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Catalytic Deoxygenation of Fatty Acids: Elucidation of the Inhibition Process

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Catalytic deoxygenation of unsaturated fatty acids in the absence of H_2 is known to suffer from significant catalyst inhibition. Thus far, no conclusive results have been reported on the cause of deactivation. Here we show that C=C double bonds present in the feed or the products dramatically reduce the deoxygenation activity of supported palladium catalysts. In the case of stearic acid deoxygenation the addition of 0.1 equivalents of a mono-unsaturated fatty acid or olefin already reduces the catalytic deoxygenation activity by 60%. This effect becomes more pronounced with an increasing number of double bonds. The inhibition is shown to be reversible in H_2 atmosphere, indicating no significant contribution from irreversibly deposited hard coke. Furthermore, the type of support material has no apparent effect on catalyst inhibition. Hence we propose that initial catalyst inhibition proceeds through reversible adsorption of C=C double bonds on the palladium active sites.

Introduction

Fossil resources such as coal, oil, and gas have contributed greatly to our modern lifestyle and will continue to do so in the coming decades. To ensure a lasting supply of energy for the longer term, we will increasingly depend on renewable resources such as biomass. Science and industry are working together to turn biomass into, for instance, biofuels that are compatible with the existing distribution infrastructure and engine technologies.

Vegetable oil-based feedstocks have gained significant interest as a sustainable resource for the production of fuels and chemicals, mainly owing to their high energy density and structural similarity to petroleum-based fuels. As such, the implementation of these compounds would require minimal changes in the present infrastructure and the internal combustion engine, which is highly beneficial for the introduction of new technologies. Especially the use of non-edible or waste fats and oils are of interest as this will not interfere with the food production.

The use of (nonrenewable) H_2 is to be avoided for the design of a sustainable process, because this has impact on the environmental footprint. H_2-free deoxygenation has been investigated frequently, and although demonstrating much potential in the deoxygenation of saturated feeds,[1] complications were reported with the use of more practical feedstocks.[2] Catalyst deactivation appeared more severe during H_2-free deoxygenation reactions and was regularly related to the presence of unsaturated compounds. Decreasing H_2 pressure during the reaction resulted in an increasing amount of unsaturated compounds and more severe catalyst deactivation.[1a,b,3] Snåre et al. screened several catalysts and reported faster deactivation if higher selectivity towards unsaturated products was obtained (e.g., if using Ru/C and Rh/C).[4]

Thus far, no conclusive results have been reported on this process of catalyst inhibition and/or deactivation during H_2-free deoxygenation. Several explanations for these phenomena, however, have been proposed in the literature. The formation of unsaturated products often also gives rise to CO in the gas stream as a direct decarbonylation product,[1e,4] which could deactivate the metal phase through poisoning.[5] However, CO poisoning could not explain observations of decreased activity after re-reduction of the spent catalysts.[6]

The formation of irreversibly deposited coke (referred to as hard coke, for example, graphitic carbon or polycyclic aromatic compounds[7]) from unsaturated compounds is also mentioned in the literature as a reason for catalyst deactivation. Lestari et al. reported the presence of trace amounts of aromatic compounds during the deoxygenation of stearic acid over Pd/C, which was related to coke formation and a decreasing surface area of the spent catalyst.[1c] The authors suggested that unsaturated products were the origin of aromatic formation and subsequent coke formation. The formation of alkenylbenzenes as side products (e.g., undecylbenzene) was indeed confirmed during the deoxygenation of fatty acids.[1d,8] Simakova et al. reported decreasing access to palladium metal clusters after catalytic deoxygenation of several fatty acids and related this to coke formation as well.[9]

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Reduced accessibility of active metal clusters could also be explained by the adsorption of unsaturated reactants or (side) products on the catalyst by the C=C double bond in the alkyl chain, as was speculated by Immer et al.[1e] Unlike in the case of hard-coke formation, the inhibition by adsorption of unsaturated reactants could be a reversible process. No further investigation was, however, performed to test and prove this hypothesis.

Ping et al. claimed that adsorption of the feed (stearic acid), solvent (dodecane), and product (heptadecane) diminished the deoxygenation activity.[6] These authors do not relate the inhibition to the presence of unsaturations but to the presence of saturated compounds instead. These conclusions are puzzling because the reduced deoxygenation activity is only reported for recycle runs, but the catalyst is also in contact with saturated compounds during the initial run. To the best of our knowledge, no other reports confirm the inhibition in deoxygenation activity by the strong adsorption of saturated compounds.

In summary, several explanations are proposed to explain the catalyst deactivation during H_2-free deoxygenation: CO poisoning, hard-coke formation, and adsorption of saturated and of unsaturated reactants/products on the catalyst surface (i.e., soft coke[7]). Possibly several of these processes are occurring simultaneously. No conclusive results have, however, been reported thus far that thoroughly elucidate the inhibition process and investigate the effect of feed, products, unsaturations, and CO formation on the inhibition process.

