

Selective Hydrogenation of Polyunsaturated Fatty Acids Using Alkanethiol Self-Assembled Monolayer-Coated Pd/Al₂O₃ Catalysts

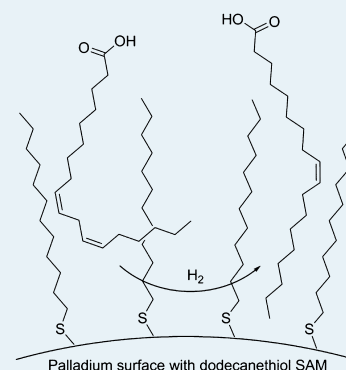
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Supporting Information

ABSTRACT: Pd/Al₂O₃ catalysts coated with various thiolate self-assembled monolayers (SAMs) were used to direct the partial hydrogenation of 18-carbon polyunsaturated fatty acids, yielding a product stream enriched in monounsaturated fatty acids (with low saturated fatty acid content), a favorable result for increasing the oxidative stability of biodiesel. The uncoated Pd/Al₂O₃ catalyst quickly saturated all fatty acid reactants under hydrogenation conditions, but the addition of alkanethiol SAMs markedly increased the reaction selectivity to the monounsaturated product oleic acid to a level of 80–90%, even at conversions >70%. This effect, which is attributed to steric effects between the SAMs and reactants, was consistent with the relative consumption rates of linoleic and oleic acid using alkanethiol-coated and uncoated Pd/Al₂O₃ catalysts. With an uncoated Pd/Al₂O₃ catalyst, each fatty acid, regardless of its degree of saturation had a reaction rate of ~0.2 mol reactant consumed per mole of surface palladium per second. Using alkanethiol-coated Pd/Al₂O₃ catalysts, the activity was reduced by a factor of 4 for polyunsaturated reactants and by a factor of 100 for the monounsaturated reactants. In contrast to the hydrophobic alkanethiol modifiers, hydrophilic thioglycerol SAM modifiers were found to strongly inhibit reaction kinetics.

KEYWORDS: polyunsaturated fatty acids, selective hydrogenation, self-assembled monolayers, palladium



Tuning the near-surface environment of heterogeneous catalysts offers a promising route for controlling selectivity in reactions of complex chemicals. The ability to control chemoselectivity of the reaction of multifunctional feedstocks is desirable for industrial reaction processes because it reduces separation costs and maximizes yield.^{1,2} Fatty acid oils are one example of an important multifunctional biorenewable feedstock that can be produced from a variety of terrestrial and marine plants and are associated with low environmental toxicity.^{3–5} Fatty acids have many industrial uses, ranging from chemicals and fuels to biological applications, personal care products, plastics, and other household commodities.^{4,5} Naturally occurring fatty acids contain a large fraction of unsaturated 18-carbon components, including linolenic acid (*cis*-9,*cis*-12,*cis*-15-octadecatrienoic, C_{18:3}) linoleic acid (*cis*-9,*cis*-12-octadecadienoic acid, C_{18:2}) and oleic acid (*cis*-9-octadecenoic, C_{18:1}), which are especially important in the production of biodiesel.⁶

Since biodiesel is an important biorenewable fuel, its production from fatty acids has been extensively studied.^{3,7–10} Critically, controlling the oxidative stability of fatty acids is vital to the quality of biodiesel that can be produced.^{11–13} Polyunsaturated molecules such as linoleic acid are susceptible to autoxidative degradation, which can produce polymers and other undesirable side products that prevent fuel from meeting regulatory standards.¹⁴ Fortunately, reducing the degree of unsaturation can increase the oxidative stability. The oxygen adsorption rate in fatty acids decreases dramatically with a decrease in the degree of unsaturation where linolenic acid,

linoleic acid, and oleic acid have oxygen adsorption rates of 800:100:1 respectively.³ Soybean oil, a major biodiesel precursor, has a reported 50–60% composition of unsaturated fatty acids, so selectively reducing its degree of unsaturation is highly desirable.^{11,13–16} The main challenge with decreasing fatty acid unsaturation is that complete saturation of the alkane tail would result in a dramatic increase in the melting temperature and viscosity of the fuel.¹⁴ Therefore, a selective reaction environment is desired to partially saturate polyunsaturated fatty acids.

