**Stability of Self-Assembled Monolayer Coated Pt/Al₂O₃ Catalysts for Liquid Phase
Hydrogenation**

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Abstract

Thiolate self-assembled monolayers have recently been demonstrated to be effective catalyst modifiers for selectivity control, but these studies have not extensively explored the long term stability of these modifiers or the effects of specific reaction conditions. Here we investigate how the performance of thiolate-modified Pt/Al₂O₃ catalysts is affected by recycling and regeneration, using the selective hydrogenation of cinnamaldehyde to cinnamyl alcohol as a probe reaction. Although modification of Pt catalysts with 3-phenyl-1-propanethiol results in high selectivity due to a ligand-specific interaction between modifier and reactant during the first use of a given catalyst, repeated recycling was shown to decrease the efficacy of this mechanism due to increasing disorder in the monolayer. However, selectivity and order could be stabilized using a thiol regeneration step or by feeding dilute concentrations of thiols in the reaction mixture. Similarly, aging in air was shown to decrease the order of the thiol and reduced the selectivity improvement of both a 3-phenyl-1-propanethiol and an octadecanethiol (C18) modified Pt/Al₂O₃ catalyst. These studies show that the ligand-specific interactions between the SAM and the reactant are particularly sensitive to conditions that can degrade the monolayer.

Keywords: alkanethiol, self-assembled monolayer, unsaturated aldehyde, hydrogenation, platinum on alumina

1. Introduction

The ability to exert control over the selectivity of a reaction with numerous competing pathways is of paramount concern in catalysis for chemicals production [1]. Catalyst design plays a fundamental role in determining selectivity, where selection of the metal composition, metal loading, support, and particle shape all can influence the selectivity and reactivity [2-5]. It is equally important to consider the long-term stability of the catalyst; as design becomes more complicated, deterioration of the catalyst under reaction conditions becomes an increasing concern. For example, the use of organic coatings has seen recent success as a method of catalyst modification [6-8]. Specifically, thiol self-assembled monolayers (SAMs) have been used as selectivity modifiers for their ability to covalently bind to a metal catalyst surface and enhance reaction selectivity through a combination of surface and near-surface effects [9-13]. These modifications to the catalyst surface, while effective, raise questions about durability over long reaction times or reuse in subsequent reactions. Durability is a particular concern in solvated reaction systems, where it is possible for thiols to dissolve into the solvent. Moreover, studies of catalyst performance over time and under different environmental conditions can provide fundamental information about the interactions of reacting species with the near-surface environment and how these interactions influence selectivity.

Alkanethiols bind to a metal surface, such as that of a Pt catalyst, in a multistep process to form a SAM, as illustrated in Scheme 1. To prepare thiolate SAMs, the substrate metal is incubated in a dilute solution of typically 1-100mM of the thiol precursor such that the thiols adsorb and rapidly saturate the surface with thiol [14, 15] forming a covalent bond [16]. The deposition step is allowed to occur over several hours in order to allow time for a slow re-organization step of thiols on the metal surface [14, 17].

Scheme 1. Formation of a C18 coating from a bulk solution. An initial fast step of bulk transport to the surface is followed by an ordering step resulting in a well-ordered self-assembled monolayer

Recently, we have shown that thiolate SAMs can be used to dramatically improve selectivity for the hydrogenation of cinnamaldehyde (Scheme 2(a)) through a combination of ligand specific and ligand non-specific interactions [12]. High selectivity to the desired product cinnamyl alcohol was achieved by modifying the catalyst with a thiol (3-phenyl-1-propanethiol) that exhibited aromatic stacking interactions with the phenyl head group of cinnamaldehyde. As shown in Scheme 2 (b), the 3-phenyl-1-propanethiol SAM is of the proper length such that non-covalent aromatic stacking interactions favor an adsorbate orientation that leads to carbonyl hydrogenation to form the desired product, cinnamyl alcohol. In addition to this ligand-specific effect, selectivity was also influenced by a non-specific surface effect induced by attachment of the thiolate sulfur atom to the metal surface.

