction product in the slurry hydrogenation of methyl ester (3), under high hydrogen pressure and elevated temperature, is the fatty alcohol, along with residual fatty-fatty ester and trace amounts of side reaction products. Fatty-fatty esters, commonly referred to as wax esters, are alkyl alkanoates. To describe a detailed reaction

pathway for the hydrogenation of methyl ester to alcohol, it was necessary to develop an experimental reaction method that would accentuate the generation of normally undesirable side reaction products. The side reaction products may be obtained under widely varying conditions of hydrogen pressure and reaction temperature used for the hydrogenation of C₁₂ methyl ester (Table 1). The ability to follow the wide variety of side reaction products allows an accurate development of hydrogenation reaction pathways and, in addition, provides a method for the more optimal design of catalyst surfaces.

EXPERIMENTAL PROCEDURES

A series of slurry-phase, semi-batch hydrogenations of methyl ester with copper chromite catalyst was carried out in a fully computer-controlled Autoclave Engineers Micro-Scale bench-top reactor system (4), referred to as a BTRS. The experimental system is a small-scale, semi-batch reactor with complete microprocessor control of temperature, pressure, flow, agitation, and liquid sampling capability for gas chromatographic analysis. The experimental conditions were: reactor volume, 100 cc; construction material, 316

TABLE 1
Selectivity Differences vs. Reaction Conditions

Reaction conditions	~2000 psig	~3000 psig
H ₂ pressure	~2000 psig	~3000 psig
Rx temperature	280°C	260°C
Catalyst slurry	1–6%	~2.5%
Reaction products		
	Alcohol	Alcohol
	Fatty-fatty ester	Fatty-fatty ester
	Aldehyde	trace
	Acetal	—
	Ethers	trace
	Ketone	trace
	Fatty acid	—
	Copper soap	—
	Even-chain alkane	trace
	Odd-chain alkane	—

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stainless steel; feed stock, 60 g C_{12} methyl ester (98%); copper chromite catalyst, 1–6 g; hydrogen pressure, 2000 psig; reactor hydrogen sweep, 75 cc/min; reactor temperature, 280°C; impeller agitation, ~450 rpm; reaction time, 1–8 h; sample frequency, 15 min, 30 min; component identification, gas chromatography (GC)/mass spectroscopy; sample analysis, GC. Experimental runs consisted typically of pressurizing a methyl ester/catalyst slurry up to 2000 psig with hydrogen, followed by a continuous flow of hydrogen through the reactor at 75 cc/min. The system temperature was brought to 280°C during a 20-min heat-up cycle. Microsamples were taken at 15- or 30-min intervals, beginning with the initiation of system heat-up. All reaction conditions were recorded by the on-line computer system provided by the BTRS. All reaction products were identified by GC/mass spectroscopy and allowed reaction sample compositions to be followed by GC. Analysis of copper chromite physical properties was provided through Micromeritics (Norcross, GA). X-ray diffraction analysis was carried out in-house (Procter & Gamble, Cincinnati, OH), with a Stoe diffractometer.

RESULTS AND DISCUSSION

Reaction pathways. A typical dodecyl methyl ester hydrogenation reaction profile, consisting of methyl ester depletion, alcohol generation, fatty-fatty ester generation and depletion, and the generation of side reaction products, as listed in Table 1, appears in Figure 1. A more detailed breakdown of a number of side reactions appears in the section entitled *Catalytic surface properties vs. reaction characteristics*. The study of the hydrogenation of dodecyl methyl ester has revealed a number of interesting side reaction products. The presence of ethers supports the hemiacetal as the transient intermediate of the reaction. Potential reaction routes appear