Previous strategies aimed at the selective hydrogenation of polyunsaturated fatty acids have included varying the composition of the metal catalyst, temperature, and hydrogenation pressure.^{11,17–19} The addition of amines to the reaction mixture has also been shown to affect the activity of Pd catalysts toward polyunsaturated fatty acid ethyl esters in sunflower oil; in some cases, providing a modest improvement in the yield of a particular monounsaturated product and inhibiting isomerization.³

Selective poisoning of catalysts is an alternative method for affecting a reaction selectivity.^{20–24} The use of alkanethiol self-assembled monolayers (SAMs) to direct the selectivity of reaction systems is one such example of selective catalyst poisoning. Alkanethiol monolayers have been used to improve the selectivity of the hydrogenation of 1-epoxy-3-butene (EpB)

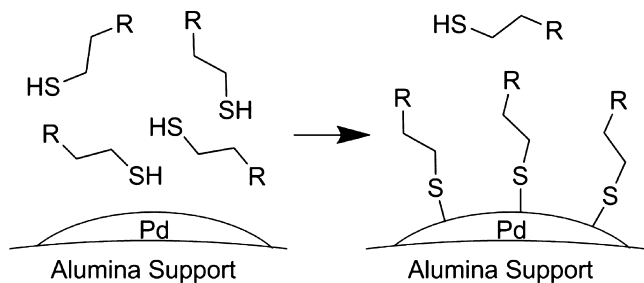
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to 1-epoxybutane as well as to affect the selectivity of allyl alcohol isomerization.^{20,22,25} In the case of 1-epoxybutene hydrogenation, modification of the Pd surface by the sulfur headgroup (as shown in Scheme 1) was found to be largely

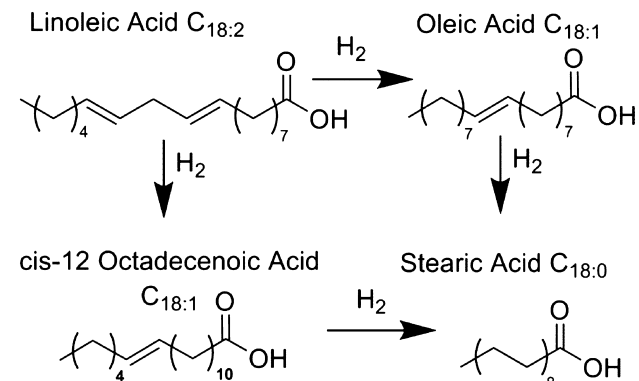
Scheme 1. Formation of alkanethiol SAMs on Pd/Al₂O₃ Catalyst



responsible for the increase in selectivity observed in these systems, and the tail group was shown to affect only the activity, not the selectivity.²⁵ However, these studies examined reactant molecules that are too small to have adsorbed states in which the reactant is chemisorbed to the metal while still interacting with more remote regions of the organic ligands.^{26,27} We hypothesized that larger reactant molecules, such as fatty acids, would interact more extensively with the organic tail-group ligands of the SAM coating.

Hydrogenation of polyunsaturated fatty acids can yield a wide range of products and isomers. The molecules of greatest interest here were the family of 18-carbon fatty acids including C_{18:3} (linolenic acid), C_{18:2} (linoleic acid), *cis*-C_{18:1} (oleic acid), and C_{18:0} (stearic acid). In addition to the differing degrees of unsaturation, each degree of saturation may be present as *trans* and *cis* isomers as well as positional isomers for a wide range of slightly different molecular configurations. For example, the hydrogenation of linoleic acid, shown in Scheme 2, provides both positional and *cis*–*trans* isomerization products for each step in the unsaturation sequence.

Scheme 2. Reaction Pathway of Linoleic Acid Hydrogenation



The hydrogenation of linoleic acid was performed for 90 min; data from a typical experimental run are shown in Figure 1 for uncoated Pd/Al₂O₃ and for dodecanethiol-coated Pd/Al₂O₃. Similar data were obtained for each of the alkanethiol-coated catalyst systems with each of the fatty acid reactants.