Scheme 2. Hydrogenation of cinnamaldehyde. (a) reaction pathway. (b) orientation effect exerted by a 3-phenyl-1-propanethiol SAM via non-covalent interactions [12]

Organic modifiers such as thiols are naturally susceptible to degradation, especially under harsh reaction conditions. For example, under hydrogenation reaction conditions in the liquid phase, it is expected that thiolates can undergo the reverse of the deposition reaction, i.e. that they will gradually desorb from the catalyst as thiols [18]. Despite the growing use of SAMs as catalyst modifiers for liquid phase reactions [9, 11, 19, 20], a systematic study of the effects of this phenomenon and its effect on catalysis has not yet been presented. Here we use the hydrogenation of cinnamaldehyde as a probe reaction to study how environmental conditions affect influence the structure and catalytic performance of SAM-coated catalysts, and to identify methods can be used to moderate these effects.

2. Experimental

2.1 Materials

A commercial 5 wt% Pt/Al₂O₃ catalyst was purchased from Sigma Aldrich. 3-Phenyl-1-propanethiol was purchased from MolPort (>95%). 1-Octadecanethiol (>99.5%), ethanol (>99.5% anhydrous, used as solvent in reactions as well as for making ethanolic solutions of

thiols for SAM deposition), tetrahydrofuran (>99.5%, used as internal standard), and the reactant cinnamaldehyde were also obtained from Sigma Aldrich, as were solvents heptane, benzene, and cyclohexane. Gasses (hydrogen, oxygen, and helium) used for catalyst preparation and reaction were Airgas ultra-high purity.

2.2 Catalyst preparation

SAM-coated catalysts were prepared from the as-purchased commercial 5wt% Pt/Al₂O₃ catalyst. The catalysts were oxidized in an 80:20 helium:oxygen mixture at 300°C for 3 hrs and then reduced at 200°C for 2 hrs or overnight under an 80:20 helium:hydrogen mixture. Once oxidized and reduced, the catalyst was immersed in an ethanolic solution of thiol precursor. Contact to air was limited; however, reaction studies showed that exposure of the catalyst to air before thiol deposition, including using the catalyst untreated as purchased, did not affect the efficacy of the SAM coating or show any changes in its characterization. The catalyst (250mg or less) was added to 40mL of thiophenol (10 mM), 3-phenyl-1-propanethiol (10 mM), or octadecanethiol (1 mM); the latter was deposited at a lower concentration due to the low solubility of octadecanethiol in ethanol. Using the maximum amount of catalyst, the 1 mM concentration corresponded to a deposition of thiol at 10x the theoretical monolayer coverage assuming a packing structure of $\sqrt{3} \times \sqrt{3}$ R30° on the active surface area of the catalyst. The active surface area was determined by chemisorption with carbon monoxide on a Quantachrome Autosorb-1 to be 2.87 m²/g for uncoated 5 wt% Pt/Al₂O₃. Over 12-24 hrs the catalyst was allowed to settle out of the thiol solution, after which time the thiol supernatant was poured off and the catalyst was rinsed in 40mL of fresh ethanol for 3-12 hours to remove weakly-adsorbed

thiol. Finally, the ethanol supernatant was poured off and the catalyst was dried in a vacuum desiccator. All thiol-coated catalysts were used the same day they were prepared unless otherwise specified for experiments probing the effects of degradation due to ambient exposure. Degradation of the catalysts was achieved by placing the catalyst uncovered in ambient laboratory conditions for the desired incubation time.

