The Effect of Free Fatty Acid on the Reactivity of Copper-Based Catalysts for the Hydrogenolysis of Fatty Acid Methyl Esters

Frank Th. van de Scheur[a], Guido U-A Sai[a], Alfred Bliek[a] and Leendert H. Staal[a,b,]*
[a]Department of Chemical Engineering, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands and [b]Unipath Ltd, Norse Road, Bedford MK41 OQG, United Kingdom

ABSTRACT: In the synthesis of fatty alcohols by hydrogenolysis of fatty acid methyl esters, small amounts of free fatty acids in the feed negatively affect the reactivity of copper-silica based catalysts. The effect of the acid was investigated in relation to the production of water, the nature of the inhibiting species, and the degree of reduction of the catalyst. Inhibition is reversible and not due to catalyst deactivation. Water is not the inhibiting species. Furthermore, formation of copper and zinc soaps was excluded. Lauric acid in the methyl ester feed reacts preferentially, but at a lower rate than the ester. Inhibition most likely stems from a preferential adsorption of the acid at the active sites of the catalyst. The consequences for practical applications are discussed.

JAOCS 72, 1027–1031 (1995).

KEY WORDS: Catalyst, copper, ester, hydrogenolysis, lauric acid, methyl palmitate, palmitic acid, reactivity, silica, water, zinc.

Fatty alcohols are important intermediates in the synthesis of surfactants. The increasing production of palm kernel oil in the Pacific Rim has renewed interest in the synthesis of fatty alcohols from natural feedstocks. Current technology for this reaction is based on slurry (1,2) or fixed-bed (3) hydrogenation of fatty acid methyl esters at pressures between 200 and 300 bar in the presence of copper–chromium oxide catalysts. Direct hydrogenation of fatty acids on copper-based catalysts also has been reported in the patent literature (4). However, esters are usually preferred to acids, because most copper-based catalysts are not sufficiently acid-resistant.

Current issues in the hydrogenolysis of methyl esters are the development of processes that work at pressures below 100 bars and the search for alternatives for chromium as a promoter in the catalyst. We have demonstrated the feasibility of lower process pressures in the liquid phase if the reaction is performed in an inert solvent, such as *n*-octane or a mineral white oil (5). As for the development of improved catalysts, zinc has been shown to be a feasible promoter in silica-supported copper catalysts for the ester hydrogenolysis (6).

The natural origin of the raw materials, e.g., coconut oil or palm kernel oil, has distinct consequences for the preparation of the feed for industrial fatty alcohol synthesis. Methyl esters can be prepared by direct transesterification of triglycerides with methanol. Consequently, the methyl ester feed consists of a mixture of esters, corresponding to the naturally-occurring range of fatty acid residues in the triglycerides. Prior to the preparation of methyl esters, extensive purification of the oil is required because of the presence of free fatty acids, phospholipids, protein residues, and metal salts. After the purification and conversion to methyl esters, the feed is essentially free of contaminants, except for an unavoidable content of free fatty acids. However, little is known about the particular influence of fatty acid on ester hydrogenolysis. The aim of this study is to gain further insight in the influence of free fatty acids on the performance of the silica-supported copper–zinc oxide catalyst. The hydrogenolysis of methyl palmitate was taken as a model reaction.

EXPERIMENTAL PROCEDURES

Catalyst preparation. A 14 wt% Cu/9 wt%ZnO/SiO_2 catalyst was prepared by homogeneous precipitation of copper and zinc nitrates onto silica. Support particles (sieve fraction 75–125 μm were obtained by grinding silica spheres; Shell S980A, Gent, Belgium). Copper(II)nitrate trihydrate and zinc(II)nitrate tetrahydrate were obtained from Merck (Darmstadt, Germany), and urea (p.a.) from Aldrich (Milwaukee, WI). The pH was raised from its initial value of 3 to the final value of pH 7 by the decomposition of urea at 363 K. The resulting precipitate was washed repeatedly with distilled water and dried for at least 16 h at 383 K. For comparison, an unpromoted 14 wt%Cu/SiO_2 catalyst was prepared in an analogous way.