In this work we report on the inhibition process during the deoxygenation of fatty acids over several Pd-based catalysts. We show that inhibition is caused by strong but reversible adsorption of unsaturated molecules by the C=C double bond on the palladium active sites. Inhibition occurs in presence of unsaturated feeds or products as well as with the presence of CO. The inhibition agents are shown to have dramatic effects on the deoxygenation activity even if present in very small quantities. However, the inhibition is demonstrated to be reversible and the presence of H_2 is essential to effectively regenerate the deoxygenation activity.

Results and Discussion

For our study into catalyst inhibition, supported palladium catalysts are chosen, as palladium is reported as the most active metal in H_2-free fatty acid deoxygenation and has been investigated most extensively.[1a, 2a,b, 3a, 4, 11] Furthermore, we used commercially available catalysts for this study to have a constant quality of catalyst over a broad range of experiments.

Pd/SiO_2 and $Pd/\gamma\text{-}Al_2O_3$ were selected because of the different deoxygenation pathways reported for these catalysts (decarboxylation for Pd/Al_2O_3 and combined decarbonylation and decarboxylation for Pd/SiO_2[12]), in combination with the different support properties (e.g., the difference in isoelectric point of 1.7–3.5 for SiO_2 and 7–8 for $\gamma\text{-}Al_2O_3$). Furthermore, Pd/C was also used because it is the most active reported catalyst for the H_2-free deoxygenation of stearic acid.[4]

Table 1. Catalyst properties.

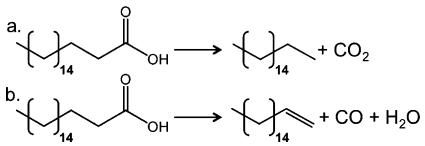
	Pd loading[a] [wt%]	BET surface area[b] [$m^2 g^{-1}$]	Pore volume[c] [$cm^3 g^{-1}$]	Dispersion[d] [%]	Average particle size[e] [nm]
Pd/SiO_2	5.07	218	0.012	6.94	16.1
Pd/Al_2O_3	4.98	106	0.003	9.64	11.6
Pd/C	4.67	n.d.[f]	n.d.	6.88	16.3

[a] Elemental analysis; [b] N_2 physisorption; [c] N_2 physisorption, t-plot micropore volume; [d] H_2 chemisorption; [e] average particle size calculated from the dispersion, as described by Scholten et al.;[10] [f] not determined

Catalyst properties are summarized in Table 1. Catalytic deoxygenation reactions were performed for 20 h at 250 °C under 7 bar N_2 pressure (4 bar at room temperature) unless noted otherwise. Pd/SiO_2 was selected as the main catalyst for this inhibition study because SiO_2 is considered to be chemically inert towards fatty acids under the reaction conditions, and also allows for spectroscopic analysis.

A stepwise investigation is essential to study the effect of potential inhibition agents and to elucidate the process of catalyst inhibition and/or deactivation. The influence of the fatty acid feed on the deoxygenation activity and product selectivity was initially investigated to confirm the relationship between unsaturations and deoxygenation activity, and to investigate the different reactions that occur.

Catalytic deoxygenation of stearic acid (SA, 97% pure) over Pd/SiO_2 results in deoxygenation to heptadecane ($C17_{sat.}$) and heptadecenes ($C17_{unsat.}$) by decarboxylation and decarbonylation, respectively (Scheme 1). In contrast, the catalytic deoxygenation activity drastically decreases if oleic acid (OA, 90%) is used as a feedstock (Figure 1). Note that the oleic acid feed contains stearic acid (≈8%) and some linoleic acid (≈2%) as impurities. No deoxygenation products are observed if using linoleic acid (LL, 99% pure) or linolenic acid (LLN, 71% pure, ≈20% LL, ≈9% OA) as a feed. If linoleic acid is used as feed, the reaction composition also contains 13 mol% oleic acid isomers and 14 mol% of other oxygenates (including mainly linolenic isomers). These are most probably formed by transfer hydrogenation of the feed.



Scheme 1. Deoxygenation pathways of fatty acids (SA shown here) in the absence of H_2 yielding a) a paraffinic product after decarboxylation and b) an olefinic product in the case of decarbonylation.

Double-bond isomerization under the applied reaction conditions poses serious challenges to analyze the products quantitatively by gas chromatography. As an example, peak overlap occurs for linolenic acid isomers with several oxygenates like alcohols, aldehydes, and cyclization products (clustered as "other oxygenates"). The accuracy of the calculated mass bal-

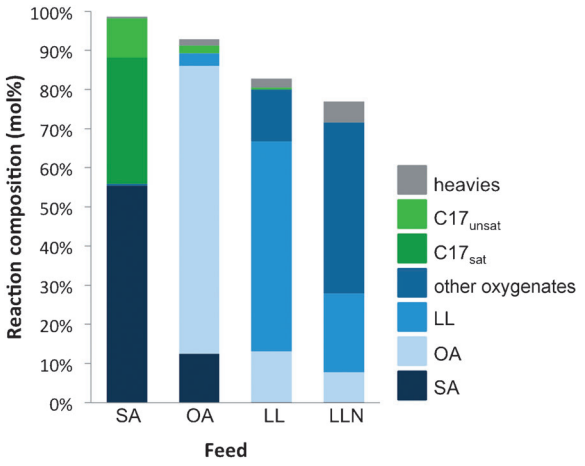


Figure 1. Reaction mixture composition after catalytic reaction of different feeds over Pd/SiO_2.

ance for that reason decreases with increasing amounts of isomers and other oxygenates.