In some of the results described below, the catalyst was regenerated between reactions. In this regeneration procedure, the spent catalyst was immersed in an ethanolic solution of the thiol precursor under the same incubation conditions as for the initial deposition. The concentration was reduced by half for the 3-phenyl-1-propanethiol-coated catalyst and by a factor of 10 for the octadecanethiol-coated catalyst. Lower thiol concentrations were required since the surface still contained a high coverage of thiols from the initial deposition. In addition, using full thiol deposition concentrations rendered the rinse step less effective in removing physisorbed thiols, a condition easily noted by a significant decrease in the reaction rate.

2.3 Reaction system

All reactions shown were run in a 100mL Parr batch reactor at 50°C pressurized to 40 bar with hydrogen gas. The reactor was prepared as described previously with 48mL solvent, 5mL THF internal standard, and 1mL of cinnamaldehyde [12]. These proportions gave an initial reactant concentration of approximately 0.15 M. For reactions of uncoated catalysts, 10 – 100mg of catalyst was used, and for coated catalysts, up to 300mg catalyst was used. Eight samples were taken at increasing time intervals over the course of a 60 minute reaction. Head pressure inside the reactor was used to push liquid samples out through the sample tube and

through a disposable filter [12, 19, 20]. By sampling the liquid with catalyst, filtering out the catalyst, and replacing the filter before each sample, the ratio of catalyst to reactor solution was considered to be constant and independent of the volume of liquid sampled. Re-pressurization of the reactor with hydrogen gas was used to push any excess liquid left in the sample loop back into the reactor mixture thereby avoiding the contamination of a future sample. Liquid samples were analyzed in an Agilent 5890A gas chromatograph equipped with a flame ionization detector. The column was an Agilent HP-5 capillary column with dimensions of 30m x 0.32mm x 0.25 μ m.

For recycle studies where thiol precursor was added to the reaction mixture, a dilute concentration of the thiol was added to the solvent/THF/reactant solution prior to the start of the reaction.

As in other studies, the rates reported here are moles of reactant per moles of surface sites of an uncoated catalyst per second. There is still uncertainty in the extent to which thiol modifiers restrict the active sites of the catalyst surface, so this method is used to create a consistent comparison between different thiol coatings and the uncoated catalyst.

2.3 Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

Fourier transform infrared spectroscopy analysis was performed with a Thermo Scientific Nicolet 6700 FT-IR. A Harrick closed cell Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) attachment was used to take IR measurements. For each sample, 50 scans at 4 cm⁻¹ resolution were taken to compile the spectra. Approximately 50mg of catalyst was used for each measurement.

3. Results and Discussion

3.1 Kinetic studies of ligand-specific and non-specific interactions

As reported in a previous publication [12], we have observed that thiol SAMs can improve the selectivity for hydrogenation of cinnamaldehyde to cinnamyl alcohol. This effect was found to be strongly dependent on the nature of the thiolate tail, where the highest selectivity was observed for a 3-phenyl-1-propanethiol SAM. Whereas the specific aromatic stacking interactions disfavored hydrogenation of the internal olefin function for the longer 3-phenyl-1-propanethiol function, they tended to favor it when the thiolate phenyl group was close to the surface, as in thiophenol. These differences in rate, tuned by tail functionality, resulted in selectivity control of the cinnamaldehyde hydrogenation pathway through a ligand-specific selectivity mechanism.

A related method for characterizing this effect is illustrated by Fig. 1, which shows the initial rates for hydrogenation of cinnamyl alcohol and hydrocinnamaldehyde, which are the intermediate, monofunctional products of cinnamaldehyde hydrogenation (Scheme 1). Over the uncoated catalyst, hydrogenation of the internal olefin of cinnamyl alcohol was approximately 40 times faster than the terminal aldehyde function of hydrocinnamaldehyde, indicating a much higher intrinsic hydrogenation rate for the internal C=C bond than the terminal C=O bond on Pt, a well-established effect [2]. Modification of the surface decreased the terminal aldehyde hydrogenation rate by approximately a factor of three for thiophenol, octadecanethiol, and 3-phenyl-1-propanethiol; i.e., the hydrogenation of the terminal aldehyde function was not strongly affected by the thiolate tail. Here, because the rate is *non-specific* to the structure of the organic modifying ligand, the effect of the modifiers on rate is expected to be primarily due to the effect

