

Fatty Methyl Ester Hydrogenation to Fatty Alcohol: Reaction Inhibition by Glycerine and Monoglyceride

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ABSTRACT: The present work demonstrates the rate-limiting effect of varying levels of both glycerine and monoglyceride through a series of batch hydrogenations of fatty dodecyl methyl ester, using copper chromite as the catalyst. Reactions were carried out at 3000 psig H₂, 280°C with catalyst levels varying between 1.25 and 1.80%. With increasing contaminant levels of glycerine (0.0, 0.1, 0.5, 5 wt%), conversion of fatty methyl ester to alcohol is correspondingly reduced (95, 89, 80, 2 wt%). On a molar basis of contaminant, monoglyceride equally reduces the conversion of methyl ester to alcohol. In both cases the latent appearance of fatty-fatty ester results from the slower hydrogenation rate. Chemistry is proposed outlining the thermal decomposition of glycerine or glyceride to intermediate components (acetol and acrolein), leading to the generation of propanediols. Experimental studies indicate that diols effectively deactivate the copper chromite catalyst, limiting the rate of fatty methyl ester hydrogenation. Catalyst deactivation is not permanent, suggesting catalyst site blockage by physical adsorption of the polyhydroxyl components. The complete understanding of this interaction holds promise for the development of glycerine/monoglyceride-insensitive catalysts. In addition, a brief overview of methyl ester hydrogenation inhibition effects of some heteroelements, water, and soap is presented.

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KEY WORDS: Catalyst inhibition, copper chromite, fatty alcohol, fatty soaps, glycerides, glycerine, hydrogenation, methyl ester, propanediol, slurry hydrogenation.

In any chemical reaction that is catalyst dependent, reaction inhibitors and catalyst poisons are of great interest. Reaction inhibitors may fall into the class of thermodynamic variables, such as reduced pressure and temperature, or inadequate reactor design leading to poor agitation. Catalyst poisons may fall into two classes: those that temporarily reduce activity and those that permanently reduce catalytic activity. Data in this area for the hydrogenation of fatty acid or fatty methyl ester to an alcohol product have usually been well guarded by industry. A brief discussion of poisons in the generation of detergent-range alcohols appears in the publication by Voeste and Buchold (1). Examples of temporary catalyst poisons

may be water, soaps, fatty acids, glycerine, and glycerides. In the case of the hydrogenation of methyl esters to alcohol, using copper chromite as the catalyst, there are compounds that may react with or irreversibly adsorb onto copper sites to deactivate the catalyst permanently. Examples of such were developed under the auspices of the Procter & Gamble Company (King, R.M., private communication), i.e., compounds containing halogens, sulfur, or phosphorus. These compounds completely and irreversibly deactivate a copper chromite catalyst. Although this paper will focus on temporary catalyst poisons, it is of interest to briefly review the background data of King on permanent catalyst poisons, classified as heteroelements. In the communication with King, dodecyl methyl ester was hydrogenated at 2000 psig H₂, 270°C, with 1% copper chromite catalyst in a batch autoclave, reacting for 1 h. The catalyst poisons investigated were *n*-octadecyl chloride, *n*-octadecyl bromide, *n*-octadecyl methane sulfonate, *n*-octadecyl thiol, and bis (diphenyl phosphino) ethane.

The effect of these poisons on the relative conversion of the methyl ester feed, at varying contamination levels, is shown in Figure 1. At the termination of each reaction, elemental microanalyses were applied to both reaction product and catalyst for determination of the corresponding heteroelement poison. In each case, the poison was found exclusively on the catalyst. These particular poisons appear to deactivate accordingly by equal molar concentrations. The effect of these poisons is permanent, eliminating any catalyst activity recovery.

Experimental studies of temporary hydrogenation catalyst poisons are presented in this publication, primarily focusing on the effects of glycerine and monoglyceride.

