# Control of Metal Catalyst Selectivity through Specific Noncovalent Molecular Interactions

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Ⓢ *Supporting Information*

ABSTRACT: The specificity of chemical reactions conducted over solid catalysts can potentially be improved by utilizing noncovalent interactions to direct reactant binding geometry. Here we apply thiolate self-assembled monolayers (SAMs) with an appropriate structure to Pt/Al_2O_3 catalysts to selectively orient the reactant molecule cinnamaldehyde in a configuration associated with hydrogenation to the desired product cinnamyl alcohol. While nonspecific effects on the surface active site were shown to generally enhance selectivity, specific aromatic stacking interactions between the phenyl ring of cinnamaldehyde and phenylated SAMs allowed tuning of reaction selectivity without compromising the rate of desired product formation. Infrared spectroscopy showed that increased selectivity was a result of favorable orientation of the reactant on the catalyst surface. In contrast, hydrogenation of an unsaturated aldehyde without a phenyl ring showed a nontunable improvement in selectivity, indicating that thiol SAMs can improve reaction selectivity through a combination of nonspecific surface effects and ligand-specific near-surface effects.
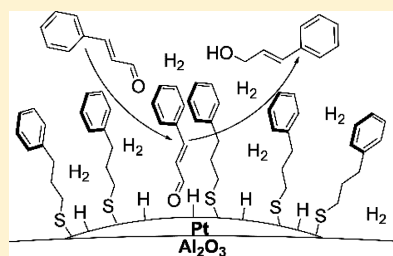
1. INTRODUCTION

Heterogeneous catalysts, such as supported transition metals, are widely used in industrial applications due to their recoverability, but they are generally far less selective toward forming desired products in comparison to organometallic or enzyme catalysts.[1] Enzyme catalysts have evolved an advantage for improving selectivity: the active site is often contained within a binding pocket, and noncovalent interactions between the reactant and binding pocket cause reactant molecules to bind in a specific orientation to the active site.[2] Similar interactions have been successfully exploited to produce branched chain alcohols as biofuels,[3] and alcohol dehydrogenase enzymes achieve selective hydrogenation of α,β-unsaturated aldehydes through alignment of the reactant molecules in a hydrophobic barrel within the catalyst structure.[4] Previous attempts to improve the chemoselectivity of heterogeneous catalysts have not generally focused on controlling noncovalent interactions and instead have focused on changing the size, shape, or composition of the surface layer.[5−8] While these methods represent powerful tools for improving selectivity through (for example) control of the electronic properties of the active site, the engineering of noncovalent interactions above the active surface may provide an additional lever for approaching optimal selectivity.

In this contribution, we deposit thiolate self-assembled monolayers (SAMs) on conventional heterogeneous catalysts to control the selectivity of an important model reaction, the hydrogenation of cinnamaldehyde (Scheme 1). By changing the functional groups of the hydrocarbon "tail" of the thiolate modifier, it is possible to adjust noncovalent interactions in the near-surface environment in a manner analogous to changing functional groups in an enzyme binding pocket.[9] Previous work has shown that self-assembled monolayers can change the

Scheme 1. Hydrogenation Pathway of Cinnamaldehyde
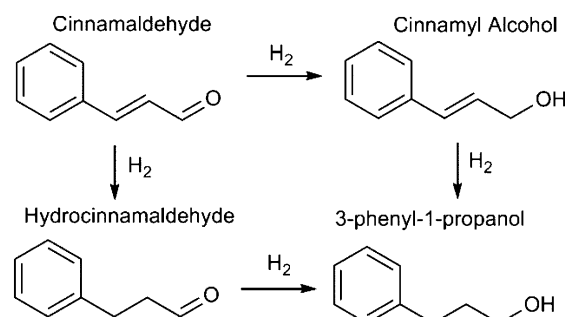
properties of the active catalyst surface *nonspecifically* through the interaction of the sulfur headgroup with the surface,[10] but here we show that it is possible to control selectivity *specifically* by precise placement of functional groups in the organic tail that (de)stabilize particular geometries of adsorbed reacting species. Interestingly, 15 years ago, Gallezot and Richard[6] speculated that such an approach might be possible, but it has not been successfully demonstrated previously.

The formation of alkanethiol SAMs on gold surfaces has been extensively characterized; such systems are deposited on a surface from a dilute thiol solution through bulk transport followed by surface adsorption and a final, slow, two-dimensional organization step to yield a well-ordered monolayer bound to the active metal surface by a metal—sulfur bond.[11−13] Alkanethiol SAMs exhibit similar well-ordered structures on palladium and platinum surfaces. For example, the wetting behaviors of

alkanethiol SAMs on palladium are similar to those observed for the same SAMs on gold, silver, and copper substrates.[14] Similarly, alkanethiols on platinum have been shown using XPS not to undergo C−S bond scission or to contain weakly adsorbed species and are oriented much closer to the surface normal than those on palladium or gold.[15] Because alkanethiol SAMs are readily fabricated in a controlled, reproducible manner, they offer an excellent way to control the near-surface environment. Regioselectivity studies have been pursued previously using organic monolayers to create favorable geometries for directing organic photoreactions,[16] and recently a wide range of organic modifiers have been successfully used to nonspecifically tune the surface of heterogeneous catalysts.[10,17−21] However, the ability to rationally and precisely tune chemoselectivity through noncovalent interactions within these monolayers has not been previously achieved.