Methyl ester synthesis and purification. Methyl palmitate was prepared according to the method of Harrison *et al.* (7). Methyl palmitate was further refined by washing with a dilute aqueous solution of sodium hydroxide to remove free fatty acids and other possible contaminants. After drying on sodium sulfate, the methyl palmitate was distilled under vacuum to achieve further purification. The result was methyl palmitate of 99.95% purity (acid value 0.1 mg KOH/g ester).

---

*To whom correspondence should be addressed at Unipath Ltd., Norse Road, Bedford MK41 OQG, United Kingdom.

Continuous-flow experiments. Activity testing was performed in a high-pressure flow reactor described elsewhere (8). A tubular flow reactor of 2 mm i.d. was filled to a bed length of 130 mm with a mixture of 100 mg of the catalyst precursor (75–125 μm) and 130 mg Shell S980A silica (75–125 μm). The entrance of the reactor was filled with silicon carbide (175–210 μm), and both ends of the reactor were fixed with plugs of quartz wool. The catalyst was calcined in an air flow of 1 mL/s by heating at 0.02 K/s to 750 K for 12 h and reduced in a hydrogen flow of 1 mL/s (Praxair 99.999%; Praxair, Hoofddorp, The Netherlands) by heating at 0.02 K/s to 600 K with a dwell time of 12 h.

The feed was prepared by dissolving appropriate amounts of methyl palmitate and *n*-heptadecane (Aldrich 12,850-3) in *n*-octane (Janssen 23.242.59; Janssen Chimica, Tilburg, The Netherlands). The *n*-octane was distilled under nitrogen in the presence of liquid sodium. Standard feed contained 20 mmoles/L of methyl palmitate and 1 mmoles/L *n*-heptadecane as internal standard in *n*-octane. To create an artificial acid value in designed experiments, small amounts of palmitic acid (Merck art. 800508) or lauric acid (Unichema Chimica BV, Gouda, The Netherlands) were added to the feed. Hydrogen was dissolved in a mixing vessel (Hofer DR1 autoclave; Andreas Hofer GmbH, Düsseldorf, Germany), at 80 bar and room temperature. The saturated liquid was fed to the reactor by a Waters 510 HPLC pump (Waters Associates, Milford, MA). The reactor was operated in the upflow mode, and the effluent was collected in a gas–liquid separator, which was kept at an argon pressure of 100 bar.

Product analysis. In the hydrogenolysis reaction, only two reaction products were detected—cetyl alcohol and cetyl palmitate. Liquid samples were analyzed by capillary gas chromatography in a Carlo Erba (Rome, Italy) Mega Series HRGC 5300 gas chromatograph equipped with a J&W Scientific (Folsom, CA) DB1 megabore column (length 15 m, i.d. 0.53 mm, film thickness 0.15 μm). Helium (Praxair, 99.9999%) was used as carrier gas. In a typical analysis, the gas chromatograph oven temperature was kept constant for 3 min at 353 K and subsequently raised to 573 K at a rate of 0.17 K/s. Methyl palmitate conversions were calculated from the peak areas by using the mass balance and the relative molecular response factors published by Ackman and Sipos (9). Conversions of methyl palmitate calculated from the mass balance were always in agreement with conversions of methyl palmitate calculated from the internal standard. The presence of copper and zinc soaps in the reactor effluent was investigated by extraction of the solution in *n*-octane with a citric acid solution in water. Aqueous solutions were analyzed by inductively coupled plasma–atom emission spectrometry (ICP/AES).

RESULTS AND DISCUSSION

Effects of fatty acid on catalyst activity were investigated by addition of varying amounts of lauric acid to the methyl palmitate feed. Lauric acid, having twelve carbon atoms, was selected to detect product formation from the acid among reaction products from methyl palmitate, which contains sixteen carbon atoms in the acyl residue. Results of the activity measurements are depicted in Figure 1. As a general feature, after an initial stabilization time, conversion of methyl palmitate is stable over the time on stream. However, lower steady-