As illustrated in Figure 1a, the hydrogenation of linoleic acid using an uncoated palladium catalyst quickly passed through

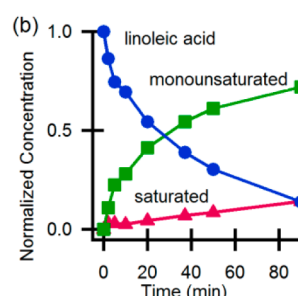
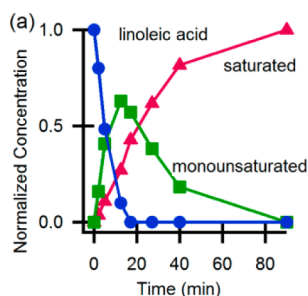


Figure 1. Kinetic data for linoleic acid hydrogenation over Pd/Al₂O₃ at 30 °C and 6 bar H₂. The initial reactant concentration was normalized to 1 for clarity: (a) uncoated Pd/Al₂O₃ and (b) dodecanethiol-coated Pd/Al₂O₃.

monounsaturated intermediates to the fully saturated product, stearic acid, with the maximum selectivity being recorded before 10% conversion. The yield to oleic acid reached a maximum of 64%, after which the series reaction resulted in a continuous decrease in selectivity. As shown in Figure 1b, application of an alkanethiol SAM coating to the Pd/Al₂O₃ catalyst dramatically increased the selectivity of linoleic acid hydrogenation to monounsaturated products. With an alkanethiol coating, the yield to monounsaturated products was >80%, and remarkably, this selectivity remained high, to >80% conversion.

Reaction data for various SAM-coated catalysts are shown in Figure 2a. Each of the alkanethiol coatings achieved a greater

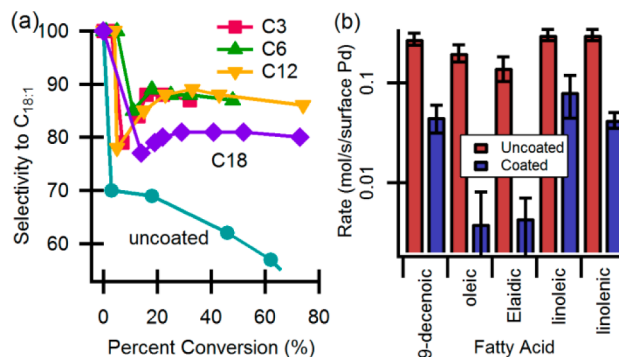


Figure 2. (a) Selectivity of linoleic acid hydrogenation to monounsaturated products as a function of conversion. C3, C6, C12, and C18 correspond to propanethiol-, hexanethiol-, dodecanethiol-, and octadecanethiol-coated Pd/Al₂O₃. (b) Turnover frequency (1/s) for the hydrogenation of oleic acid (*cis*-9-octadecenoic acid), elaidic acid (*trans*-9-octadecenoic acid), linolenic acid (*cis,cis,cis* 9-12-octadecadienoic acid), and linolenic acid (*cis,cis,cis* 9-12-15-octadecatrienoic acid) over alkanethiol-coated (average rate of C3, C6, C12, and C18 coatings) and uncoated catalysts. Reaction rate measured as the moles of reactant consumed per mole of exposed surface Pd per second.

selectivity to monounsaturated products than the uncoated catalyst. The initial variation in selectivity shown at low conversions in Figure 2a may be due to limited GC sensitivity to the products at low conversions. The addition of alkanethiol SAMs to the Pd/Al₂O₃ catalyst was also responsible for a decrease in the overall reaction activity, consistent with previous SAM catalysis studies.^{22,25} Although an alkanethiol SAM may block some surface sites, the extent of this effect is unclear (see the Supporting Information for more details), and we have therefore reported rates as the moles of reactant

consumed per mole of exposed surface metal per second using the dispersion of the catalyst metal.

Experiments measuring the hydrogenation rates of different unsaturated fatty acids (Figure 2b) show that SAM coatings reduce the hydrogenation rate much more for $C_{18:1}$ fatty acids, resulting in an enhanced yield of the intermediate (monounsaturated) product. That is, whereas the rate of hydrogenation on uncoated catalysts was fairly uniform (0.1–0.3 mol/s/mol surface Pd) for all reactants tested, the hydrogenation rate on coated catalysts decreased by an order of magnitude for $C_{18:1}$ fatty acids compared to the $C_{18:2}$ fatty acid. Because each of the different alkanethiol tail lengths affected the selectivity and rate in approximately the same way, the activities for the reaction of each fatty acid over the C3-, C6-, C12-, and C18-coated catalysts were averaged in Figure 2b as “coated”.