EXPERIMENTAL PROCEDURES

A series of slurry-phase batch hydrogenations of dodecyl methyl ester with copper chromite catalyst was carried out in a 1-L, baffled, stirred reactor designed by Autoclave Engineers (Erie, PA). The experimental system is a small-scale batch reactor with complete microprocessor control of temperature, pressure, agitation, and liquid sampling capability for gas chromatography (GC) analysis. The experimental conditions were: reactor volume, 1000 mL; material of construction, 316 stainless steel; feed stock, 400 g C₁₂ methyl

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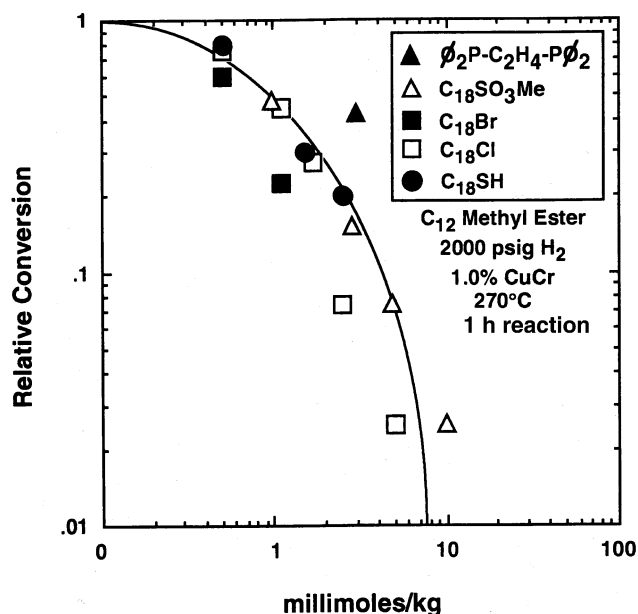


FIG. 1. Relative conversion of dodecyl methyl ester vs. millimoles/kg of permanent catalyst poisons. $\phi_2P-C_2H_4-P\phi_2$, bis (diphenyl phospheno) ethane; $C_{18}SO_3Me$, *n*-octadecyl methane sulfonate; $C_{18}Br$, *n*-octadecyl bromide; $C_{18}Cl$, *n*-octadecyl chloride; $C_{18}SH$, *n*-octadecyl thiol.

ester (98%), copper chromite catalyst (Engelhard), 4–7.2 g; hydrogen pressure, 3000 psig; reactor temperature, 280°C; impeller agitation, 2000 rpm; reaction time, 1 to 2 h; sample period, ~20 min; sample analysis, GC, Hewlett-Packard 5880 (Palo Alto, CA). The preferred GC column was a fused-silica capillary column (HP SPB-5, 30 m, 0.25 mm i.d., 0.25 μ m film thickness). The GC conditions were: initial temperature, 100°C; final temperature, 325°C; injection temperature, 350°C; detector temperature; 350°C; ramp rate, 10°C/min; and run time, 45 min. Experimental runs typically consisted of charging the reactor with ester/catalyst slurry and varying levels of catalyst inhibitors of interest, followed by raising the pressure to ~300 psig hydrogen. The reactor temperature was then ramped to 280°C, at which time the hydrogen pressure was increased to 3000 psig. Microsamples were taken through 0.5 μ m sintered filter-tipped sample lines at ~20-min intervals. All reaction products were identified by GC–mass spectroscopy (Finnigan 4500; San Jose, CA). Reaction sample compositions were followed by GC analysis.

RESULTS and DISCUSSION

Water, fatty soaps, fatty acids (2), glycerine, and glycerides fall into the class of temporary catalyst poisons from which activity loss may be recovered. In this current work, the effect of water upon the hydrogenation of methyl esters has been further investigated at higher hydrogenation pressure which approaches that of commercial processes.

Effect of water. A series of batch hydrogenations of dodecyl methyl ester was run (3000 psig H_2 , 280°C, 1.80% fresh CuCr catalyst) with varying levels of water in the methyl ester

feed stock. Figure 2 shows the relative conversion of the methyl ester as a function of the water level. Under these reaction conditions, significant levels of water reside in the liquid phase, effectively blocking catalyst sites.