Small amounts of heavies (e.g., stearyl stearate, stearone, and other dimers) are also present in the reaction mixture after reactions with unsaturated feeds, as analyzed by gas–liquid chromatography. The amount of heavies is increasing with the amount of unsaturations in the feed, as shown in Figure 1. Hydrocarbon cracking products (C13–C16 alkanes) were not found in the product mixture.

These results confirm that the presence of C=C double bonds in the feedstock has severe detrimental effects on the deoxygenation activity. A more systematic approach is essential to elucidate the inhibition process, because several potential inhibition products are present in the reaction mixture, such as unsaturated feed and products, heavies and possibly other side products.

The impact of potential inhibition agents was investigated by monitoring the effect of small amounts (0.05–0.6 equiv. relative to stearic acid) of inhibition agent on the turnover number (TON) during the catalytic deoxygenation of stearic acid. In Figure 2, the TONs are shown as a function of the molar equivalents of inhibition agent. Note that TON is defined as conversion to C17 hydrocarbons [mmol] per surface palladium [mmol]. As shown in Figure 2a, the addition of only 0.05 equivalents of oleic acid to the reaction mixture is enough to significantly decrease the TON (>30%), which further deceases to only 6% of the original TON with the addition of 0.4 equivalents oleic acid.

If inhibition is caused solely by the presence of the C=C double bond, comparable inhibition is expected if an olefin is used as inhibition agent. As shown in Figure 2b, pentadecene (C15:1) indeed gives a comparable effect on the TON during the catalytic deoxygenation of stearic acid. These results show that the presence of unsaturated feed and products have a similar inhibiting effect on the deoxygenation activity. This inhibitory effect by unsaturated compounds suggests inhibition initiated by adsorption of the C=C double bond on the catalyst surface and possibly subsequent side reactions or coke formation. In the case of inhibition by competitive adsorption between the carboxyl group and the C=C double bond, the adsorption of the C=C double bond must be irreversible or much stronger than adsorption of the carboxyl group to explain the substantial inhibition at relatively low concentrations.

Except for product inhibition in the presence of olefins, CO poisoning could also occur through adsorption on the palladium metal surface, because Pd/SiO_2 was shown to be also active in fatty acid decarbonylation.[1e,4–5] To investigate the inhibition by CO formation we used hexadecanal as an inhibition agent, which is selectively decarbonylated to form CO and pentadecane (Scheme 2). Comparable mechanisms are reported if using octadecanal or ethanal as the feed with heptadecane and methane as decarbonylation products, respectively.[2d,13]

As shown in Figure 2c, a decrease in TON is observed if hexadecanal was added to the reaction mixture. As GC analysis of the reaction mixture reveals full conversion to pentadecane within 2 h, and as pentadecane itself does not inhibit the reaction (Figure 2d), CO poisoning is indeed inhibiting the deoxy-

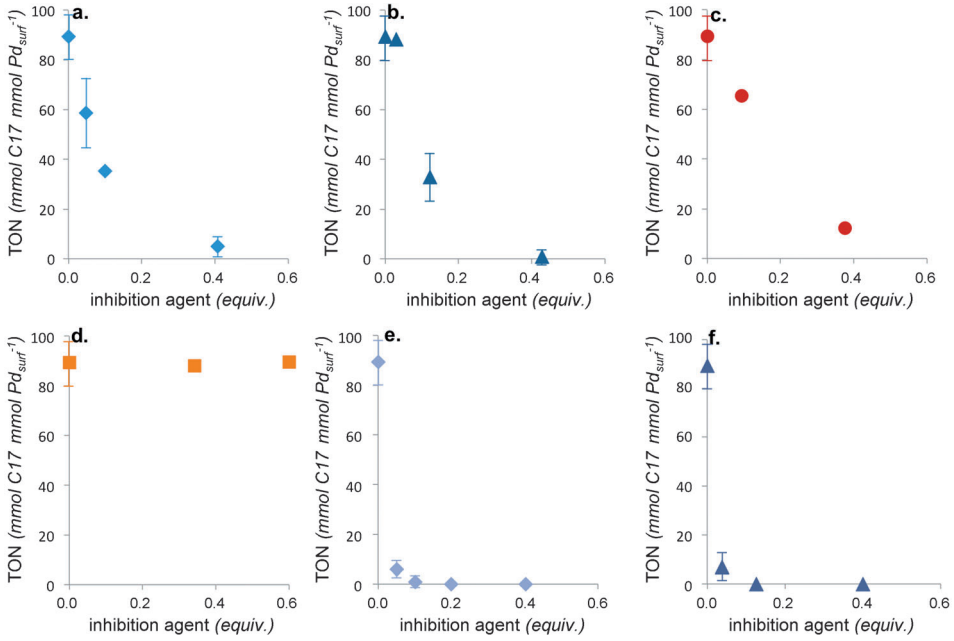
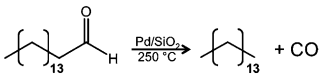