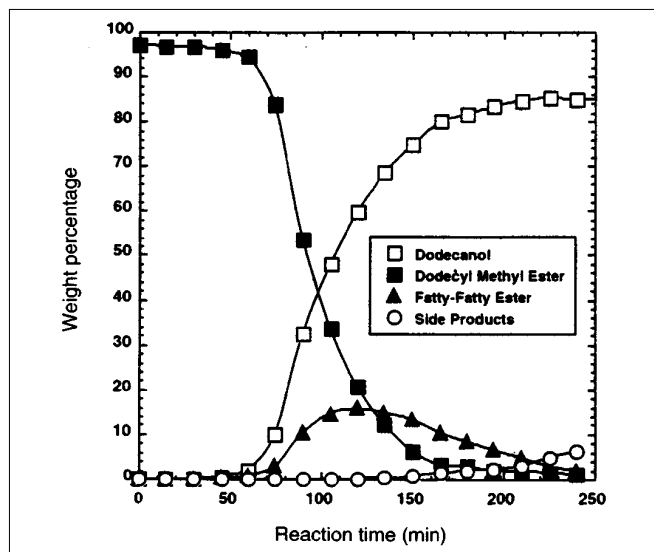


FIG. 1. Typical fatty methyl ester hydrogenation.

in Figure 2. Except for the hemiacetal, which is inherently unstable, all reaction products appearing in Figure 2 have been observed during semi-batch hydrogenations of dodecyl methyl ester. The ability to measure these products provides a refined tool for additional characterization of catalyst surface modification.

Catalytic surface properties vs. reaction characteristics. A series of plant-produced copper chromite catalysts were generated at various calcination temperatures, to produce the physical properties shown in Table 2. Powder x-ray diffraction patterns were developed for each of the five samples. These patterns appear in Figure 3. The diffraction patterns clearly show an increase in the overall background of the samples with decreasing calcination temperature, as well as a broadening of the diffraction peaks. A direct comparison of the samples generated at 399 and 538°C indicates virtually a complete loss in resolution of certain reflections, especially in the 30 to 40° two-theta region. This is an indication of a decrease in surface crystallinity with decreasing calcination temperature. There is also a significant increase in catalyst surface area with decreasing calcination temperature. The fact that certain reflections are not observed in the higher surface area samples may indicate changes in the crystalline phase of the catalyst as the surface area increases (decreasing calcination temperature). Such differences in surface morphology suggest significant differences in catalyst activity and selectivity. Application of the hydrogenation conditions described previously allows the study of such differences.

Using the described variations of copper chromite catalyst, a series of hydrogenations of dodecyl methyl ester were carried out. The first series focused upon the rate of reaction, specifically the depletion of dodecyl methyl ester and the generation of dodecanol (Figs. 4 and 5). Catalysts calcined at lower temperatures were more active than those calcined at higher temperatures. The surface area of the catalyst increased with decreasing calcination temperature. Considering only surface area available for generation of hydrogen atoms, the results of Figures 4 and 5 are expected. The profile for generation and depletion of the fatty-fatty ester (dodecyl dodecanoate) appears in Figure 6. However, the ratios of the dodecyl methyl ester depletion rates are not equal to the ratios of surface area. This suggests that different surface morphologies are present, as previously indicated by the powder x-ray diffraction patterns of Figure 3.

Alkane generation, dodecane, is demonstrated in Figure 7. Alkanes are the result of pyrolysis reactions during ester hydrogenation, as shown in the potential reaction routes of Figure 2. The alkene, dodecene, may be generated by thermal decomposition of dodecyl dodecanoate, and may be followed by the hydrogenation of the double bond to the alkane, dodecane. To a lesser extent, the alcohol product may dehydrate to form the alkene, which can then be hydrogenated to form the alkane. Both ether forms, the symmetrical and unsymmetrical, may be hydrogenated, with some difficulty, to form an alcohol and the alkane.