of surface sulfur. In contrast, the rate of cinnamyl alcohol hydrogenation (i.e., reduction of the internal olefin) was *specific* to the tail structure, with thiophenol causing the least reduction in rate and 3-phenyl-1-propanethiol causing a dramatic rate decrease. This large (nearly two order-of-magnitude) rate difference is attributed to non-covalent interactions between the aromatic functions of the reactant and thiolate tail. As discussed previously, interactions between 3-phenyl-1-propanethiol-derived monolayers and phenylated oxygenates suppress the accumulation of adsorbates that adopt a flat-lying orientation on the Pt surface, since an upright orientation is stabilized by the aromatic stacking interactions (as depicted in Scheme 1(b)) [12]. The flat-lying configuration has been shown to be associated with hydrogenation of the internal olefin function, suggesting that 3-phenyl-1-propanethiol strongly suppresses accumulation of such intermediates (Scheme 1b). All of the coatings suppress cinnamyl alcohol reactivity to a significant extent, likely because flat-lying geometries are generally disfavored when the surface is covered by an organic modifier species that occupies surface sites [12].

Fig. 1. Hydrogenation of cinnamyl alcohol and hydrocinnamaldehyde solvated by ethanol. Reaction rate is displayed as the moles of reactant consumed per mole of surface metal sites per second.

Such modification of the near surface environment by thiol modifiers has been shown to be effective, but preliminary studies showed the layer could be susceptible to degradation [12]. The primary focus of the following sections is to understand both how non-specific and specific thiolate-reactant interactions are affected by recycling- and aging-induced structural changes in the monolayer.

3.2 Recyclability of thiol SAM-coated catalysts

The effects of recycling were investigated for three types of catalysts: an uncoated Pt/A₂O₃, an octadecanethiol (C18) coated Pt/A₂O₃ catalyst, and a 3-phenyl-1-propanethiol-coated Pt/A₂O₃ catalyst. As discussed above, the C18 modifier has been associated with selectivity improvement due to the influence of sulfur on surface reactivity, while the 3-phenyl-1-propanethiol coating exhibits additional enhancements in selectivity due to non-covalent near-surface interactions. It is important to note that C18 and 3-phenyl-1-propanethiol modifiers produce monolayers surface coverages that are identical within experimental error [12]. Post-reaction, the spent catalysts were recovered by allowing them to settle out of solution, decanting the solution, and then drying the catalyst in air. In the most basic method of catalyst recycling, the catalyst was used in a fresh reaction mixture immediately following the drying step. Cinnamyl alcohol selectivity versus conversion plots for these catalysts are shown in Fig. 2.

Fig. 2. Recycle reactions for catalysts which were reused without any regeneration procedure. (a) uncoated catalyst (b) C18-coated catalyst (c) 3-phenyl-1-propanethiol-coated catalyst

Figure 2 shows the cinnamyl alcohol selectivity as a function of conversion for the uncoated, C18-coated, and 3-phenyl-1-propanethiol-coated catalysts. Even on the uncoated catalysts, selectivity was not found to be a very strong function of conversion. The weak dependence of selectivity on conversion until very high conversion has been previously observed and attributed to the suppression of cinnamyl alcohol hydrogenation by the presence of hydrocinnamaldehyde [2]. For simplicity, below we will generally compare selectivity measured at 50% conversion. The uncoated Pt/Al₂O₃ catalyst selectivity at 50% conversion improved after recycling from 28% to 45%. This improvement was attributed to the deposition of carbonaceous species during the initial reaction period, which may selectively poison the undesired reactions. CO-DRIFT spectra reported in Fig. S1 (as well as the analysis presented in Section 3.3 below) were consistent with the presence of carbonaceous deposits on the surface following reaction. Partial coverage of the catalyst surface by spectator species may reduce the number of binding sites and/or the binding affinity of the double bond in α,β -unsaturated aldehydes [2, 21-24]. The C18-coated catalyst selectivity showed little dependence on recycling, with selectivity remaining within experimental error during the three recycle reactions. This was also supported by Fig. S1,

which showed that the nature of the available sites on a C18-coated catalyst were constant over multiple recycle reactions.