The question remains whether water may inhibit the reduction of fresh catalyst to its active form, in addition to blocking active sites by occlusion. To clarify the role of catalyst reductive state, a series of methyl ester hydrogenations under the above conditions were run. For comparative purposes, samples were taken 20 min into each hydrogenation run. In the absence of water, fresh copper chromite catalyst allowed a methyl ester conversion of 50%, whereas a second use of the catalyst resulted in a conversion of 62.5%. The increased conversion for the second run is due to a now fully reduced catalyst. When fresh catalyst is used in the presence of 5000 ppm water, the conversion of methyl ester is only 11.5%. The use of fully reduced catalyst, in the presence of 5000 ppm water, results in a conversion of 31.3%. These data suggest that water not only may occlude active catalyst sites but also may inhibit the reduction of cupric oxide to its zero valence state active form. Fully reduced catalyst appears to be relatively immune to low levels of water contamination (500 ppm). However, commercial slurried reactor systems may be sensitive to low water levels owing to continuous fresh catalyst addition required to maintain activity.

Effect of soap. Fatty soaps, owing to their low solubility in methyl ester feed stocks, may also temporarily reduce the hydrogenation activity of copper chromite. A series of batch hydrogenations of dodecyl methyl ester was run (3000 psig H_2 , 280°C, 1.80% fresh CuCr catalyst) as a function of sodium laurate contamination level. The percentage relative conversion of methyl ester vs. the sodium laurate level appears in Figure 2. These data were generated using fresh copper chromite catalyst, reduced through its use in the hydrogenation

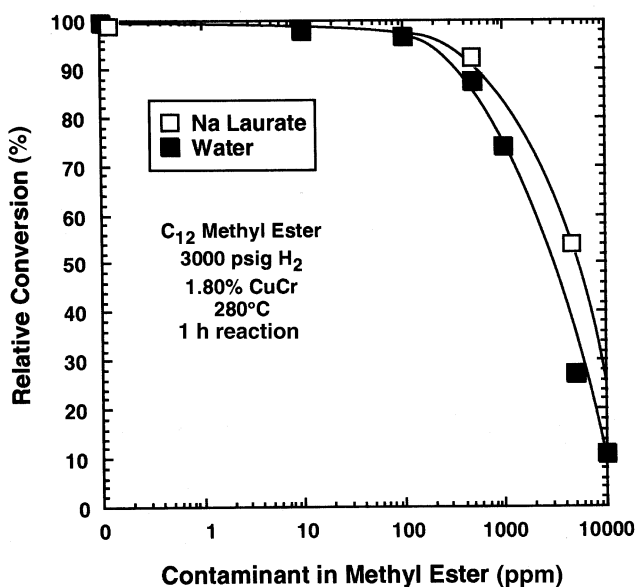


FIG. 2. Relative conversion of dodecyl methyl ester vs. level of water and soap contamination.

tion reaction. It is believed that the mechanism by which soap deactivates the catalyst is similar to that suggested for water, i.e., active site occlusion and reduction inhibition. High-purity methyl ester feed containing minimal levels of fatty soap is key in maintaining high catalyst activity and hydrogenation reaction rate.

Effect of glycerine and monoglyceride. In the generation of methyl ester via the methylation of triglycerides, low levels of both glycerine and glycerides in the methyl ester product may exist. Various unit operations (water washing, distillation, etc.) may be used to further purify the methyl ester prior to its hydrogenation to alcohol product. In the following section, the inhibition effects of both glycerine and monoglyceride are discussed. It is well known that glycerine and glycerides (mono-, di-, and tri-) may inhibit the activity of copper chromite catalyst, significantly reducing the conversion of methyl ester to alcohol product (1). However, it is not clear if it is these components, or their reactive/decomposition intermediates that cause catalyst inhibition. The effect of intermediate components is discussed in a later section.

Glycerine. Dodecyl methyl ester was hydrogenated, under batch conditions, in the presence of various levels of glycerine. In each case, the catalyst was fresh copper chromite, reduced during the hydrogenation reaction. Figures 3, 4, and 5 are plots of the methyl ester depletion by hydrogenation, dodecanol product generation, and the generation and depletion of the intermediate fatty-fatty ester dodecyl dodecanoate, respectively.