These data show that by coating the catalyst with a SAM, the selectivity to monounsaturated fatty acid products can be dramatically increased over the uncoated catalyst system. In addition, that increase in selectivity is exhibited to 80% conversion, so although there is a loss of rate over alkanethiol coated catalysts, a reaction system can be run at a greater overall production rate of monounsaturated fatty acid than a system with uncoated catalyst, which must run at <10% conversion to maintain the same selectivity to monounsaturated products. Interestingly, we also observed that in the monounsaturated product, the ratio of unsaturation at the 9 and 12 positions was less than 2:1 on uncoated catalysts, but for coated catalysts it was typically greater than 3:1.

The hydrogenation of linolenic acid $C_{18:3}$ was also investigated and showed results consistent with the hydrogenation of linoleic acid. Again, the uncoated catalyst resulted in completely saturated products with low selectivity to partial hydrogenation. As shown in Figure 3b, the addition of an

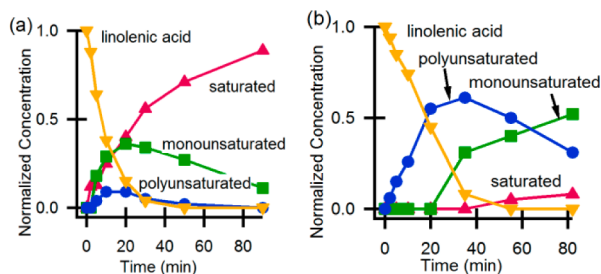


Figure 3. Kinetic plot data of linolenic acid hydrogenation over Pd/ Al_2O_3 : (a) uncoated Pd/ Al_2O_3 and (b) dodecanethiol coated Pd/ Al_2O_3 .

alkanethiol coating increased the selectivity to unsaturated products to as much as 80% (at 80 min), by reducing the production of saturated fatty acid. Figure 3b highlights the trends of linolenic fatty acid hydrogenation, but when more catalyst was used, 80% selectivity was specifically achieved to monounsaturated fatty acid, in a kinetic result resembling Figure 1b. Supported by Figure 2b, the rate of consumption of linolenic acid $C_{18:3}$ was similar to the rate of linoleic acid $C_{18:2}$ consumption over both coated and uncoated catalysts. These results indicate that regardless of the position or the degree of unsaturation, alkanethiol monolayers can be used to direct hydrogenation to products with one degree of unsaturation.

Included in Figure 2b, kinetic data were also obtained for the hydrogenation of 9-decenoic acid to compare with the rates of

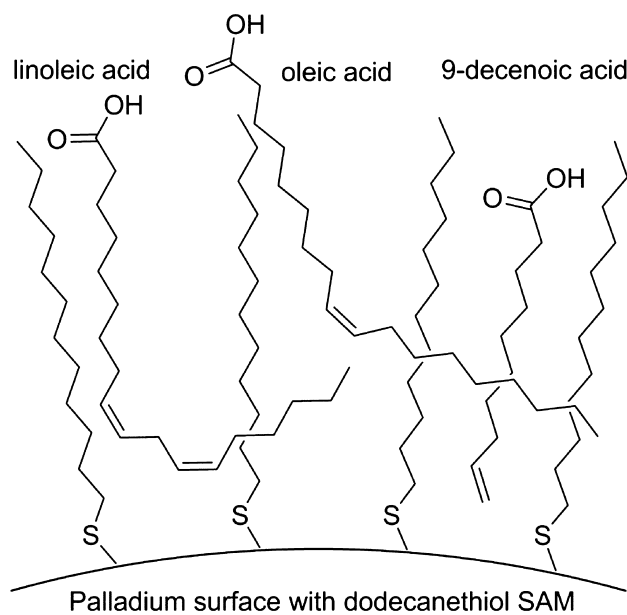
hydrogenation of 18-carbon monounsaturated fatty acids. 9-Decenoic acid was chosen because it contains a double bond at the same position with respect to the fatty acid headgroup as both elaidic acid and oleic acid, with 9-decenoic acid lacking the eight-carbon terminal alkyl chain. Although the rates of oleic and elaidic acid hydrogenation were much lower on alkanethiol-coated catalysts, the rate of 9-decenoic acid hydrogenation was not as dramatically affected by the presence of an alkanethiol coating on the catalyst surface. This suggests that hydrogenation of the targeted double bond may depend more on its position from the terminal end of the fatty acid rather than its position relative to the fatty acid head.