The hydrogenation of *α,β*-unsaturated aldehydes, such as cinnamaldehyde, to their respective unsaturated alcohols is among the most widely studied classes of model reactions for understanding methods to promote chemoselectivity.[5,6,22−26] In addition, the production of unsaturated alcohols is a less favorable yet more industrially valuable pathway for the fragrance and pharmaceutical industries.[6] The selectivity of this reaction has been shown to be highly dependent on the precious metal used, and since platinum is among the most selective for producing the desired cinnamyl alcohol product, it was chosen as a starting point for this study.[5]

2. EXPERIMENTAL METHODS

2.1. Materials. A 5 wt % Pt/Al_2O_3 catalyst was purchased from Sigma-Aldrich. 1-Propanethiol (C_3SH), 1-hexanethiol (C_6SH), 1-dodecanethiol ($C_{12}SH$), 1-octadecanethiol ($C_{18}SH$), thiophenol, thiophene, benzyl mercaptan, and 2-phenylethanethiol were all obtained from Sigma-Aldrich. 3-Phenyl-1-propanethiol (>95%) was obtained from MolPort, and 4-phenyl-1-butanethiol (>95%) was obtained from Ukrorgsyntez, Ltd. Ethanol (>99.5%) used as a solvent during SAM deposition and in the reactor was from Sigma-Aldrich. Tetrahydrofuran (>99.5%) internal standard and the reactants cinnamaldehyde and prenal were also obtained from Sigma-Aldrich. All gases (H_2, O_2, and He) used for catalyst preparation and reaction were Airgas ultrahigh purity.

2.2. Surface Area and Preparation of Catalysts. The commercial uncoated 5 wt % Pt/Al_2O_3 was characterized by chemisorption of hydrogen on a Quantachrome Autosorb-1 to determine the active surface area. The catalyst was reduced in situ at 473 K for 16 h, after which chemisorption with CO indicated an active surface area of 2.87 m^2/g and a dispersion of 26.6%. The particle size was measured by TEM as 3.9 ± 1.1 nm.

SAM-coated catalysts were prepared by immersing the catalyst in an ethanolic solution of 10 mM for thiols that were liquid at room temperature and 1 mM for thiols that were solid at room temperature. After 12−16 h, the thiol solution was poured off and the catalyst was rinsed for 3 h in ethanol to remove any physisorbed thiols. Finally, this ethanol supernatant was poured off and the catalyst was dried under vacuum for 20 min in a vacuum desiccator. All thiol-coated catalysts were used the same day they were prepared unless specified otherwise.

Phenylated SAM coatings used for the hydrogenation of cinnamaldehyde were susceptible to subtle changes of the deposition procedure, including aging in air. Aging of the thiol coating in air (ambient laboratory conditions) significantly altered the selectivity of the 3-phenyl-1-propanethiol coating, reducing the selectivity from 90% to near 15% for times longer than 1 week; this is hypothesized to be due to degradation of the SAM layer. Numerous effects can contribute to the degradation of an alkanethiol SAM, including ozone oxidation in air enhanced by time and light.[27] In addition, SAM-coated surfaces degrade under solvated conditions, though this degradation is minor up to 25

h.[28] To minimize degradation in this study, all reactions were run for 1 h, minimizing any degradation of the SAM surface in situ. Aging was achieved by leaving a dry catalyst exposed to ambient laboratory conditions for the desired time.

2.3. Reaction System. Reactions were run in a 100 mL Parr semibatch reactor at 50 °C pressurized to 40 bar with hydrogen gas. Reactor contents were prepared as 48 mL of ethanol solvent, 5 mL of THF internal standard for the GC analysis, and 1 mL of reactant, giving the system a reactant concentration of approximately 0.15 M. Solvent choice has been shown not to significantly influence the selectivity of the reaction, and light alcohols such as ethanol have been shown previously to give the highest rates.[6] For reactions of uncoated catalysts between 10 and 50 mg of catalyst was used, and for coated catalysts, up to 300 mg of the catalyst was used. All reactions were run for 60 min, during which eight 1.5 mL liquid samples were taken. Hydrogen pressure was used to push liquid samples out through the sample tube and through a disposable filter, which was replaced after each sample. By sampling the liquid with catalyst and filtering out the catalyst, we were able to keep the ratio of catalyst to reactant constant within the reactor independent of how much liquid was sampled. Liquid samples were taken in vials and analyzed in an Agilent 5890A gas chromatograph with a flame ionization detector. The column was an Agilent HP-5 capillary column with dimensions of 30 m × 0.32 mm × 0.25 μm.