There is significant reduction in the hydrogenation reaction rate as the level of glycerine in the feed methyl ester is increased. At or near the 5% glycerine level, the hydrogenation reaction is almost completely suppressed. This may be more clearly seen in Figure 5, which profiles the intermediate dodecyl dodecanoate generation (transesterification) and de-

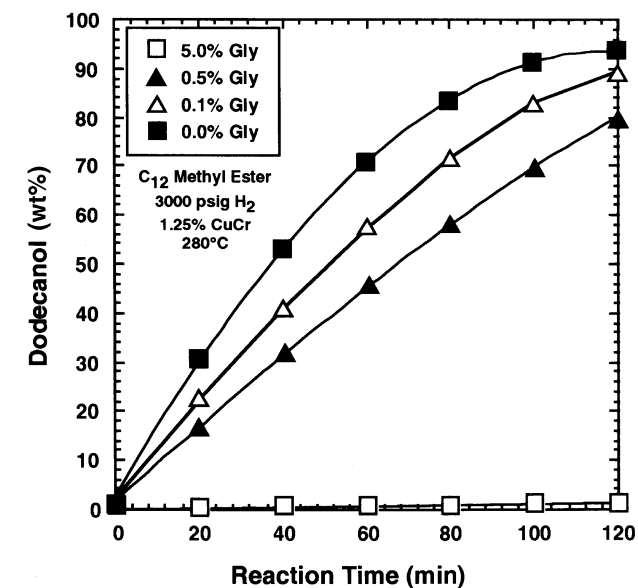


FIG. 4. Dodecanol generation vs. time as a function of glycerine (Gly) contamination.

pletion by hydrogenation. As the alcohol generation decreases with increasing glycerine level, so follows the generation of the fatty-fatty ester, the appearance of its maximal level increasingly delayed. Behavior of this glycerine-spiked system is similar to hydrogenations under unfavorable thermodynamic conditions, i.e., low H_2 pressure or low temperature.

Monoglyceride. Varying levels of monoglyceride were added to batch hydrogenation reactions of fatty methyl ester to fatty alcohol. The monoglyceride was the 1-monolauryl-rac-glycerol. The catalyst, which was fresh copper chromite, was reduced during the hydrogenation reaction. The limiting

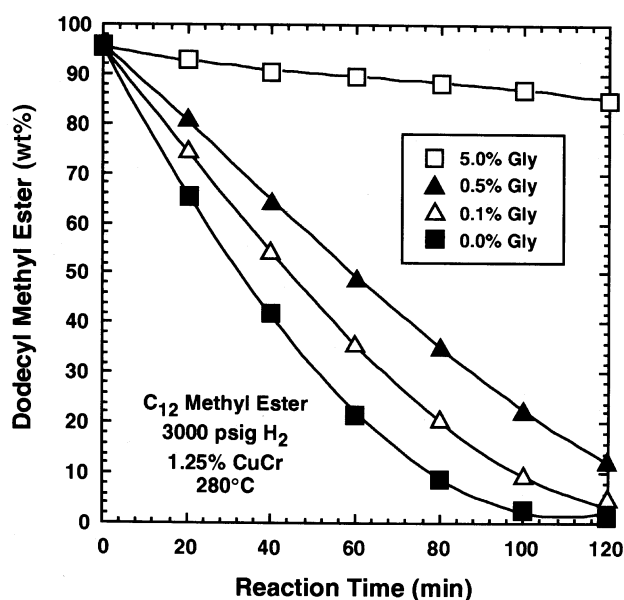


FIG. 3. Dodecyl methyl ester hydrogenation (depletion) vs. time as a function of glycerine (Gly) contamination.