The most dramatic effect of recycling was the decrease in selectivity for the 3-phenyl-1-propanethiol coated catalyst (Fig. 2 (c)). Such a decrease in selectivity is consistent with the hypothesis that a ligand-specific interaction is necessary to achieve high selectivity, and that this interaction effect is highly sensitive to subtle changes in the monolayer structure [12]. As the specific interaction effect of the thiol is compromised, the selectivity will decrease to parity with the non-specific selectivity improvement of the C18 coating. As seen in Fig. 2, over the course of sequential recycle reactions, the selectivity of each catalyst converges towards 50% selectivity. This is consistent with the hypothesis that there is degradation of the ligand specific 3-phenyl-1-propanethiol interaction, but also that the selective poisoning of sulfur on the surface still results in selectivity improvement over that of the uncoated catalyst.

Table 1: Recycle procedures used for regenerating catalysts between reactions. For the recycle method of adding thiols to the reaction solution, the “Recycle with no regeneration” technique was used with thiol added to the reaction mixture.

Recycle with no regeneration	Recycle with catalyst regeneration
1 Run reaction	1 Run reaction
2 Allow catalyst to settle	2 Allow catalyst to settle
3 Decant reactant supernatant solution	3 Decant reactant supernatant solution
4 Dry in desiccator under vacuum	4 Dry in desiccator under vacuum
5 Run subsequent reaction	5 Deposit catalyst overnight in thiol solution
	6 Decant and rinse for 4 hours in ethanol
	7 Decant and dry catalyst in desiccator under vacuum
	8 Run subsequent reaction

We hypothesize that a critical factor to maintaining the performance of thiol-coated catalysts in solution is maintaining an adequate surface coverage of the thiolate under reaction conditions. Therefore, we used an alternative recycle method of regenerating the SAM-coated

catalysts before reusing them in a subsequent reaction, referred to as the “regeneration-recycle” procedure. Here, the catalysts were dried and decanted after reaction and then immersed in a thiol solution similar to that used for initial deposition, but at a lower concentration (methods section) to limit physisorption of thiols on the catalyst surface. This procedure was expected to replenish the thiols that had desorbed into the solution during reaction. In the case of the uncoated catalyst, pure ethanol containing no thiols was used for the immersion step.

Fig. 3. Recycle reactions for catalysts which were regenerated by re-depositing them in the thiol precursor. (a) uncoated catalyst, deposited and rinsed in pure ethanol (b) C18-coated catalyst (c) 3-phenyl-1-propanethiol-coated catalyst

Shown in Fig. 3 (a), rinsing of the uncoated catalyst with ethanol after recycle resulted in near-constant selectivity for all runs, in contrast to the procedure of simply re-using the catalyst without an ethanol rinse (Fig. 2 (a)). This result suggested that the rinsing step removed adsorbed organic molecules produced during the reaction, and that the removal of these molecules affected selectivity. The C18-coated catalyst was greatly influenced by this recycle-regeneration procedure, which saw the selectivity increase from 50% to 79% selectivity during the 3rd reaction. The selectivity of the 3-phenyl-1-propanethiol-coated catalyst at 50% conversion fell somewhat from 93% in the first reaction to 82% by the third reaction, but the decrease was much less significant than the decrease observed for the simple recycle experiment (without regeneration) discussed in Fig. 2.