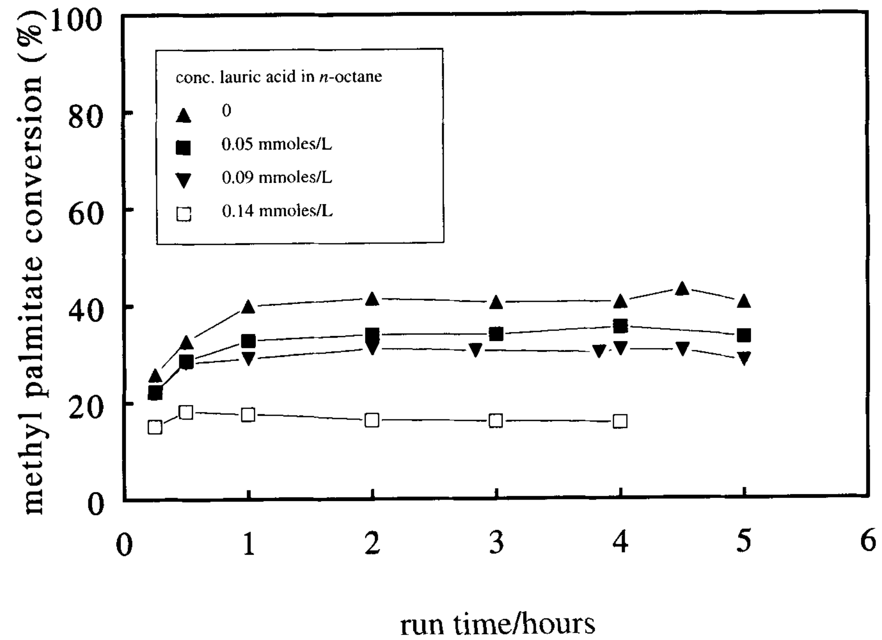

FIG. 1. Effect of the addition of small amounts of lauric acid to a feed containing methyl palmitate. Conditions: Catalyst weight divided by molar flow of methyl palmitate (direct measure of the residence time) (*W/F*) = 250 kg catalyst (cat.) s/mole, $C_{ester + acid}$ (293 K, 1 atm) = 20 mmoles/L, $T_{reactor}$ = 470 K.

state catalyst activities are observed at higher concentrations of lauric acid in the feed. As shown in Figure 1, a decrease in methyl palmitate conversion from 41 to 34% is found at a lauric acid concentration as low as 0.05 mmoles/L in *n*-octane. This concentration of lauric acid corresponds to 0.25% of the methyl palmitate concentration (20 mmoles/L) in the feed. At a lauric acid concentration of 0.14 mmoles/L, a methyl palmitate conversion of only 16% is observed.

As to product formation from the acid, analysis by ICP/AES showed copper and zinc to be absent in the reactor effluents. Hence, soap formation has not occurred. The high hydrogen concentration prevents formation of copper- and zinc-laurates. This is to be expected for copper metal and even for oxidic copper, but is not obvious for oxidic zinc species at the catalyst surface.

In addition to forming a soap, lauric acid can be converted by esterification and hydrogenation reactions. Lauric acid esters were not detected, but the presence of lauryl alcohol in the reactor effluent was established by gas-chromatographic analysis. Yield of lauryl alcohol was up to 75% of the amount of lauric acid in the feed. In contrast, the conversion of the methyl ester was between 18% and 40%, depending on the acid concentration. Apparently, lauric acid reacts preferentially to methyl esters.

In view of the stable methyl palmitate conversion as a function of the time on stream, the detrimental effect of acid on the catalyst reactivity is rather due to inhibition of the reaction rather than to catalyst deactivation. This is confirmed by the recovery of the original reactivity, which is shown in Figure 2. At a feed of 20 mmoles/L methyl palmitate (99.95% purity) in *n*-octane, the average methyl palmitate conversion was about 60%. In a subsequent experiment, a mixture of 0.8 mmoles/L of palmitic acid and 20 mmoles/L of methyl palmitate in *n*-octane was used as the feed. A relatively high concentration of palmitic acid, not representative for practical applications, was chosen to obtain a substantial effect. In this case, the methyl palmitate conversion was about 20%, which remained constant as a function of the time on stream. Apparently, no irreversible deactivation had occurred by the addition of palmitic acid. To verify this, the same catalyst was used in a subsequent experiment with pure methyl ester feed. The methyl palmitate conversion turned back to the original conversion level of 60%. Hence, addition of acids has an inhibiting effect on the rate of the reaction, rather than a deactivating influence on the catalyst. The lower reactivity in the presence of 0.8 mmoles/L of palmitic acid was reproducible.