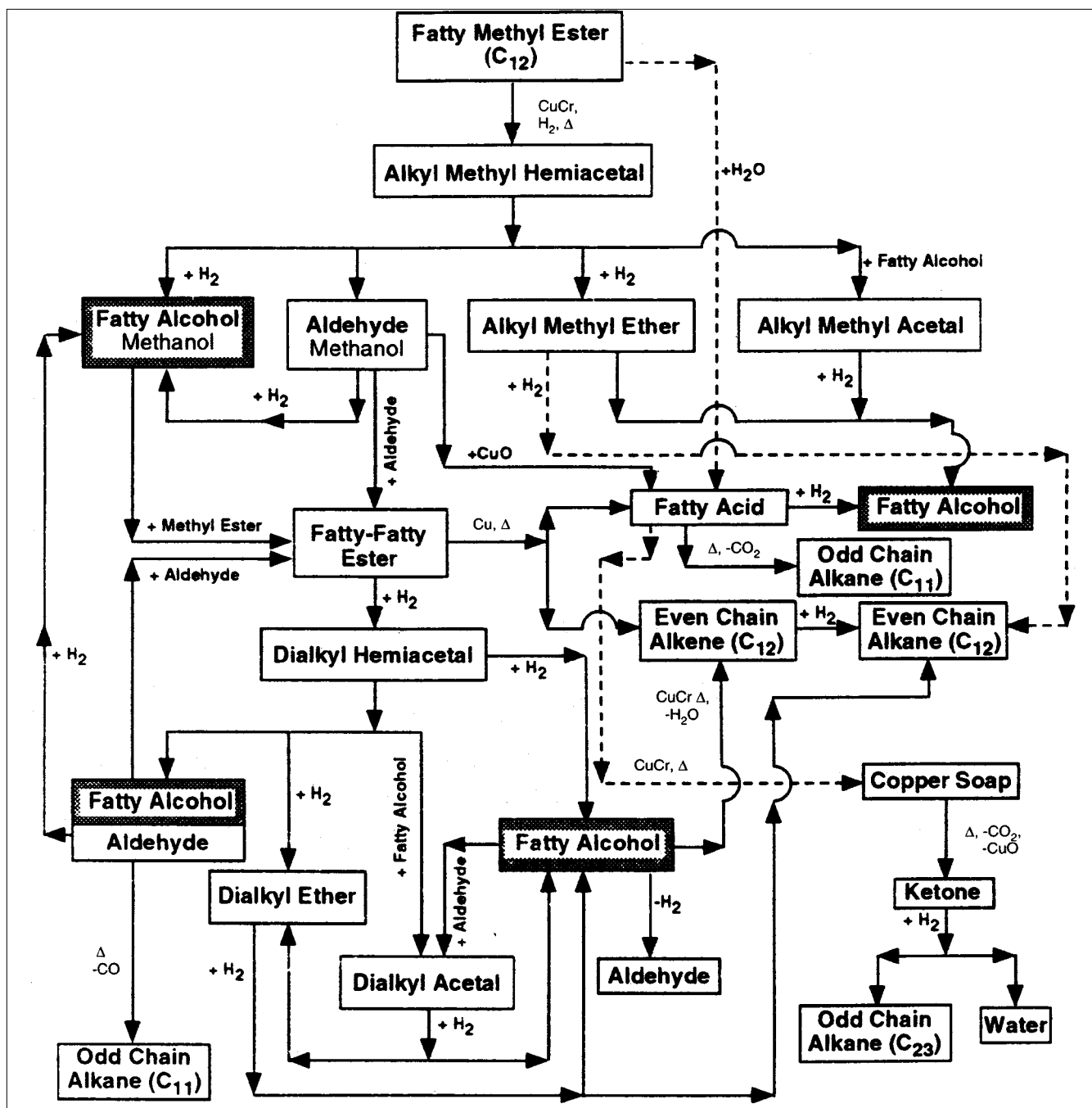


FIG. 2. Potential reaction routes in the hydrogenation of alkyl methyl ester.