Another method of maintaining the thiolate surface coverage, and thus the efficacy, of a thiol-coated catalyst was to add thiol to the reaction solution at a dilute concentration. This recycle technique has already been described in ref. [12] but is treated in further detail here with rate data and surface characterization to complement the discussion. The technique of adding thiols to the reaction solution has been used for the hydrogenation of epoxybutene in ethanol [19], a system where addition of thiol was hypothesized to maintain a critical equilibrium coverage of thiol in the reaction solvent. One of the key effects observed in this method was a sharp decrease in the rate, likely due to thiol outcompeting the reactant for surface sites. Shown in Fig. 4, very dilute concentrations of thiols, 0.005mM C18 and 0.3mM 3-phenyl-1-propanethiol, were used in the reaction mixture to minimize the decrease in reaction rate while still allowing the study of reaction selectivity.

Fig. 4. Recycle reactions where thiol was added to the reaction mixture (a) C18-coated Pt/Al₂O₃ with 0.005mM C18 added to the reaction solution (b) 3-phenyl-1-propanethiol-coated Pt/Al₂O₃ with 0.3mM 3-phenyl-1-propanethiol added to the reaction solution. Panel (b) adapted from ref. [12]

Here, the C18-coated catalyst showed a higher selectivity for the first reaction than a C18-coated catalyst run in a pure solvent; however, this increase was observed only for the first reaction, after which it returned to the range of 50%, consistent with observations for a fresh C18-coated catalyst in a reaction mixture without thiol.

The 3-phenyl-1-propanethiol-coated catalyst retained high selectivity when thiols were added to the reaction mixture, as shown in shown in Fig. 4 (b). In contrast to a basic recycle, this method of introducing thiols to the reaction mixture shows that selectivity can be maintained, potentially as a method of compensating for desorption of thiols into reaction solution. However, this method of improving selectivity can potentially decrease the rate of reaction, an undesirable effect discussed below. In fact, the rate decrease observed for the 3-phenyl-1-propanethiol coating was such that conversions of only approximately 10% were achieved even over the 60 minute experimental run time.

By coating a catalyst surface, thiol SAMs naturally reduce the rate of reaction as compared to an uncoated catalyst [10], similar to other methods of blocking surface sites, such as coking [25]. This simple effect is illustrated in Fig. 5 (a) where, for the first reaction, the rate of reaction for the coated catalysts is approximately 1/3 of the rate on the uncoated catalyst. In subsequent reactions after recycling, the hydrogenation rate over the uncoated catalyst decreases, so that by the third reaction its rate is within experimental error of the C18 coated catalyst, and approaching that of the 3-phenyl-1-propanethiol-coated catalyst. This trend was consistent with the convergence of the selectivities of the uncoated, C18-coated, and 3-phenyl-1-propanethiol-coated catalysts shown in Fig. 2, for the basic recycle procedure.

Fig. 5. Rate data for each of the recycle procedures. (a) Recycle without regeneration (b) recycle with catalyst regeneration (c) recycle with thiols added to the reaction mixture.

All rates were calculated as the moles of reactant (cinnamaldehyde) consumed per surface site of an uncoated Pt/Al₂O₃ catalyst per second (methods section)

The regeneration for the uncoated catalyst, which consisted of a rinse in pure ethanol, stabilized the rate and the selectivity, again suggesting that carbonaceous deposits left on the catalyst surface could be largely removed with the ethanol wash. The rates for the coated catalysts, shown in Fig. 5 (b), were also stabilized with the recycle-regeneration procedure. The lack of change in the rate for the C18-coated catalyst is surprising when considering that the recycle regeneration procedure increased the selectivity of this reaction from 50% to 79%. Interestingly, as discussed in detail in the Supplementary Information, this increase in selectivity appears to be accompanied by (and perhaps a result of) leaching of small Pt particles, as indicated by a combination of ICP-OES and CO chemisorption. The rate over the 3-phenyl-1-propanethiol-coated catalyst was also stabilized for the regeneration-recycle procedure, but with a slight decrease in selectivity. This decrease might be due to similar changes in the morphology of the catalyst as were observed for the C18 coating (though such changes were less apparent, as indicated in the Supplementary Information), or from degradation of the ligand specific interaction between the SAM and cinnamaldehyde from some buildup of carbonaceous material on the surface of the catalyst, which will be discussed in section 3.3.