2.4. Selectivity and Rate Calculations. Reaction rates for both the coated and uncoated catalysts were calculated as the moles of reactant consumed per mole of surface metal per second. The calculations were made using the dispersion of the uncoated Pt/Al_2O_3 catalyst and the initial slope of the consumption of reactant per time at short time intervals where the slope could be approximated as linear. This is the same approach for calculating rates as in our previous SAM-coated catalysis work.[10,29,30] Further characterization is required to determine which sites alkanethiol SAMs cover and which type of site is active in the reaction system with or without the SAM coating. In order to avoid confusion or present a misleading turnover frequency (TOF), we instead report the rates as moles of reactant consumed per mole of surface metal per time. Error bars in the reported rates are computed from replicate measurements and error in the initial slope estimation. Reaction selectivity was calculated as the conversion to a particular product divided by the total conversion to all products. Therefore, the selectivity always totaled 100%. Error bars in selectivity were calculated from repeat measurements.

2.5. Thin Film PM-RAIRS. Thin films of platinum were prepared by electron beam evaporation onto soda lime glass slides. The slides were cleaned with a nanostrip solution (sulfuric acid/peroxide/buffer) for 10 min at 95 °C, rinsed in DI water for 10 min, and then cleaned in a UV ozone plasma machine at 150 W for 3 min, rinsed in DI water, and blown dry. An adhesion layer of 30 nm of Ti followed by 150 nm of Pt was deposited onto the cleaned slides. Thiol coatings were deposited to the platinum thin films at the same concentration used to prepare thiol-coated catalysts. When they were removed from solution, platinum thin films were blown dry with nitrogen rather than under a vacuum desiccator, as had been done for the catalysts.

PM-RAIRS (polarization modulation−reflection absorption infrared spectroscopy) data were taken using a Thermo Scientific Nicolet 6700 spectrometer with a Thermo Scientific TOM (tabletop optical module) PM-RAIRS attachment. The PEM (photoelastic modulator) was made by Hinds Instruments and the synchronous sampling demodulator by GWC Technologies. The signal was received by a Thermo Scientific MCT-A (mercury cadmium telluride) detector cooled with liquid nitrogen. In order to hold the cinnamaldehyde or prenal liquid in place to take the IR scan, an Edmund Optics (1 mm × 50 mm) zinc selenide coverslip was used. Zinc selenide is IR inactive and therefore served as a way to maintain a uniform thin film of cinnamaldehyde or prenal while not disrupting the infrared signal on the surface. Some incident light was reflected from the surface of the zinc selenide coverslip before reaching the platinum surface, but this light was not focused at the detector and so could not interfere with the measured signal. The coverslip had an antireflective coating rated from 3 to 12 μm to allow as much light to pass through as possible. The coverslip was clipped in place over top of the liquid sample so as not to interfere with the signal. Error bars of the

η^1/η^2 ratio were calculated from repeat measurements on freshly prepared slides.

3. RESULTS AND DISCUSSION

3.1. Noncovalent Control of Selectivity. Over an uncoated Pt/Al_2O_3 catalyst (Figure 1a), cinnamyl alcohol was
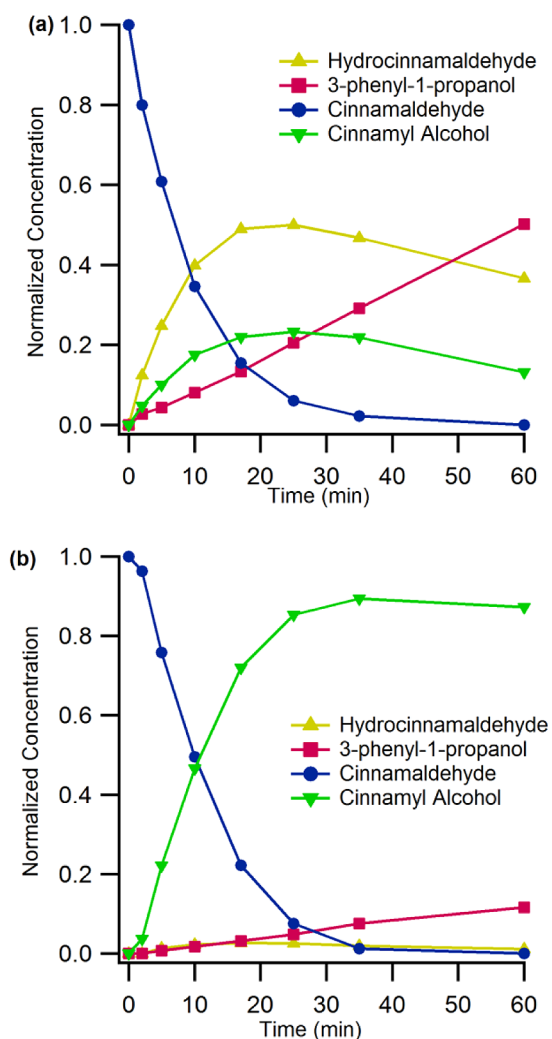