The odd-chainlength alkane, undecane, appears at low concentrations during the latter portions of the hydrogenation reaction (Fig. 8). Its generation depends upon thermal decompositions. As shown in Figure 2, there are a number of aldehyde (dodecanal) sources, generated from the two hemiacetal forms. Dodecanal may thermally decompose to form the alkane, undecane, and carbon monoxide. Thermal degradation of dodecyl dodecanoate has been shown to be a source of the even-chainlength dodecane. It may also

provide a route to odd-chainlength undecane. The fatty-fatty ester may thermally decompose to form dodecanoic acid and alkene. Dodecanoic acid may undergo further thermal decomposition to form undecane and carbon dioxide.

The primary source of the alkane tricosane ($C_{23}H_{48}$) is through thermal decomposition of dodecyl dodecanoate. The fatty acid decomposition product, dodecanoic acid, may react directly with copper chromite catalyst to form the copper

TABLE 2
CuCr Physical Properties vs. Calcination Temperature

Catalyst number	Calcination temp. (°C)	BET area (m ² /g)	Pore vol. (mL/g)	Pore size (Å)	Catalyst dia. (μ)
1	399	44.8	0.31	276	1.66
2	427	35.9	0.24	268	1.58
3	460	25.8	0.19	296	1.28
4	516	18.5	0.16	344	1.23
5	538	13.4	0.09	280	1.02