Finally, the procedure of adding thiols to the reaction mixture was shown to have a significantly deleterious effect on the rate of reaction. Shown in Fig. 5 (c), C18 was added to the reactor at the lowest consistently measurable dose of 0.005 mM. Here, the rate of the first reaction was within experimental error of the C18 catalyst without added thiol; however, subsequent dosing resulted in a dramatic decrease in the rate to nearly immeasurable values. Higher concentrations, not shown, completely suppressed the reaction yielding no measurable

conversion over a 60 minute reaction. Error bars in Fig. 5 (c) are large as a result of decreased reproducibility in repeat experiments where subtle differences in the dosed thiol had a strong effect on the rate of the reaction. The 3-phenyl-1-propanethiol rate was relatively stable with 0.3 mM thiol in the reaction solution, decreasing only by a factor of 3. Such decreases in rate for this procedure were consistent with previous studies where thiols exhibited highly competitive affinity for the near surface region [19]. Thus, the method of including thiols in the reaction mixture appears to offer promise for maintaining high selectivity, but the concentration must be finely tuned (in this case, to levels below 0.3 mM) to prevent significant loss of activity.

3.3 Characterization of Recycled Catalysts

In order to characterize the coverage of thiols on the catalyst surface and monitor potential coking, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used to study two infrared regions of interest, the carbonyl C=O stretching region from 1550-1750 cm^{-1} and the hydrocarbon C-H stretching region from 2850-3150 cm^{-1} . These regions were used to characterize the order of the SAM layer, to identify the presence of remaining carbonyl species from the reaction and to measure carbonaceous species. As shown in Fig. 6 (a), the pre-reaction uncoated catalyst, as expected, showed no significant features in either the C-H stretching region or the C=O stretching region, with only a small deflection at 1650 from the beginning of the Pt fingerprint region. Recycling the catalyst without regeneration led to organic deposits. Post-reaction spectra showed the presence of an aldehyde stretch at 1675 cm^{-1} indicating some remaining aldehyde, as well as C-H stretches between 3000 cm^{-1} and 3100 cm^{-1} , indicating the presence of hydrocarbons deposited from the reaction mixture.

Fig. 6. DRIFT spectra of catalysts before reaction 1 and after reactions 1, 2, and 3 for catalyst recycle with no regeneration or thiol added to the reaction solution. Reactions run with ethanol solvent over (a) uncoated Pt/Al₂O₃, (b) C18-coated Pt/Al₂O₃, (c) 3-phenyl-1-propanethiol-coated Pt/Al₂O₃, (d) C18-coated Pt/Al₂O₃ with added 0.005M thiol added to the reaction mixture. The peak at 1670 cm⁻¹ indicates the presence of aldehyde on the recycled catalyst surface. The peaks between 3000 cm⁻¹ and 3100 cm⁻¹ indicate the presence of hydrocarbons on the catalyst surface.