Figure 1. Kinetic plots for the hydrogenation of cinnamaldehyde: (a) hydrogenation over an uncoated 5 wt % Pt/Al_2O_3 catalyst; (b) hydrogenation over a 3-phenyl-1-propanethiol coated 5 wt % Pt/Al_2O_3 catalyst.

produced at levels much lower than those of hydrocinnamaldehyde at all times and conversions. In fact, the selectivity to cinnamyl alcohol was constant at 25% (Figure 2) over a broad range of conversions (20−90%), in agreement with previous reports.[5,6]

To tune noncovalent interactions in the near-surface environment, SAMs comprised of a number of organic ligands (Scheme 2) were employed. Prenal, a branched nonaromatic α,β-unsaturated aldehyde, was used as a reactant for control experiments. Because all α,β-unsaturated aldehydes contain the same reactive double bond and aldehyde at their terminal end, they can be expected to respond similarly to changes in the electronic properties of the catalyst surface; however, cinnamaldehyde contains a phenyl group, resulting in additional spatial constraints within the crowded surface region[6] as well as
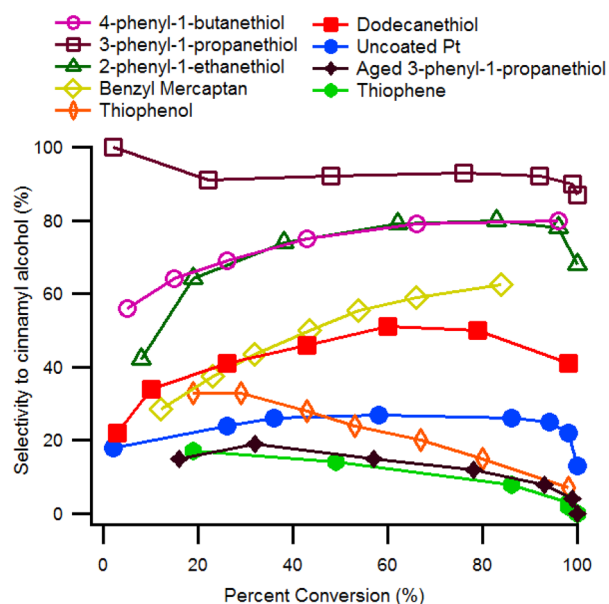

Figure 2. Selectivity to cinnamyl alcohol for the hydrogenation of cinnamaldehyde over Pt/Al_2O_3 catalysts. All reactions were carried out at 40 bar of hydrogen pressure and 0.15 M initial cinnamaldehyde concentration in ethanol solvent. Alkanethiol SAMs nonspecifically increased the selectivity to cinnamyl alcohol (C_3SH, C_6SH, and $C_{18}SH$ shown in Figure S5 (Supporting Information)) over the uncoated case, but phenylated SAMs showed the ability to dramatically increase or decrease the selectivity depending on the location of the phenyl ring with respect to the surface.

Scheme 2. Molecules Used in the Hydrogenation System: (a) Thiol SAMs Used To Coat the Pt/Al_2O_3 Surface; (b) Cinnamaldehyde and Prenal Reactants
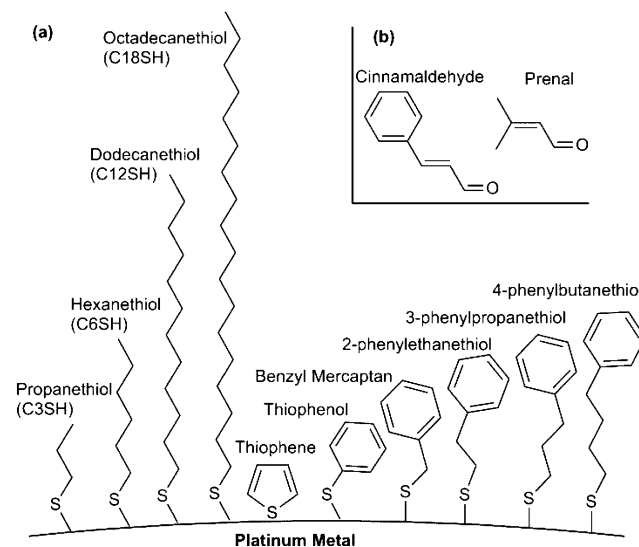
the potential for additional noncovalent aromatic stacking interactions. Whereas linear alkyl ligands are not expected to interact preferentially with a particular region of the cinnamaldehyde reactant, phenylated ligands can interact with cinnamaldehyde's phenyl group through aromatic π−π stacking.[31] For example, cinnamaldehyde exhibits much smaller contact angles with phenyl-terminated Pt surfaces than with alkyl-terminated surfaces (Figure S1, Supporting Information). By changing the vertical position of the modifying phenyl group within the SAM layer, it is hypothetically possible to control the

orientation of the cinnamaldehyde with respect to the active surface via these $\pi-\pi$ stacking interactions. Prenal, which lacks an aromatic moiety, exhibits no such specific interaction with phenylated SAMs.