Figure 2. The effect of a) OA, b) pentadecene, c) hexadecanal, d) pentadecane, e) LL, and f) 1,7-octadiene on the TON during SA deoxygenation over Pd/SiO_2. Error bars are shown to illustrate the deviation when multiple experiments are performed.



Scheme 2. Decarbonylation of hexadecanal to CO and pentadecane.

genation activity under inert atmosphere. It should be noted that H_2O is also formed during decarbonylation of fatty acids (Scheme 1), which could decrease CO poisoning, because water-gas-shift reactions would yield H_2 and CO_2 instead.[4,14]

Linoleic acid is used as an inhibition agent to study the effect of multiple unsaturations on the TON. As shown in Figure 2e, the inhibition of linoleic acid on the deoxygenation activity is much stronger than that observed with the mono-unsaturated compounds: the addition of only 0.05 equivalents of linoleic acid already decreases the TON with 95%. The decrease in activity is an order of magnitude higher than with oleic acid or pentadecene. As it is known that linoleic acid adsorbs more strongly on metal surfaces because of the multiple unsaturation (i.e., chelating effect), it is possible that it monopolizes the catalyst surface already at lower concentration.[15] The addition of only 0.05 equivalents of linoleic acid would indeed be enough to cover the total palladium surface of the catalyst. Theoretically, an amount of linoleic acid of only 2 mg $g_{cat.}^{-1}$ would already be enough for a monolayer of linoleic acid on the palladium metal surface.[16]

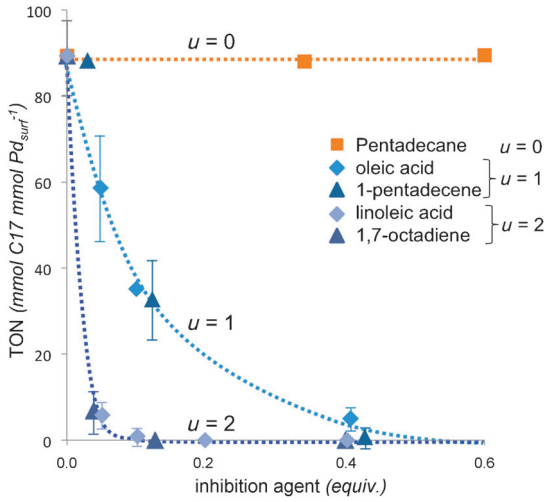


Figure 3. The effect of unsaturations on the TON during SA deoxygenation over Pd/SiO_2. u = Number of unsaturations in the inhibition agent.

As the carboxylic acid group of the fatty acid was shown to have no significant effect on the inhibition process (Figure 2a, b), comparable inhibition is expected for linoleic acid and a diolefin such as 1,7-octadiene.[17] In Figure 2f, it is shown that the addition of 0.05 equivalents of 1,7-octadiene as inhibition agent almost entirely suppresses the deoxygenation activity.

The overlay of the inhibition curves of the fatty acids and olefins clearly demonstrates the correlation between the amount of unsaturations and the impact on the deoxygenation activity (Figure 3). However, these results do not indicate whether the inhibition is initiated by reversible adsorption on the catalyst surface (i.e., soft coke) or by irreversible adsorption and conversion of the adsorbed species to, for instance, polycyclic aromatic compounds or graphitic carbon (i.e., hard coke).

To investigate whether the inhibition is reversible, catalytic deoxygenation reactions of stearic acid with inhibition agent were performed in N_2 atmosphere (7 bar), in which the reaction atmosphere was switched from N_2 to H_2 (7 bar) after 20 h at 250 °C. The reactions were subsequently continued for another 20 h under H_2 atmosphere. H_2 is known to adsorb on the palladium surface and Pd–H is considered as very efficient in the hydrogenation of unsaturated species.[18] In the case of reversible inhibition, the deoxygenation activity is expected to restore after switching to H_2 atmosphere as a result of hydrogenation of the unsaturated inhibition agents. The deoxygenation reactions were performed with stearic acid and 0.4 equivalents of inhibition agent present, because this amount of inhibition agent was shown to considerably inhibit the deoxygenation (Figure 2).