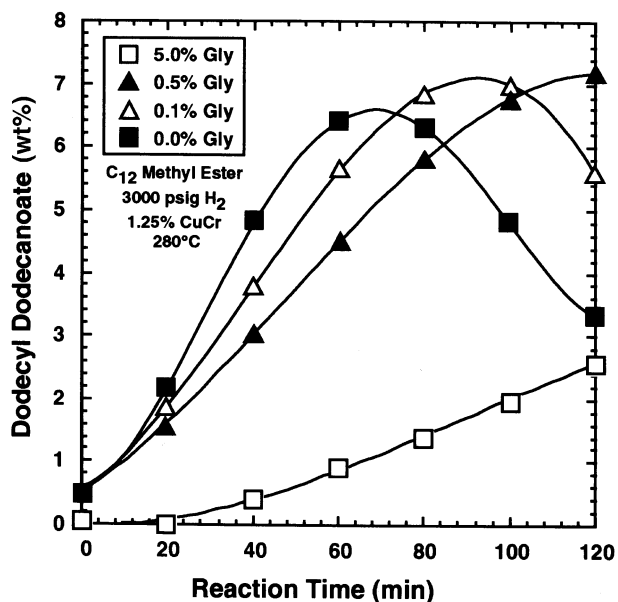


FIG. 5. Dodecyl dodecanoate generation and depletion vs. time as a function of glycerine (Gly) contamination.

effect of the monoglyceride upon the hydrogenation of dodecyl methyl ester, the generation of dodecanol alcohol product, and the generation/depletion of the fatty-fatty ester dodecyl dodecanoate component follows similar profiles as presented for glycerine. As in the previous case with glycerine, suppression of the methyl ester hydrogenation rate is observed, resulting in generation of lower amounts of the alcohol product. Again, the latent appearance of the fatty-fatty ester dodecyl dodecanoate results from the slower hydrogenation rate.

It is of interest to compare the effects of both glycerine and the monoglyceride. As will be discussed shortly, the reaction products of both compounds may cause deactivation through the same mechanism. In Figure 6, the final saponification values for the hydrogenation of dodecyl methyl ester to dodecanol alcohol product (2-h reaction under the indicated conditions) are plotted against various molar concentrations of both glycerine and monoglyceride. Pure dodecyl methyl ester has a saponification value of ~253. It appears that, on a molar basis, the limiting effect of glycerine and monoglyceride on hydrogenation is the same. This suggests that the molecular interaction with the copper chromite surface may be the same for both molecules or that both molecules may form a common intermediate that interacts with the surface sites. The latter theory is favored since the overall structure of both species is so different, i.e., 3-carbon chain vs. a 15-carbon chain. The following section discusses the potential decomposition chemistries of both glycerine and monoglyceride to form intermediates that may interact with the catalyst surface. The catalyst surface interaction of these intermediates is discussed in detail.

Glycerine/monoglyceride decomposition chemistry. In the alcohol product distillation purification step that often follows