Using a catalyst coated with a 3-phenyl-1-propanethiol SAM (Figures 1b and 2) increased the hydrogenation selectivity of cinnamaldehyde to greater than 90%, indicating a highly favorable specific interaction between the properly spaced phenyl ring from the SAM and the phenyl ring of the cinnamaldehyde. 2-Phenylethanethiol and benzomercaptan modifiers improved selectivity to a lesser extent, while catalyst modification with thiophene and thiophenol decreased selectivity. In other words, the highest selectivity was associated with a three-methylene spacer between the S atom and the phenyl ring, a structure that approximately matches that of cinnamaldehyde. Over long time intervals, at 100% conversion, the series reaction to produce 3-phenyl-1-propanol occurred; however, high selectivity was observed even at conversions of 90%.

A longer 4-phenylbutanethiol coating showed an increase in selectivity similar to that of the 2-phenylethanethiol coating, but not as good as the 3-phenylpropanethiol coating, indicating a peak in selectivity at the proper spacing length of the cinnamaldehyde molecule. The longer spacer also decreased the rate of reaction by a factor of 2 compared to the shorter phenylated SAM cases. An even larger rate decrease was seen for the hydrogenation of benzaldehyde (C_6H_5CHO) on uncoated and 3-phenyl-1-propanethiol-coated catalysts (Table S1, Supporting Information). That is, in cases where the spacer length in the modifier is greater than the distance between the phenyl ring and the carbonyl function in the reactant, the reaction rate is suppressed. This result suggests that if aromatic stacking interactions occur too far above the surface, the carbonyl function is hindered from reaching the surface.

The molecular order of the phenylated SAMs for these hydrogenation experiments was critical to their efficacy. Well-ordered SAMs contain few surface vacancies and exhibit a standing-up adsorption geometry, while poorly ordered SAMs adopt a lying-down structure and are prone to C–S bond scission due to greater tail disorder on the catalytic surface.[29,32] For the hydrogenation of cinnamaldehyde, the quality of the SAM was shown to have a dramatic impact on the selectivity of the reaction. A 3-phenyl-1-propanethiol SAM that had been aged for 1–3 weeks in air decreased the selectivity to cinnamyl alcohol to lower than that for the uncoated case (Figure 2), similar to the effect caused by shorter phenylated SAMs, consistent with a strong dependence on the position of the SAM phenyl ring relative to the catalyst surface. The 2-phenylethanethiol SAM was even more sensitive to aging, showing a decrease in selectivity after less than 1 day. Degradation of SAMs within the reaction solution was also considered, as shown in Figures S2 and S3 (Supporting Information). The results show that there is some selectivity loss when the catalyst is recycled without regeneration, but this can be avoided by maintaining a small concentration of thiols in solution. A detailed investigation of the effects of various recycling procedures is in progress.

Metal particle size has been shown previously to significantly affect the selectivity of cinnamaldehyde hydrogenation, where large particles, with larger flat facets, favor selective hydrogenation and small particles with large curvature have low selectivity to cinnamyl alcohol.[6] The 5 wt % Pt/Al_2O_3 catalyst used here had a measured average particle size of 3.9 ± 1.1 nm, but we also studied a 0.5 wt % Pt/Al_2O_3 catalyst particle size of 0.8 ± 0.1 nm. For these smaller particles, as shown in Figure S4

(Supporting Information), the selectivity was improved for thiol-coated catalysts in comparison to the uncoated case, but the increase in selectivity did not depend on the functionality of the coating. This loss of ligand-specific selectivity control suggests that, for small particles with high curvature, the ligand-specific control is difficult to maintain.

Alkanethiol SAMs formed from propanethiol, hexanethiol, dodecanethiol, and octadecanethiol were all shown to increase the selectivity of the reaction (Figure 2 and Figure S5 (Supporting Information)) to up to 60% selectivity. These selectivity values were improved over those of the uncoated case, but they were not specific to the length of the thiol tail, similar to the nonspecific effect typically seen from sulfur poisoning. This result suggests that a nonspecific selectivity improvement may be realized through modification by inorganic sulfur sources, as has been observed previously in the hydrogenation of 1-epoxy-3-butene on alkanethiol- and H_2S-modified Pd catalysts.[10] Studies of H_2S-modified Pt (reported in the Supporting Information) for cinnamaldehyde hydrogenation showed a decrease in rate with no improvement in selectivity. However, we cannot rule out the possibility that a different form of exposure to H_2S or another inorganic sulfur source can improve selectivity; as reported elsewhere, sulfur deposition for selectivity modification is difficult to control.[26,33−36]

Whereas the phenylated SAMs exerted specific control on the basis of their tail lengths, the alkanethiol modifiers nonspecifically enhanced the reaction selectivity. Previous studies have shown that unsaturated alcohol selectivity is increased by weakening the binding strength of the desired product to the catalyst surface,[37,38] and the same adsorption weakening effect is hypothesized to be responsible for the nonspecific increase in selectivity over alkanethiol-coated catalysts.