In Figure 4 the results for the described N_2/H_2 sequence reactions are compared with those for the catalytic reactions performed under either N_2 or H_2 atmosphere. No deoxygenation is observed under N_2 atmosphere if 0.4 equivalents of pentadecene was present (Figure 4a). Under H_2 atmosphere however, the pentadecene was fully hydrogenated to pentadecane (not shown in the figure) and 38 mol% of the stearic acid is converted to heptadecane. The N_2/H_2 sequence reaction resulted in reaction composition comparable to that for the catalytic reaction of 20 h under H_2 atmosphere (Figure 4a). These

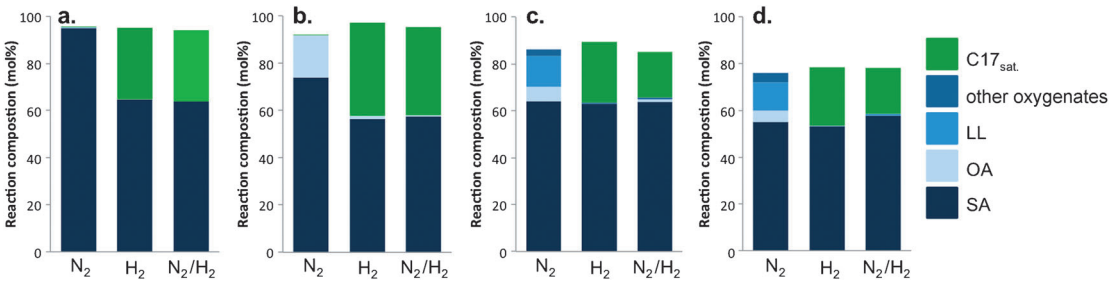


Figure 4. Reaction composition after SA deoxygenation over Pd/SiO_2 in the presence of the amount of 1.3 mmol of a) pentadecene, b) OA, c) LL, and d) LLN as the inhibition agent. Catalytic experiments were performed under N_2 atmosphere (20 h), H_2 atmosphere (20 h), and switching from N_2 to H_2 atmosphere (N_2/H_2 sequence, 2×20 h).

results demonstrate that the inhibition is reversible in H_2 atmosphere and that deoxygenation activity is restored by hydrogenation of the pentadecene.

If oleic acid is used as the inhibition agent (Figure 4b), full hydrogenation of the inhibition agent resulted in restored deoxygenation activity and comparable reaction compositions relative to pentadecene. As the deoxygenation activity and product selectivity are highly comparable to reactions performed under H_2 atmosphere, it can be concluded that the inhibition by 0.4 equivalents of mono-unsaturated compounds is fully reversible with the introduction of 7 bar H_2 at 250 °C. Deoxygenation activity was also restored if linoleic acid or linolenic acid were used as inhibition agent (Figure 4c, d). However, the heptadecane yields were slightly lower for the N_2/H_2 sequence reactions than in the H_2 reactions. This can be explained by the fact that two or three times as many double bonds, respectively, are present in the inhibition agents.

The reversibility of the deoxygenation activity indicates that initial inhibition is caused by strong but reversible adsorption of the unsaturated compounds. H_2 was shown to "clean" the catalyst surface, most likely by adsorption on the palladium surface, which subsequently hydrogenates the adsorbed unsaturated species followed by desorption. These results show that the formation of irreversibly deposited hard coke does not significantly contribute to the initial inhibition process.

Note that the mass balances are not complete if either linoleic or linolenic acid are added to the reaction mixture (Figure 4c, d). As the mass balances appear independent of the reaction atmosphere (N_2 or H_2) and reaction time (20 or 40 h), the loss in mass is presumably caused by adsorption on the catalyst surface. A monolayer of fatty acids on the SiO_2 surface would already contain up to 12 mol% feed.[16] Chemisorption and physisorption on the catalyst surface could thus possibly account for the observed apparent mass loss.

Although Soxhlet extraction of the spent Pd/SiO_2 catalyst removed part of the adsorbed species, chemisorbed organic deposits remained present on the catalyst surface, shown by thermogravimetric analysis (TGA). The amount of organic deposition increased if more unsaturations were present in the feed; from 27 mg $g_{cat.}^{-1}$ in the case of stearic acid up to 64 mg $g_{cat.}^{-1}$ if using linolenic acid as feed (see the Supporting Information, Table S1). Comparable amounts of organic depositions were present after reaction with oleic acid or pentadecene as the feed, confirming the correlation between organic deposition and the presence of C=C double bonds. The organic deposition is clearly not solely present on the palladium active sites because the maximum amount of chemisorbed feed on the palladium metal surface would be between 0.2 and 2 mg $g_{cat.}^{-1}$, depending on the coordination to the palladium surface.[16] However, as mentioned earlier, a monolayer of fatty acid on the SiO_2 surface contains up to 240 mg feed $g_{cat.}^{-1}$, which could be the case for these spent catalysts (Table S1).