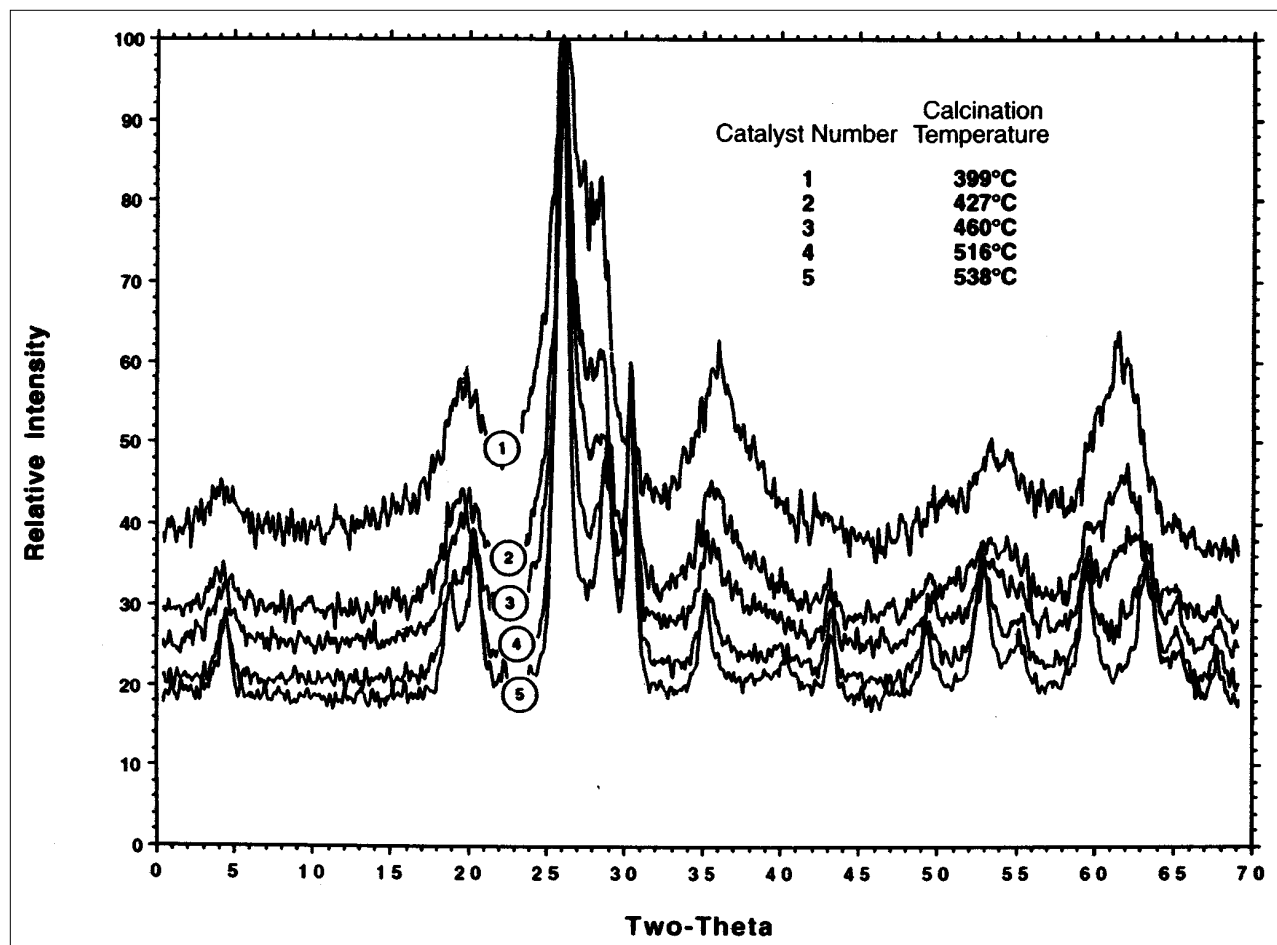


FIG. 3. Powder x-ray diffraction patterns of copper chromite catalyst.

soap, cupric dodecanoate. Cupric dodecanoate may thermally decompose to form carbon monoxide, cupric oxide, and tricosane (Fig. 9). Additional sources of the fatty acid, other than from dodecyl dodecanoate, may be through hydrolysis of the dodecyl methyl ester feed stock or through oxidation of the aldehyde, dodecanal. However, as the copper chromite catalyst becomes fully reduced during hydrogenation, the source of water, for hydrolysis, and copper oxide, for oxidation, becomes minimized.

Two forms of ether are generated during the hydrogenation of dodecyl methyl ester. These are the unsymmetrical

dodecyl methyl ether and the symmetrical didodecyl ether. The generation profile of the didodecyl ether appears in Figure 10. As shown in Figure 2, the reaction route of this species is through hemiacetal formation derived from the hydrogenation of dodecyl dodecanoate. The hemiacetal may be hydrogenated to form the symmetrical ether. It is also proposed that the hemiacetal may react with fatty alcohol to form acetal, which, upon further hydrogenation, may form the symmetrical ether. Although it is difficult, the ether itself may undergo further hydrogenation to form alcohol and alkane.

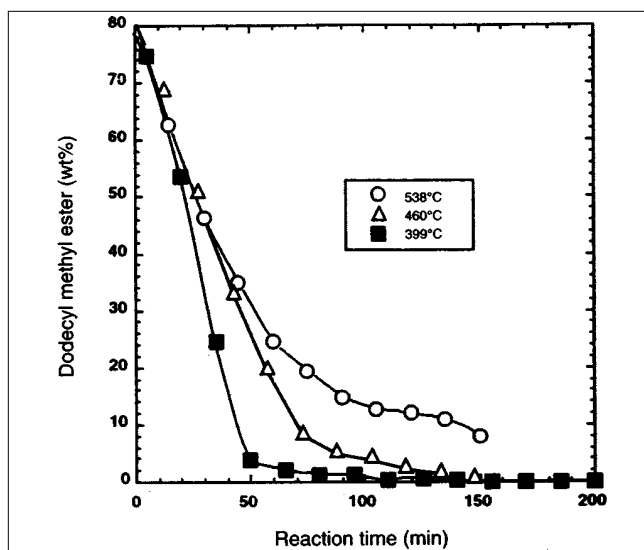


FIG. 4. Depletion of dodecyl methyl ester vs. catalyst calcination temperature.