3.2. Hydrogenation of Prenal. To test this hypothesis, we also investigated the hydrogenation of a nonaromatic α,β-unsaturated aldehyde, prenal, which contains the same reactive groups as cinnamaldehyde without a phenyl moiety. Whereas cinnamaldehyde showed specific control of selectivity via phenylated thiols, prenal hydrogenation selectivity was insensitive to the presence of a phenyl group in the SAM. Prenal hydrogenation selectivity (Figure 3) increased similarly for each of the alkanethiol-coated catalysts as well as the 2-phenyl-ethanethiol- and the 3-phenyl-1-propanethiol-coated platinum catalysts. This suggested a lack of specific interaction effects between the thiol coating and the reactant; the general increase in selectivity was consistent with previous hydrogenation studies of small molecules over thiol-coated catalysts due to changes in the electronic properties of the catalyst surface.[10] These results indicate that, although nonspecific electronic effects can increase the selectivity of the reaction, the position of the phenyl ring from the surface provides the extra functional handle with which to direct selectivity still higher or lower from there.

The low selectivity observed for catalysts modified with thiophene and thiophenol was likely due to the close proximity of the aromatic functional group to the surface. For example, thiophene is known to undergo extensive C–S bond-breaking reactions on noble metal surfaces,[39] consistent with a greater deposition of surface sulfur observed in this study (Figure S6 (Supporting Information)).

3.3. PM-RAIRS Study of Reactant Binding Geometry. We hypothesize that the direction of selectivity change (i.e., increase or decrease) for the hydrogenation of cinnamaldehyde is controlled in part by the orientation of adsorbed cinnamaldehyde in relation to the surface (Scheme 3) via the interaction of its
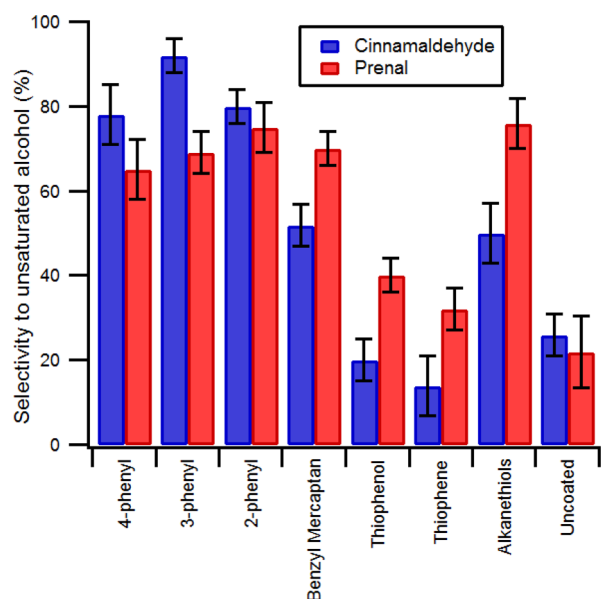
Figure 3. Selectivity of cinnamaldehyde and prenal hydrogenation to its respective unsaturated alcohol. The alkanethiols C_3SH, C_6SH, $C_{12}SH$, and $C_{18}SH$ were averaged for one data point. Reactions were run at 40 bar of H_2 and 50 °C and 0.15 M reactant solvated in ethanol. The selectivity was reported at 50% conversion.

Scheme 3. SAM-Enhanced Orientation of Cinnamaldehyde with the Catalyst Surface: (a) Cinnamaldehyde Interacting with an Uncoated Platinum Surface through the C=C Double Bond; (b) 3-Phenyl-1-propanethiol SAMs Favoring Aldehyde Hydrogenation by Creating an Upright Molecular Orientation
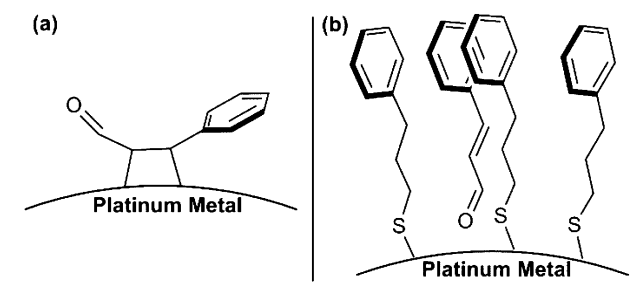
phenyl moiety with the phenyl ring of the SAM. For the 3-phenyl-1-propanethiol SAM, the distance between the phenyl ring and surface is such that cinnamaldehyde is directed to a standing-up orientation in which only the aldehyde group interacts with the surface.

It has been shown previously that binding in a horizontal configuration favors C=C hydrogenation, while binding in a vertical orientation favors C=O hydrogenation.[40] In order to probe binding geometries, polarization modulation reflection−absorption infrared spectroscopy (PM-RAIRS) was used to examine how the adsorption of cinnamaldehyde varies in the presence of different thiol coatings. The advantage of this technique is the ability to isolate the spectra of adsorbed molecules in the presence of an isotropic solution phase. Because PM-RAIRS requires an optically reflective surface, the study was performed on a thin film of platinum (150 nm) deposited on a silica glass wafer. Thiol SAM-coated surfaces were prepared in ethanolic solutions identical with the solutions used to prepare

catalysts. Each spectrum was normalized to its background and adjusted to a zero baseline between 2500 and 2600 cm^{-1}.