IR spectroscopy was performed to investigate the nature of the chemisorbed organic deposits on the spent catalysts. The fresh catalyst (before reaction) exhibits H_2O bending vibrations at 1638 cm^{-1} (O–H scissors) and a broad O–H stretch band at approximately 3300 cm^{-1}, which can both be assigned to adsorbed H_2O on the catalyst surface (Figure 5). After reaction with pentadecene or stearic acid as the feed, also C–H stretch vibrations at 3005 cm^{-1} (from C=C–H) and vibrations at approximately 2924 and 2854 cm^{-1} (CH_2 asymmetric and CH_2 symmetric stretch, respectively) are visible. The adsorbed unsaturated species could be product related if stearic acid was used as the feed because olefins are produced during the reaction (Figure 1) and are shown to inhibit deoxygenation activity by adsorption on the catalyst surface (Figure 2b). The presence of a small vibration at approximately 1710 cm^{-1} (C=O stretch vibrations) could also indicate feed-related species on the catalyst surface.[19] The C=O stretch vibrations at 1710 cm^{-1} appeared more clearly in the spectra after the reaction with unsaturated fatty acids, confirming the presence of feed-related adsorbates. Combined with the absence of symmetric and asymmetric COO^- bands (1410 and 1556 cm^{-1}), this could indicate that fatty acids are not chemisorbed as a carboxylate onto the catalyst surface but instead mainly interact with the surface by means of the carboxylic acid group.[19,20]

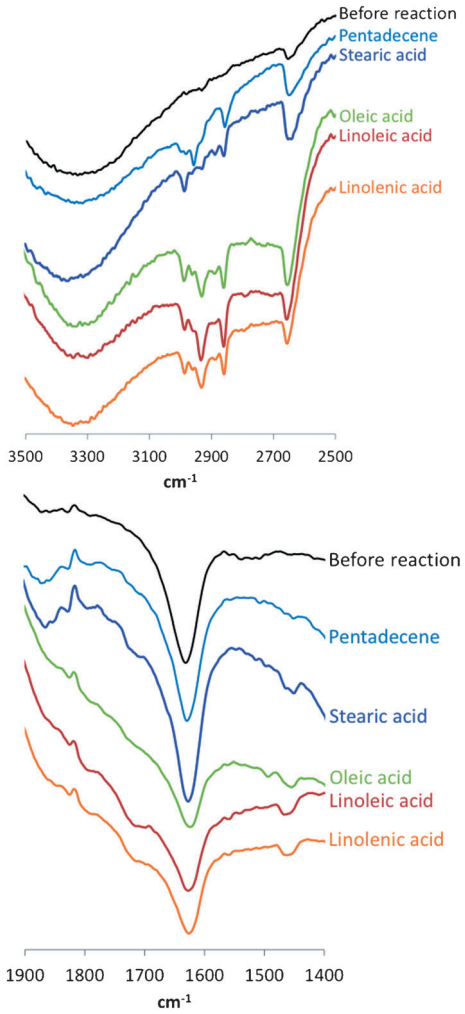


Figure 5. Details of the IR spectra of the fresh Pd/SiO_2 catalyst ("before reaction") and the spent catalysts using SA, OA, LL, and LLN as the feed, respectively.

The IR data confirm the adsorption of olefinic adsorbates after the reaction with stearic acid. Feed-related unsaturated adsorbates appear to be present after reaction with unsaturated feeds. It should, however, be noted that these spectroscopic data indicate the presence of chemisorbed molecules on the support surface and not on the palladium active sites, as was also concluded from TGA.

Although the palladium surface is active in the deoxygenation of fatty acids, the support material is known to greatly affect the deoxygenation activity.[4,12] The influence of the support material on the deoxygenation activity was indeed confirmed by measuring the deoxygenation activities for several supported palladium catalysts, shown in the Supporting Information (Table S2). For that reason, it is expected that the inhibition process is also affected by the type of support material.

To test this hypothesis, catalytic reactions were performed over Pd/SiO_2, Pd/Al_2O_3, and Pd/C by using pentadecene and oleic acid as inhibition agents. The TON without inhibition agent was set at unity to correct for the differences in deoxygenation activity.

From Figure 6 it is seen that comparable inhibition occurs for the different catalysts if plotting the relative TON as a function of the amount of inhibition agent. Thus, although deoxygenation activity is dependent on the catalyst support, there is no correlation between support material characteristics and catalyst inhibition. Differences in, for instance, the coordination of the feed and products to the support material or differences in metal–support interaction apparently do not significantly contribute to the inhibition process. Instead, these results indicate that inhibition is predominantly caused by the adsorption of unsaturated compounds on the active palladium surface, independent of the support material used.