Hydrogenation products or surface species originating from fatty acid can be responsible for inhibition of ester hydrogenolysis. As suggested by Daage and Bonnelle (10), surface hydroxyl groups cannot be excluded as inhibiting species for hydrogenation reactions on copper-based catalysts. Furthermore, water is formed in the hydrogenation of palmitic acid. As product analysis did not include the determination of water in reactor effluents, the influence of water on the reactivity was studied by the addition of water to the feed. For a good comparison, the concentration of water was chosen equal to the acid concentration in the preceding experiment with added palmitic acid. As is shown in Figure 2, the methyl palmitate conversion in the presence of water is equal to the methyl-palmitate conversion in the first standard experiment without water. Because water has no influence, the negative effect of palmitic acid on the rate of reaction is thought to stem from the adsorption of the acid itself or from inhibition by a surface intermediate directly related to the acid.

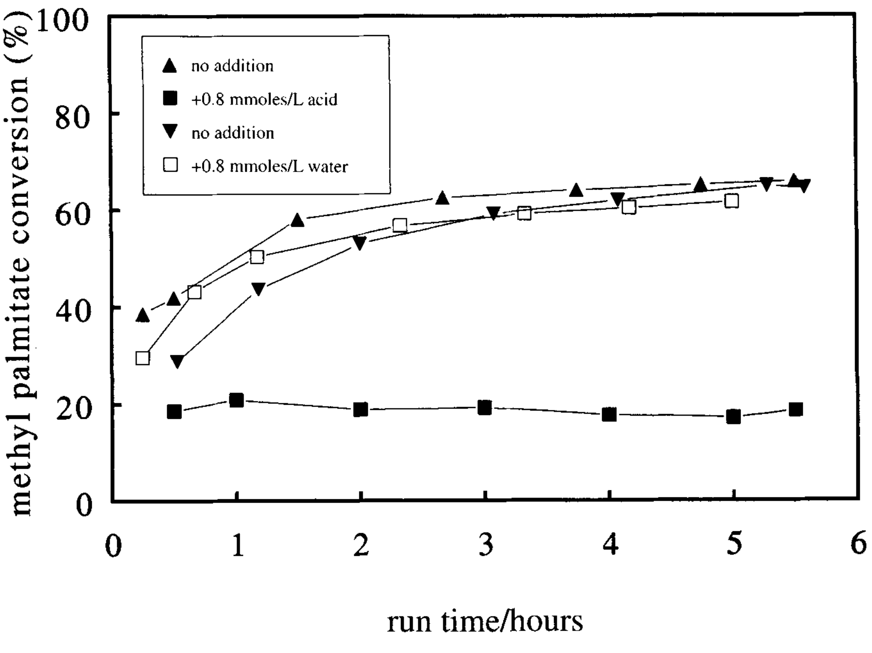

FIG. 2. Effect of the addition of palmitic acid and water to a feed containing methyl palmitate. Conditions: *W/F* = 500 kg cat. s/mole, C_{Ester} (293 K, 1 atm) = 20 mmoles/L, $T_{reactor}$ = 470 K. See Figure 1 for abbreviations.

Inhibition by the acid was suggested by Thomas *et al.* (11), who investigated the effect of water on the reactivity of a Raney copper catalyst in the hydrogenolysis of dimethyl succinate. The inhibition of the reaction was proposed to stem from the formation of succinic acid or succinic anhydride. The present experimental results give evidence of the negative effect of the acid on the rate of ester hydrogenolysis. The absence of an effect of water in this study may be connected with the presence of a silica support or with the use of *n*-octane as a solvent. In the patent literature, Poels *et al.* (12) have reported positive effects of water addition on the stability of a copper-based catalyst in the fatty alcohol synthesis. Hence, water may bring about different effects, depending on the choice of the catalyst and the experimental conditions.