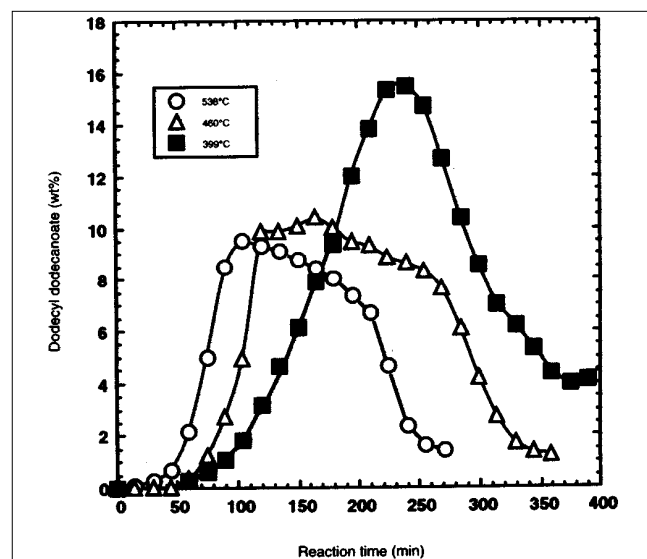


FIG. 6. The generation/depletion profiles for dodecyl dodecanoate vs. catalyst calcination temperature.

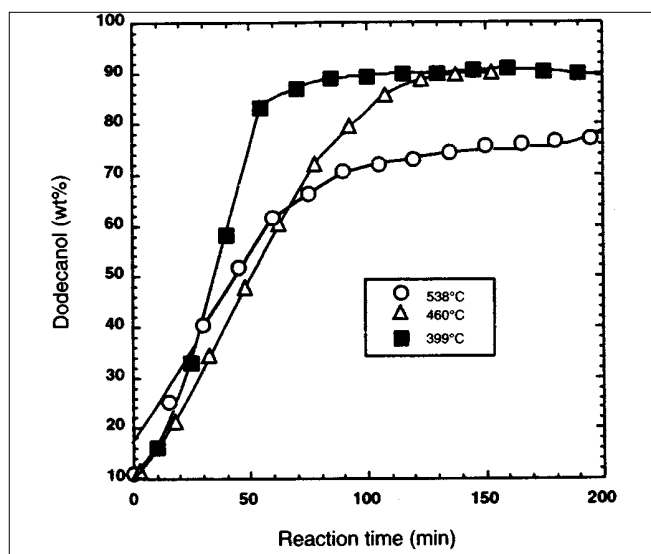


FIG. 5. Dodecanol generation vs. catalyst calcination temperature.

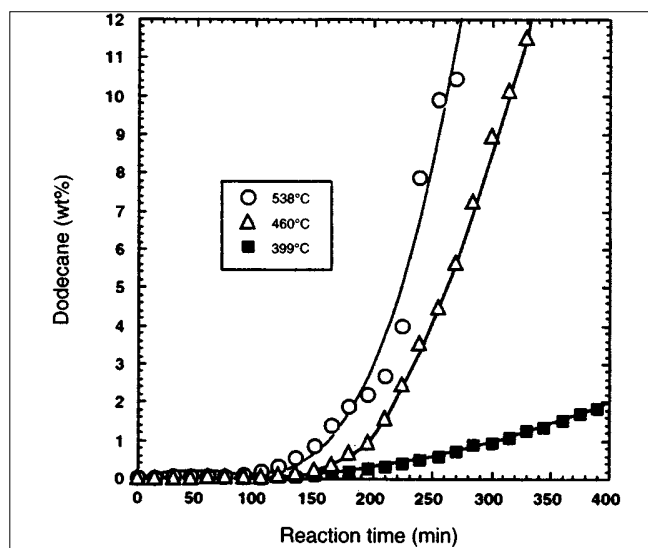


FIG. 7. Dodecane generation vs. catalyst calcination temperature.

There is a wide variation in the levels of side reaction products that are created with catalysts generated under different calcination temperatures. Confirmation of the differences in selectivity may be firmly established by plotting, for example, dodecanol product vs. dodecane. This is shown for hydrogenations with catalysts calcined in the two extreme cases of temperatures studied, 538 and 399°C (Fig. 11). If the selectivity for both were the same, then the curves would have superimposed upon each other. No superimposition confirms the change in selectivity. This large selectivity change occurs for all side reaction products when plotted against the alcohol product.