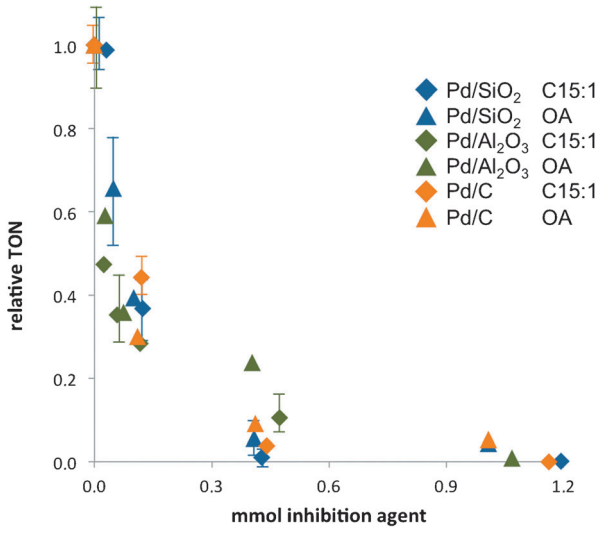


Figure 6. Relative TONs as a function of the amount of inhibition agent if using Pd/SiO_2 (◆/▲), Pd/Al_2O_3 (◆/▲), and Pd/C (◆/▲) as catalyst. The TON without inhibition agent was set at unity. Pentadecene (C15:1, ◆) and OA (▲) were used as inhibition agents.

In summary, we reported the significant influence of small amounts of unsaturated species on the deoxygenation activity in the absence of added H_2. Although in the literature the formation of hard coke was suggested by several authors as a reason for the catalyst deactivation, we showed that the reversible adsorption of unsaturated species (soft coke) on palladium is the initial and main reason for the inhibition of deoxygenation activity.

In comparison of our results with the work presented by Ping et al., possibly not the abundantly present saturated compounds caused the catalyst deactivation, but instead small amounts of unsaturated compounds that could be formed during the reaction.[6] Ping et al. reported the removal of the organic deposits with more severe washing steps and showed subsequent restored catalyst activity, which confirms our results in the present work demonstrating the reversibility of the inhibition.

Conclusions

The inhibition during H_2-free deoxygenation of fatty acids over supported palladium catalysts is highly dependent on the presence of unsaturated compounds. Significant feed and product inhibition occurs if unsaturated compounds are present, even in low concentrations. The reversibility of the inhibition under H_2 atmosphere indicates that hard-coke formation does not significantly contribute to the initial deactivation process. Instead, adsorption on the support by the C=C double bond was inferred. The nature of the support material does not contribute to the inhibition process. This could be explained by the adsorption of the unsaturations on the palladium surface as main inhibition process.

Overall, we demonstrated that the reversible adsorption of unsaturated molecules with the C=C double bond on the palladium active sites significantly contributes to catalyst inhibition. The presence of H_2 is therefore essential to retain catalytic deoxygenation activity.

Experimental Section

Chemicals

The following catalysts were used for this investigation: Palladium on silica powder (5 wt% Pd/SiO_2) reduced dry (Strem Chemicals Inc., Escat 1351); Palladium on alumina powder (5 wt% Pd/Al_2O_3) reduced (Strem Chemicals Inc., Escat1241); Palladium on activated carbon (5 wt% Pd/C) reduced dry powder (Strem Chemicals Inc.). The following chemicals were used without further purification treatments: Methanol, HPLC gradient 99.9% (GC) (Actu-All Chemicals); Chloroform, HPLC (stabilized with ethanol) 99.9% (Actu-All Chemicals); trimethylsulfonium hydroxide (TMSH), purum, ≈0.25 M in methanol (Sigma–Aldrich); dodecane, ReagentPlus ≥99% (Sigma–Aldrich); Tetradecane, olefin-free ≥99% (GC) (Sigma–Aldrich); *n*-hexane, PEC Grade 97.0% (Actu-All Chemicals); 1,7-octadiene, 98% (Sigma–Aldrich); Pentadecane, ≥99% (Sigma–Aldrich); 1-pentadecene, 98% (Sigma—Aldrich); heptadecane 99%, (Sigma–Aldrich); hexadecanal, >97% (TCI Europe N.V.); 1-heptadecanol, 98% (Sigma–Aldrich); stearyl alcohol, >99% (GC) (TCI Europe N.V.); stearic acid, 97% (Acros Organics), oleic acid, tech., 90% (Sigma–

Aldrich); oleic acid, reagent grade ≈99% *(Sigma–Aldrich)*; linoleic acid, ≥99% (SAFC, Sigma–Aldrich); linolenic acid, ≈70% (GC) (Sigma–Aldrich); 1-phenylundecane, 99% (undecylbenzene) (Sigma–Aldrich); pyrene 98% (Sigma–Aldrich); 2,3-benzanthracene, 98% (tetracene) (Sigma–Aldrich); 18-pentatriacontanone (stearone) (Alfa Aesar); Stearic anhydride (TCI Europe N.V.).

Catalytic testing

The catalyst (typically 0.5 g) was activated prior to catalytic reactions in a plug-flow reactor in which the catalyst was heated to 150 °C (5 °C min^{-1}) in nitrogen (3.0 Linde, 200 mL min^{-1}) atmosphere, dried for 30 min and subsequently reduced at 150 °C for 2 h in hydrogen (5.0 Linde, 200 mL min^{-1}). After reduction, the catalyst was flushed with nitrogen at 150 °C to remove all hydrogen from the reactor and catalyst surface and cooled to RT in nitrogen (200 mL min^{-1}). The plug-flow reactor was subsequently transferred to a glove box to add solvent, reactant and internal standard prior to catalytic reactions.