As for the nature of adsorbed species, there is ample support from the literature. Fatty acids will bind to copper metal and to oxidic species. Insight in the interaction of a fatty acid with a copper metal surface is provided by the work of Hu *et al.* (13), who studied the adsorption of stearic acid on copper surfaces with Fourier-transform infrared and raman spectroscopy. Adsorption on copper metal appeared to be mainly physisorption, and an oxide film strongly promoted chemisorption. Rapid chemisorption of stearic acid was observed at 433 K, resulting in the formation of a cupric stearate surface film. Additional information on the adsorption of acids on copper surfaces is furnished by Rynkowski *et al.* (14). Evidence of carboxylate formation was found as a result of the reaction of benzoic acid with an oxidized copper surface. The chemisorption of an acid on copper under hydrogenation conditions has been discussed by Svachula *et al.* (15), who studied the kinetics of the double-bond hydrogenation of acrylic acid on a copper catalyst. Adsorption of the carboxylic group was proposed to be the first elementary step in this reaction.

A specific aspect of catalyst preparation by homogeneous precipitation is the low catalyst reducibility. The degree of reduction of copper in the $Cu/ZnO/SiO_2$ catalyst is typically around 90% after reduction at 600 K. Experiments were performed with an unpromoted Cu/SiO_2 catalyst to discriminate between acid adsorption at oxidic sites and acid adsorption at copper metal sites. This catalyst was severely reduced at 750 K for 12 h, aiming at complete elimination of positively charged copper. Figure 3 shows the conversion of methyl palmitate as a function of the run time for the severely reduced Cu/SiO_2 catalyst. In the presence of palmitic acid, the conversion of methyl palmitate is much lower than the methyl palmitate conversion in its absence. Clearly, inhibition of the reaction by the acid occurs on copper metal sites. The presence of oxidic sites is apparently not required for acid chemisorption, as was suggested by previous studies.

The reaction steps of surface intermediates in ester hydrogenolysis have been proposed to proceed on copper metal (16). In contrast to the acid, esters bind to copper surfaces by dissociation, forming acyl and methoxy groups. The carboxylate species will be more stable than the acyl species, hence the inhibiting effect of the acid on ester hydrogenolysis. The negative effect of the acid on the activity of the Cu/SiO_2 catalyst is comparable to the effect on the $Cu/ZnO/SiO_2$ catalyst (Figure 2). This suggests that, for the zinc-promoted catalyst, copper metal crystallites form the stage for reaction of the ester and inhibition by the acid. Apparently, the acid and the ester compete for the same active sites. The inhibition of the reaction rate by small amounts of fatty acid is highly relevant to practical applications of ester hydrogenolysis. Commer-

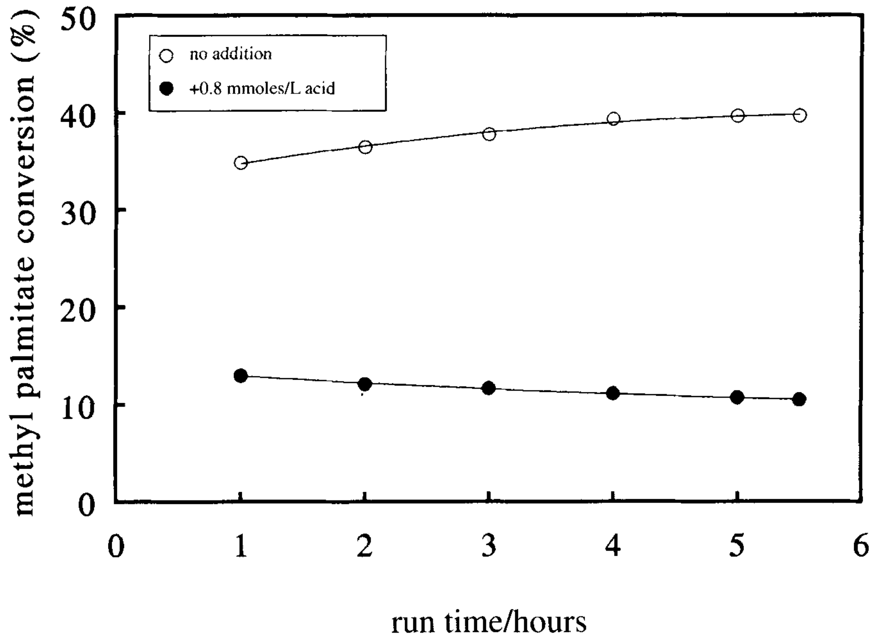

FIG. 3. The effect of palmitic acid on the activity of a severely reduced Cu/SiO_2 catalyst in the hydrogenolysis of methyl palmitate. Conditions: *W/F* = 250 kg cat. s/mole, C_{Ester} (293 K, 1 atm) = 20 mmoles/L, $T_{reactor}$ = 470 K. See Figure 1 for abbreviations.