It has been shown that, as the calcination temperature of copper chromite catalyst is lowered, there is a corresponding decrease in surface crystallinity. The decrease in crystallinity and the increase in catalyst surface area correspond well with increased catalytic activity and selectivity. The generation of the primary product, alcohol, is favored along with a suppression of all pyrolysis products (i.e., alkanes). Over exceedingly long reaction residence times, side reaction products may be suppressed when a low-temperature-calcined copper chromite catalyst is used. Figure 12 is a comparison of dodecanol generation and stability in semi-batch reactions beyond the point of maximum conversion.

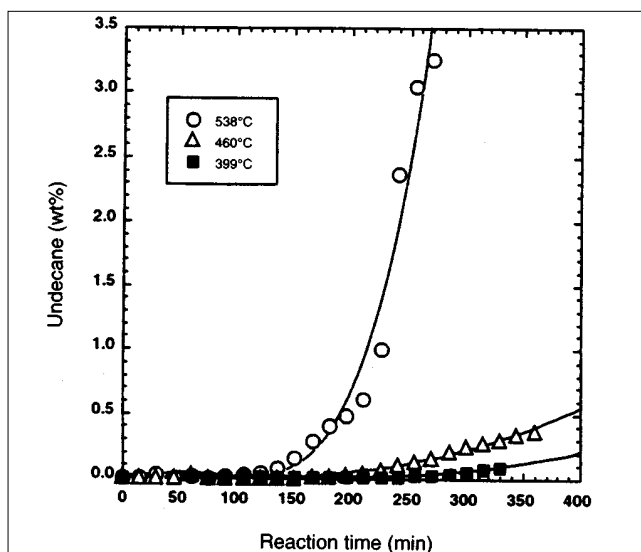


FIG. 8. Undecane generation vs. catalyst calcination temperature.

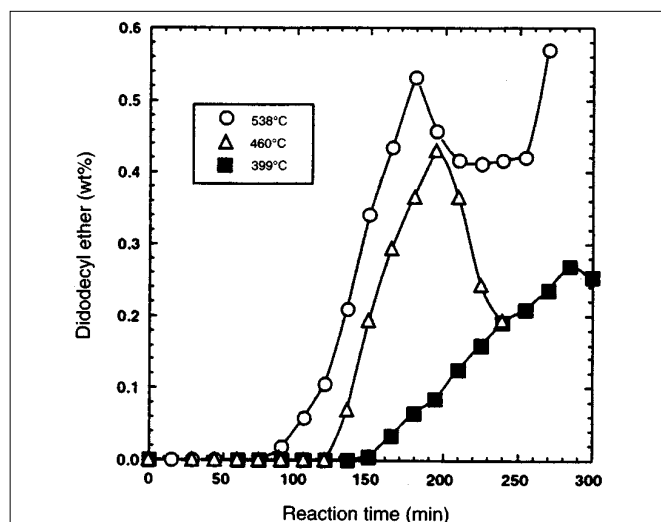


FIG. 10. Didodecyl ether generation vs. catalyst calcination temperature.