The mechanism for these effects is still not entirely clear. Previous studies have suggested that the position of a double bond within a fatty acid molecule should not strongly affect its reactivity toward hydrogenation over an uncoated Pd/C catalyst.¹⁸ With respect to SAM-coated Pd catalysts, the effects of SAMs on reaction selectivity were previously attributed to the poisoning effects of sulfur on the catalyst surface.^{22,25} In the case of gas-phase ethylene hydrogenation, application of linear alkanethiol SAMs decreases the reaction rate by a factor of 100 (compared with uncoated catalyst), far greater than the effect observed here for hydrogenation of a single olefin group of polyunsaturated fatty acids.²⁸ We hypothesize that the difference is smaller for the liquid phase hydrogenation of fatty acids because of the high coverage of unreactive species on an uncoated catalyst. Here, the site-blocking effects of SAMs are relatively less important when the surface is likely to contain a higher coverage of competitively adsorbed, unreactive species, such as the (much heavier) reactant or solvent. Such a view is consistent with the observation that alkanethiol SAMs also decrease olefin hydrogenation rates by less than an order of magnitude for 1-epoxy-3-butene, which is known to form strongly adsorbed spectator species on the surface during reaction.^{22,25,29,30} Thus, it appears that the creation of high-coverage structures with SAMs decreases olefin hydrogenation rates to a smaller extent in “stickier” reaction environments.

Our prior studies have indicated that adsorbed alkanethiols do not strongly affect activation barriers for gas-phase olefin hydrogenation, but primarily alter the site densities.²⁵ It is furthermore not clear how electronic modification of the surface by sulfur would decrease the rate of hydrogenation of olefin functions at different positions on a fatty acid molecule. Rather than an electronic mechanism, we therefore propose a geometric mechanism whereby $C_{18:1}$ fatty acids have more difficulty interacting with an alkanethiol-coated surface than polyunsaturated fatty acids. We hypothesize that when a fatty acid chain contains more than one degree of unsaturation, such as linoleic acid, shown in Scheme 3, it has the appropriate shape to reach that catalyst surface and react within an alkanethiol monolayer; in contrast, a $C_{18:1}$ fatty acid (which has only a single “kink”) does not. As demonstrated in Figure 2b and illustrated in Scheme 3 for the hydrogenation of 9-decenoic acid, monounsaturated fatty acids can better react on a coated surface when the double bond is at the terminal end of the molecule.

Unfortunately, a direct measurement of how thiolate SAMs affect orientation or uptake of different fatty acids on the catalyst is lacking. Previous researchers successfully measured the adsorption of fatty acids onto montmorillonite surfaces via solution depletion acid base titration.³¹ Attempts to use such a technique in our case did not yield statistically significant results because of the relatively low active surface area per mass of

Scheme 3. Proposed Interaction Mechanism of Fatty Acids with an Alkanethiol Coated Palladium Catalyst^a



^aMonounsaturated fatty acids are excluded from interacting with the surface.

material compared with the prior studies. For the same reason, GC analysis of the supernatant liquid was not effective for characterizing adsorption of the different fatty acids.

In addition to alkanethiol monolayers, a polar thioglycerol monolayer was deposited on the palladium catalyst surface, which reduced the activity of this catalyst beyond system sensitivity. The reaction rate over these thioglycerol coatings was at least 4 orders of magnitude smaller than the rate of reaction over alkanethiol-coated catalysts, consistent with repulsion of the oily regions of the fatty acid tails from the near surface environment. This contrasts strongly with previous studies of 1-epoxy-3-butene hydrogenation and nitrostyrene hydrogenation, in which selectivity and activity differences between hydrophobic and hydrophilic coatings were minor and implicate interactions between SAM tails and fatty acid reactants (as opposed to modification by the sulfur headgroup) in the selectivity-promotion mechanism.^{25,32}

The fatty acid compositions of sunflower oil and rapeseed oil, two important biorenewable feedstocks, have naturally <30% C_{18:1} fatty acids, with the makeup consisting of various degrees of polyunsaturated fatty acids.^{3,6} The mechanism by which alkanethiol SAMs increase hydrogenation selectivity of polyunsaturated C₁₈ fatty acids to monounsaturated C_{18:1} fatty acids requires further study, but as a result of this effect, any feedstock mixture of 18-carbon fatty acids with differing degrees of unsaturation, such as sunflower or rapeseed oil, can be reacted selectively to monounsaturated products.

■ ASSOCIATED CONTENT

Supporting Information

Materials; catalyst preparation; reaction conditions; contact angle measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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