There are distinct differences between the spectra collected after adsorption of cinnamaldehyde on each of the four surfaces (Figure 4a). Peaks in the frequency range 1500−1750 cm^{-1} correspond to the vibrational modes of C=C double bonds as well as C=O aldehyde stretches. The large qualitative differences in peak structure in this region suggested that the various coatings had a strong effect on the cinnamaldehyde adsorption geometry. In contrast, the general structure of the prenal spectra was insensitive to the various coatings (Figure 4b). Previous studies have used a combination of experimental vibrational spectroscopy and density functional theory (DFT) to identify the stretching modes in this region associated with binding configurations of prenal and crotonaldehyde (2-butenal) on platinum and tin-doped platinum surfaces.[24,37] The DFT studies identified numerous binding configurations, two of which are especially prominent in high-coverage conditions on Pt: the η^1 configuration (associated with C=O hydrogenation) where the molecule is bound through the carbonyl oxygen lone pair electrons in an upright geometry similar to that in Scheme 3a and the η^2 configuration (associated with C=C hydrogenation) where the molecule is bound in a di-σ_{CC} configuration through its C=C double bond parallel to the surface similar to the position shown in Scheme 3b.[24,41] Assignments from the prior studies (Table S2 (Supporting Information)) were used together with spectra of related molecules such as hydrocinnamaldehyde (Figure S7 (Supporting Information)) to assign peaks for the adsorption of cinnamaldehyde and prenal on platinum thin films. The peaks at 1683 and 1687 cm^{-1} corresponded to the aldehyde stretches of an η^2 binding configuration for cinnamaldehyde and prenal, respectively, and the peaks at 1575 and 1545 cm^{-1} corresponded to the aldehyde stretches of the η^1 binding configuration, respectively. The spectra in Figure 4a show a relative increase in the prominence of the η^2 binding configuration in comparison to the η^1 binding configuration for thiophenol SAMs, which exhibit low selectivity to the unsaturated alcohol. Conversely, the highly selective 3-phenyl-1-propanethiol SAM shows a stronger signal from the η^1 binding configuration. Since the η^1 binding configuration is associated with C=O hydrogenation while the η^2 binding configuration is associated with C=C hydrogenation, the effect observed for cinnamaldehyde orientation on these surfaces is consistent with the selectivity data for the hydrogenation of cinnamaldehyde. This effect was quantified in Figure 4c, where peaks identified in Figure 4a,b were integrated (Figures S8 and S9 (Supporting Information)) and a ratio of the η^1/η^2 peak area for cinnamaldehyde and for prenal was each compared to its reaction selectivity for each SAM coating. Cinnamaldehyde reaction selectivity was shown to trend directly with this ratio, while the adsorbed states of prenal were uncorrelated with the ratio of peak intensities. Consistent with previous studies, this suggests a different mode of selectivity enhancement for prenal which is nonspecific to the organic function of the SAM and has been previously attributed to a weakened adsorption state of prenal on the catalyst surface.[24]

As the electronic properties of a catalyst are altered, the selectivity typically improves at the expense of reactivity, consistent with the weakening of reactant adsorption to a catalyst surface.[24,26] Generally the catalysts investigated here showed a tradeoff between activity and selectivity, as would be expected for a modified catalytic system, but the 3-phenyl-1-propanethiol SAM did not compromise activity (Figure 5) due to
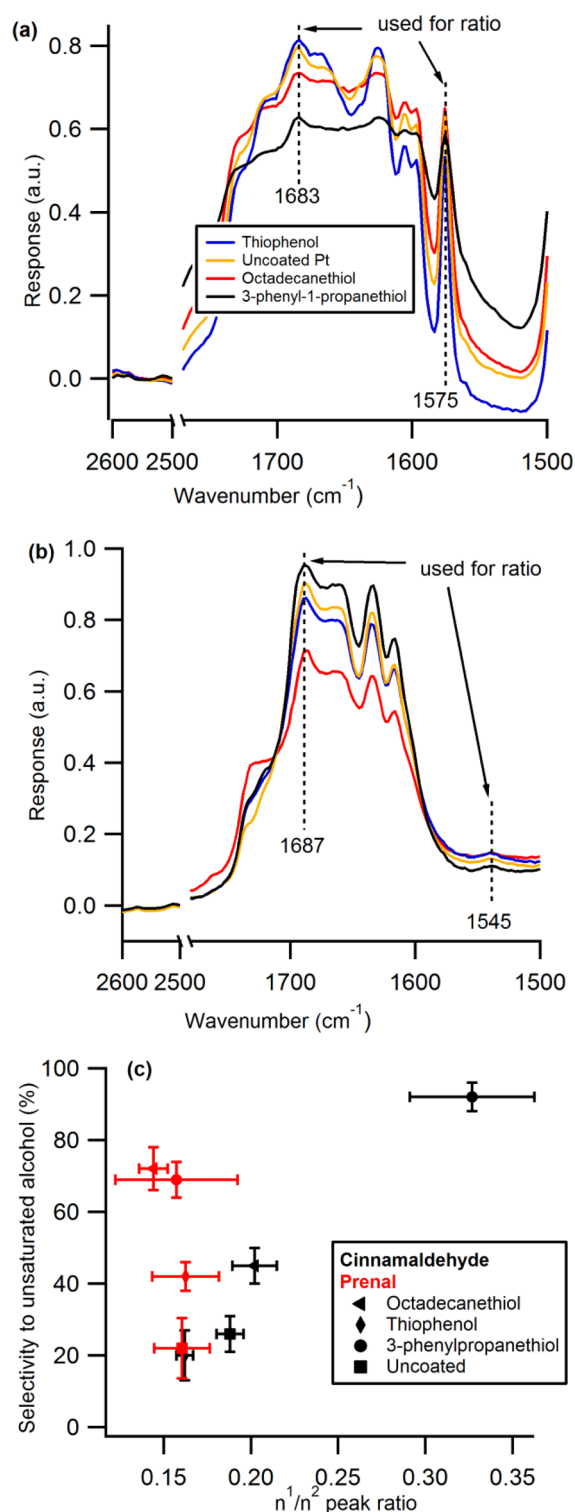
Figure 5. Rate versus selectivity to unsaturated alcohol for both uncoated and SAM-coated Pt/Al_2O_3 catalysts. Rates are shown as the moles of reactant consumed per moles of surface platinum per second. Alkanethiols C_3SH, C_6SH, $C_{12}SH$, and $C_{18}SH$ were averaged for one data point.