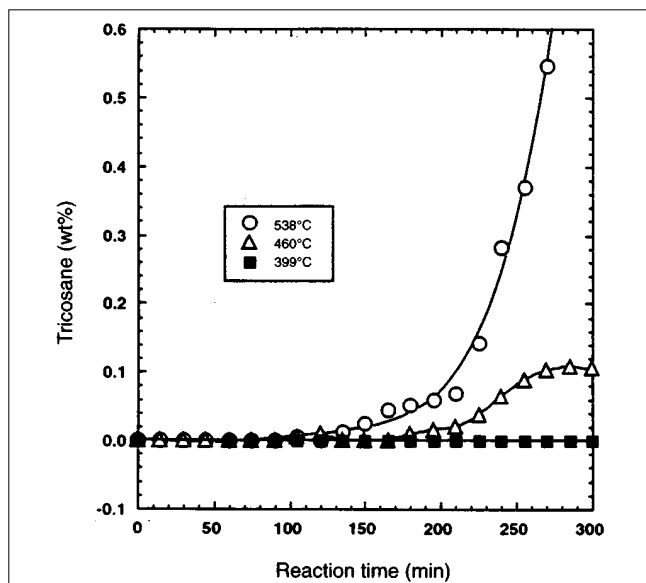


FIG. 9. Tricosane generation vs. catalyst calcination temperature.

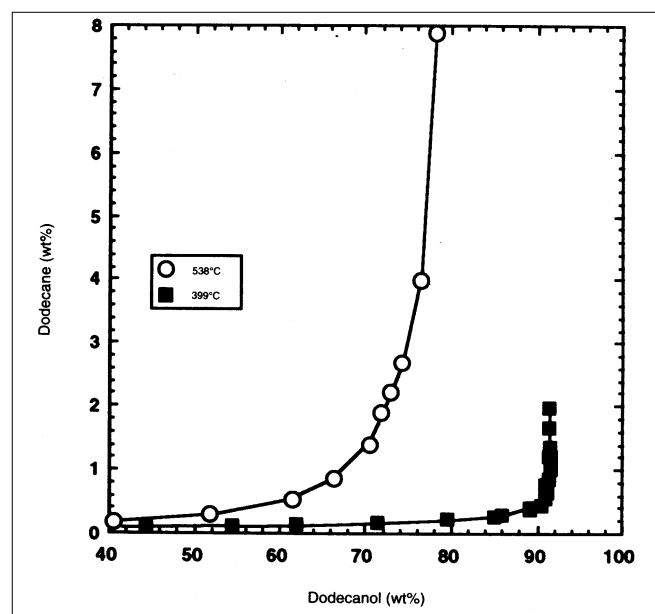


FIG. 11. Selectivity: dodecane vs. dodecanol at catalyst calcination temperatures of 538 and 399°C.

The high-surface-area, low-calcination-temperature catalyst does not allow the thermal degradation of the dodecanol product through the alkane side reactions. However, significant degradation of dodecanol occurs when using a catalyst of low surface area, produced through high calcination temperature. Although not experimentally measured, the data suggest that the low-surface-area catalyst (high calcination temperature) may have relatively large crystalline sites that are less active than the multiple, small crystalline sites of high-surface-area catalyst (low calcination temperature). These differences in surface morphologies need further analytical definition and should be stud-

ied further by hydrogenation reaction techniques here described.

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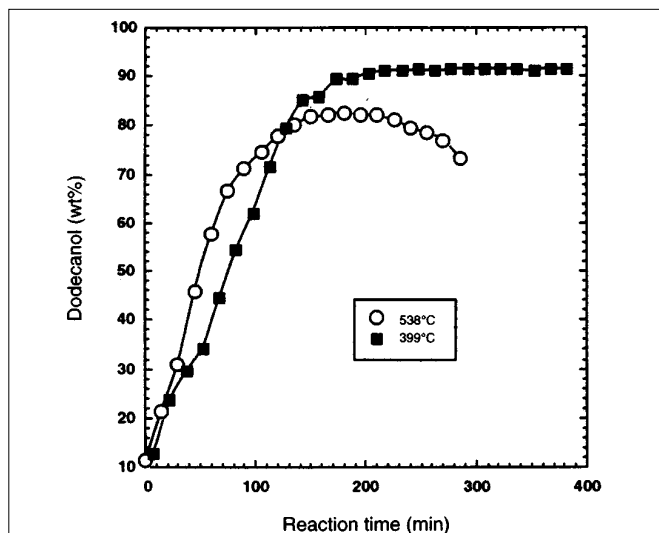


FIG. 12. Dodecanol generation/stability vs. catalyst calcination temperature.

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