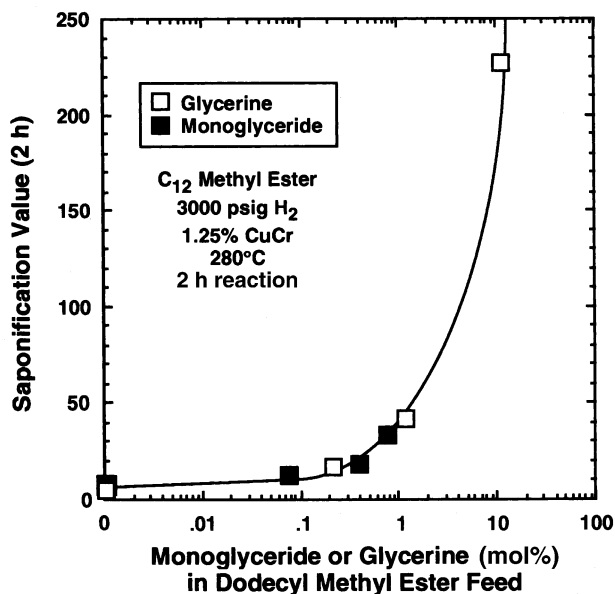


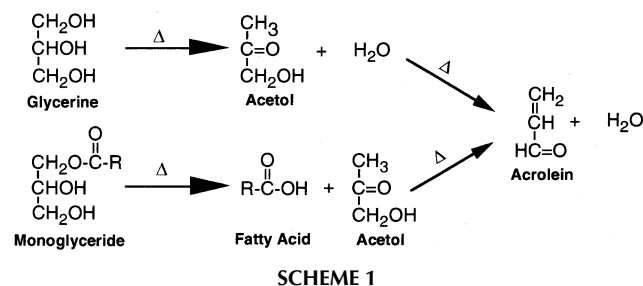
FIG. 6. Final saponification value vs. mole percentage glycerine or monoglyceride contamination. Pure dodecyl methyl ester has a saponification value of ~253.

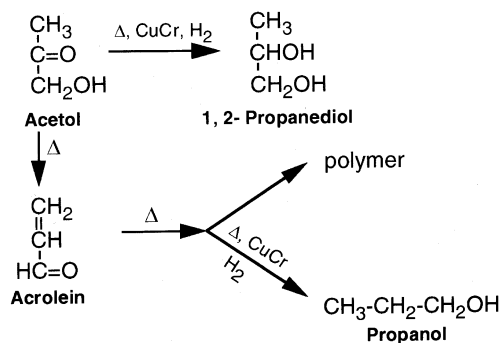
methyl ester hydrogenation, low levels of propanol have been detected in a number of commercial processes. In the works of Hurd (3) and Miner and Dalton (4), the thermal decomposition of glycerine is suggested, with the accompanying route for monoglyceride decomposition, as shown in Scheme 1. In both cases, acetol is formed as the transient intermediate. Acetol is then further reduced to form acrolein. In the presence of hydrogen and copper chromite catalyst, acetol and acrolein may easily be reduced to the 1,2- propanediol and propanol, as shown in Scheme 2. The low levels of propanol that may be found in distilled alcohol product are derived from the thermal decomposition of either glycerine or the monoglyceride. Acrolein, in the absence of inhibitors, may also easily polymerize to highly cross-linked solids (5) which are infusible and insoluble in common solvents.

Effect of propanol and propanediol. Dodecyl methyl ester was hydrogenated under batch conditions in the presence of propanol and, separately, 1,2-propanediol. In these cases, the catalyst was fresh, reduced during the hydrogenation reaction. As expected, propanol was found to have no rate-limiting effect upon the hydrogenation of methyl ester to alcohol product. It does not appear that this monohydroxyl compound interacts with the catalyst surface in a way that limits the activity of the catalyst.

Acetol and acrolein have little chance of existing under the conditions for the hydrogenation of methyl ester. However, in considering the hydrogenation of methyl ester containing 1% of the polyhydroxyl contaminant, 1,2-propanediol, there is a limiting effect upon the rate of hydrogenation of the methyl ester, as shown in Figure 7. This effect also exists for the generation of the alcohol product, dodecanol. As expected, the generation and depletion of the fatty-fatty ester dodecyl dodecanoate is similarly limited, owing to the generation of lower amounts of alcohol. Although not shown, the same results are obtained when hydrogenating methyl ester in the presence of 1% 1,3-propanediol.

Catalyst activity recovery. A series of three batch hydrogenations of dodecyl methyl ester was performed to determine whether copper chromite activity loss from glycerine is recoverable (3000 psig H₂, 280°C, 1.80% copper chromite catalyst). Consider the following experimental series of methyl ester hydrogenations: Run 1: fresh copper chromite catalyst used to hydrogenate dodecyl methyl ester, in the absence of glycerine (conversion = 90.6% @ 45 min reaction time); Run 2: reaction product of Run 1 drained from reactor,





SCHEME 2

leaving original catalyst charge, recharged with methyl ester and 5% glycerine (conversion = 58.3% @ 45 min reaction time); and Run 3: reaction product of Run 2 drained from reactor, leaving original catalyst charge, followed by multiple washes with heated methanol, recharged with methyl ester and 0% glycerine (conversion = 93.7% @ 45 min reaction time).