Catalytic experiments were performed in a multiple reactor system (Parr, model MRS 5000) containing six 75 mL vessels with magnetic stirring. Pressure and temperature were monitored continuously during catalytic tests using this setup. The reaction mixture was stirred (1100 rpm) to avoid external mass transfer limitations. It was determined that pore diffusion limitations are negligible according to the Weisz–Prater criterion (the liquid-phase effective diffusivities were estimated according to Wilke and Chang[21]). In a typical reaction, amounts of 1 g feed and 18 g dodecane (25 mL) as a solvent were used. Tetradecane (0.5 g, 2.5 mmol) was used as an internal standard for quantitative analysis by GC.

Product analysis

Reaction-mixture work-up after reaction and cooling was performed with a chloroform methanol mixture (2:1) that was heated to 40 °C to ensure complete dissolution of the fatty acid. A sample was subsequently taken from the mixture and methylated by mixing with trimethylsulfonium hydroxide, an in situ esterification reagent to derivatize carboxylic acids for accurate gas–liquid chromatography quantification. Soxhlet extraction of the spent catalyst was performed (by using chloroform, methanol, and hexane) to remove physisorbed organic species from the catalyst surface before further analysis.

Analysis of the reaction mixture (products with molecular weights between ≈180–350 g mol^{-1}) was performed on a Thermo Focus gas chromatograph equipped with an automatic injection system (AS3000 autosampler). GC program: Hold 1 min at 50 °C, ramp 20 °C min^{-1} to 170 °C, ramp 5 °C min^{-1} to 195 °C, ramp 15 °C min^{-1} to 225 °C, then ramp 5 °C min^{-1} to 250 °C and hold at 250 °C for 15 min. The following parameters and settings were used: Varian CP-FFAP (free fatty acids) GC column (25 m × 0.32 mm × 0.30 μm), 290 °C injection port temperature, 1 μL injection volume, split injection mode, 20 mL min^{-1} split flow, column flow of 1.1 mL min^{-1}, hydrogen and air flow control, ignition threshold 0.5 pA, and flame ionization detector at 270 °C.

Analysis of high-boiling-point substrates (e.g., stearyl stearate and stearone) was performed on an Interscience Trace 1300 gas chromatograph equipped with an automatic injection system (AS1310 autosampler). GC program: Hold 1 min at 50 °C, ramp 15 °C min^{-1} to 150 °C, ramp 7 °C min^{-1} to 180 °C, ramp 15 °C min^{-1} to 280 °C, ramp 7 °C min^{-1} to 350 °C and hold 10 min at 350 °C. The following parameters and settings were used: Varian Select biodiesel for glycerides (15 m × 0.32 mm × 0.45 μm), 370 °C injection port temperature, 1 μL injection volume, splitless injection mode, 60 mL min^{-1} split flow, ignition threshold 0.5 pA, 350 mL min^{-1} air flow, 35 mL min^{-1} hydrogen flow, 40 mL min^{-1} makeup gas flow, and flame ionization detector at 380 °C.

Catalyst analysis

Nitrogen physisorption was performed at −196 °C by using a Micromeritics Tristar 3000V, 6.04 Å. The obtained data were used to calculate the BET surface area. Prior to the physisorption measurements, the samples were dried at 200 °C for approximately 14 h under nitrogen flow. Micropore volumes and external surface areas were determined by using t-plot analysis.

Total palladium surface area and palladium dispersion was determined by hydrogen chemisorption measurements using a Micromeritics ASAP 2020 apparatus. The samples were dried at 120 °C in He flow for 30 min and subsequently reduced in 50% H_2/He flow at 250 °C for 2 h (5 °C min^{-1}). The H_2 adsorption isotherms were measured at 150 °C, and calculations for the percentage Pd dispersions were performed assuming a complete Pd reduction with the stoichiometry of one hydrogen atom adsorbed per Pd surface atom.

Elemental analysis was performed at the Mikroanalytisches Laboratorium Kolbe to determine the exact palladium loading of the dried catalysts.

Organic deposits on the catalyst surface were analyzed by TGA with a PerkinElmer STA 6000. Samples were heated with a heating rate of 10 °C min^{-1} from 30 °C to 800 °C by using nitrogen as a purge gas with a flow rate of 30 mL min^{-1}. 180 μL ceramic pans were used to hold the sample. The total organic content was estimated from the weight loss between 150 and 800 °C.

FTIR spectra of the fresh and spent catalysts were obtained on a Varian Scimitar 1000 FT-IR spectrometer equipped with a DTSG detector. The spectra were collected in the range 4000–650 cm^{-1} (measurement resolution at 4 cm^{-1}) by using attenuated total reflectance with a diamond w/ZnSe lens single reflection plate with 512 co-added scans. The sample chamber was purged with N_2 gas for at least 10 min before scanning.

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