cially available feedstocks have acid values around 1 mg KOH/g methyl ester (99.5% purity). Deacidification down to an acid value below 0.1 mg KOH/g methyl ester (99.95% purity) is highly recommended, and might be essential for a low-pressure solvent process.

Against the background of this study, it is important to note that direct fatty acid hydrogenation is also practiced. The feasibility of fatty acid hydrogenation seems to be in contradiction to the current experimental results, which clearly show inhibition by the acid. However, this discrepancy does not exist in practice. The Lurgi process for fatty alcohol synthesis operates in the slurry phase, and fatty acids are mixed with a 250-fold excess of fatty alcohol (1,2). Wax esters are formed in the first stage of the reactor, before the hydrogenolysis reaction actually starts. Subsequently, these wax esters are converted to fatty alcohols. This procedure counteracts acid attack on the catalyst and prevents soap formation. In general, stable surface carboxylate formation is thus avoided. However, it seems inevitable that, also in the hydrogenolysis stage, some free fatty acid is present. Accordingly, the negative effect of acid on the catalyst activity is relevant both for methyl ester hydrogenolysis and for fatty acid hydrogenation.

REFERENCES

1. Buchold, H., *Chem. Eng. 90*:42–43 (1983).
2. Voeste, Th., and H. Buchold, *J. Am. Oil Chem. Soc. 61*:350–352 (1984).
3. Eierdanz, H. in *Proceedings of the World Conference on Oilseed Technology and Utilization*, AOCS Press, Champaign, 1993, pp. 217–220.
4. Schuett, H., U.S. Patent 4,804,790 (1989).
5. van de Scheur, F.Th., J.J. Vreeswijk and L.H. Staal, in *Proceedings of the World Conference on Oilseed Technology and Utilization*, AOCS Press, Champaign, 1993, pp. 453–457.
6. van de Scheur, F.Th., and L.H. Staal, *Applied Catalysis 108*:63–84 (1994).
7. Harrison, J., *Chemistry and Industry 1968*, 1968, p. 1568.
8. Bonné, R.L.C., Ph.D. Thesis, Hydrodemetallisation of Ni-TPP and VO-TPP over Sulfided Molybdenum and Vandium Catalysis, University of Amsterdam, Amsterdam, 1992.
9. Ackman, R.G., and J.C. Sipos, *J. Chromatog. 16*:298–305 (1964).
10. Daage, M., and J.P. Bonnelle, *Appl. Catal. 16*:355–374 (1985).
11. Thomas, D.J., D.L. Trimm, M.S. Wainwright and N.W. Cant, *Chem. Eng. and Proc. 31*:241–245 (1992).
12. Poels, E.K., D.R.E. Polman and J.J. Vreeswijk, GB Patent 2250287 A1 (1992).
13. Hu, Z.-S., S.M. Hsu and P.S. Wang, in *Surface Science Investigations in Tribology*, edited by Y.-W. Chung, A.M. Homola and G.B. Street, A.C.S. Symposium Series 485, 1992, pp. 195–216.
14. Rynkowski, J.M., S. Affrossman, J.M.R. McAllister and R.A. Pethrick, *Surf. Sci. 182*:1–18 (1987).
15. Svachula, J., J. Tichy and J. Machek, *Appl. Catal. 38*:53–59 (1988).
16. Kohler, M.A., N.W. Cant, M.S. Wainwright and D.L. Trimm, in *Proceedings of the 9th International Congress on Catalysis*, Vol. 5, edited by M.J. Phillips and M. Ternan, Calgary, 1988, pp. 1043–1050.

[Received September 9, 1994; accepted June 5, 1995]