The first hydrogenation, in the absence of glycerine, was typical. The hydrogenation goes to near completion, with the latent decrease in fatty-fatty esters, as seen in Figure 5. As expected, the addition of 5% glycerine to the second run drastically reduces catalyst activity and the corresponding reaction degree of completion. With multiple hot methanol washes of the catalyst charge, the catalyst activity rebounds to a level comparable to its original.

The response of the catalyst to the methanol washes confirms that glycerine and its corresponding decomposition products are temporary catalyst poisons which, when removed from the catalyst surface, allow complete activity recovery. The same conclusion may be made for the monoglyceride species.

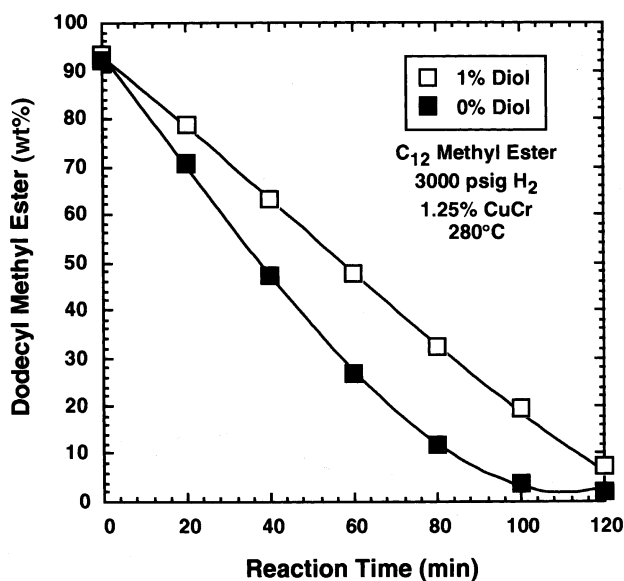


FIG. 7. Hydrogenation of dodecyl methyl ester with time in the presence or absence of 1,2-propanediol.

A distinction should be made concerning catalyst activity loss in the presence of these compounds. As discussed for the presence of water, the question remains as to whether these components inhibit the reduction of fresh catalyst to its active state, physically adsorb occluding active sites, or both. Consider the hydrogenation of dodecyl methyl ester under the following three conditions (3000 psig H_2 , 280°C, 1.25% copper chromite catalyst): Condition 1: Hydrogenation of methyl ester using fresh catalyst that is reduced to its active form during the reaction. There is no glycerine present in this case (conversion = 91.6% @ 45 min reaction time). Condition 2: Hydrogenation of methyl ester using fresh catalyst that is reduced to its active form during the reaction. There is initially 5% glycerine present in this case (conversion = 10.4% @ 45 min reaction time). Condition 3: Hydrogenation of methyl ester using the same catalyst used in Condition 1 (now fully reduced), however, in the presence of 5% glycerine (conversion = 58.3% @ 45 min reaction time).

Clearly, fresh unreduced catalyst subjected to contaminant glycerine incurs a significant inhibition of catalyst reduction to its active form. This may be seen in comparison to the case of reduced catalyst subjected to glycerine. Although activity loss by physical adsorption is certainly significant (Condition 3), loss due to catalyst reduction inhibition is dominant in the use of fresh catalyst.

In summary, extensive methyl ester hydrogenation experiments, in the presence of glycerine or monoglyceride, indicate that there exists a common thermal decomposition product which may hydrogenate to propanediol. There is a potential for the diol to react with unreduced surface copper. However, under the conditions of methyl ester hydrogenation, such a complex would likely not survive to cause permanent activity loss. Rather, activity loss is probably due to site occlusion by physical adsorption of the polyhydroxyl compound.

Polyhydroxyl compounds such as glycerine or the diols are extremely oleophobic and, given the opportunity, prefer to reside on the catalyst surface rather than remain in the reacting liquid. Levels as low as 0.1% may significantly reduce the rate of methyl ester hydrogenation.

Catalyst activity may be completely recovered by removal of the components adsorbed on the catalyst sites, shown by washing the catalyst with heated methanol to restore activity. In practice, activity recovery should occur with continued catalyst use in the absence of inhibitors.

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