production was indistinguishable, within experimental error, on the uncoated and 3-phenyl-1-propanethiol-coated catalysts (Table S1 (Supporting Information)). As also shown in Table S1, the effect of a phenylated SAM with a longer alkyl spacer is hypothesized to further decrease the rate of reaction.

4. CONCLUSIONS

Here we demonstrate that thiol modifiers can improve the selectivity in hydrogenation of α,β-unsaturated aldehydes by a combination of electronic effects and specific noncovalent interactions of the reactant in the near-surface environment. The selective hydrogenation of both prenal and cinnamaldehyde to the desired unsaturated alcohols was enhanced with a thiol-coated catalyst surface, but the selective hydrogenation of cinnamaldehyde was further controlled through interactions of its phenyl ring with aromatic ligands within the SAM-coating layer. The selective hydrogenation of α,β-unsaturated aldehydes is commonly achieved through active site modification,[6,22] but here we demonstrate that ligand-specific control exhibited by phenylated SAMs can create a reaction environment that functions in analogy to biological catalysts. This ability to exercise control over the selective hydrogenation of cinnamaldehyde by ligand-specific interactions provides a promising new method for controlling a reactive system beyond modifying the active site of heterogeneous catalysts.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Text, tables, and figures giving contact angle measurements, ICP-AES analysis, peak assignments and IR analysis, and recycle studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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Figure 4. PM-RAIRS analysis of reactant adsorption geometry. (a) Cinnamaldehyde and (b) prenal adsorbed on thiophenol-coated platinum, uncoated platinum, octadecanethiol-coated platinum, and 3-phenyl-1-propanethiol-coated platinum thin film surfaces. (c) Deconvolution of the spectra to obtain the ratio of η^1 to η^2 C═O peaks shown with selectivity data for cinnamaldehyde and prenal hydrogenation. Error bars were calculated from replicate measurements.

its different mode of selectivity improvement with cinnamaldehyde. Although the rate of cinnamaldehyde consumption decreased by a factor of 3, the rate of cinnamyl alcohol
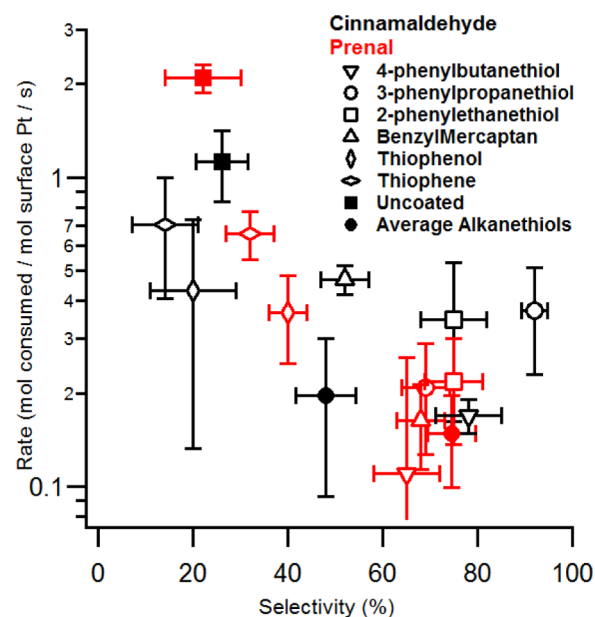
Notes

The authors declare no competing financial interest.

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