For the C18-coated catalysts, the C-H stretching region is particularly valuable for characterizing the ordering of the SAM. The peak position of the asymmetric methylene stretch (ν_a) is related to the intrinsic organization within an alkanethiol SAM, where a lower frequency indicates greater order within the monolayer [15, 17, 26-28]. In Fig. 6 (b) for the non-

regeneration recycle, the asymmetric methylene stretch was observed on the pre-reaction catalyst at 2923 cm^{-1} and increased to 2926 cm^{-1} after reaction 3, indicating a decrease in the order of the monolayer, though the peak area was relatively constant [26]. Interestingly, as shown in Fig. 6 (d), the procedure of adding C18 to the reaction mixture was able to maintain the ν_a peak position at 2923 cm^{-1} , consistent with the catalyst retaining high selectivity via this method. The 3-phenyl-1-propanethiol monolayer, shown in Fig. 6 (c), exhibited an alkyl CH stretch at 2973 cm^{-1} that decreased significantly in magnitude after the first reaction. Such a change in the IR spectrum is indicative of a change in the structure of the 3-phenyl-1-propanethiol coating, and is correlated to a decrease in efficacy.

The recycle-regeneration procedure showed the ability to stabilize the selectivity of the uncoated and 3-phenyl-1-propanethiol-coated catalyst and to increase the selectivity of the C18-coated catalyst. The DRIFT spectra shown in Fig. 7 were collected for the catalyst before the first reaction, after the second reaction, after the second regeneration (pre-run 3), and after the third reaction. As discussed above, the “regeneration” of an uncoated catalyst involved immersion of the catalyst in an ethanol solution prior to re-use, followed by an ethanol rinse of the catalyst. This recycle procedure was shown to decrease the intensity of peaks in the hydrocarbon region and the aldehyde region, for example comparing the post-reaction 2 spectra of Fig. 7 (a) to the pre-reaction 3 spectra. Considering this in conjunction with the stabilization of the rate and selectivity data, this again indicates that ethanol was likely effective in removing some of the hydrocarbons deposited from the previous reaction and restoring the surface of the uncoated catalyst.

Fig. 7. DRIFT spectra of catalysts having undergone a recycle-regeneration procedure. (a) uncoated Pt/Al₂O₃ (b) C18-coated Pt/Al₂O₃ (c) 3-phenyl-1-propanethiol-coated Pt/Al₂O₃

Finally, the 3-phenyl-1-propanethiol-coated catalyst, having shown a loss of its signature methylene stretch at 2973 cm⁻¹ post reaction, was restored with the recycle-regeneration procedure, although some coking was still observable on the catalyst surface. This indicated that the redeposit procedure could mostly restore the ligand-specific properties of the initial 3-phenyl-1-propanethiol-coated catalyst (also shown by the selectivity data in Fig. 3 (c)), but was slightly inhibited by some remaining organic material on the catalyst surface.

3.4 Effects of catalyst aging in air

The recyclability of thiol SAM-coated catalysts lends insight into the sensitivity of reaction selectivity on the detailed structure of the catalytic interface. Another possible way in which that SAM near surface environment can be perturbed is through degradation in air [29]. It was previously shown [12] that aging a 3-phenyl-1-propanethiol-coated catalyst in air decreased its selectivity to cinnamyl alcohol. A detailed investigation of this effect is reported in Fig. 8 (a).

Fig. 8. Effect of aging in air of 3-phenyl-1-propanethiol-coated and C18-coated Pt/Al₂O₃ catalysts on the (a) reaction selectivity and (b) reaction activity

The cinnamyl alcohol selectivity for the 3-phenyl-1-propanethiol-coated catalyst decreased sharply from 94% to 38% in only 24 hours of air exposure and continued to decrease below the selectivity of an uncoated catalyst. The C18-coated catalyst also showed a susceptibility to aging in air, but the change in selectivity was more gradual with aging time.

The differing selectivity losses for these two catalysts can be explained by their differing modes of selectivity enhancement. The 3-phenyl-1-propanethiol coated catalyst was shown to have an inherently high selectivity due to the ligand-specific interaction exhibited between the

phenyl ring of the thiol and the phenyl ring of the cinnamaldehyde. Only a slight decrease in the order of the thiol monolayer is expected to have a significant impact on the selectivity of the catalyst, since the spacing of the phenyl ring from the surface was shown to be paramount to the ligand specific interaction. In contrast, the C18-coated catalyst, which was shown to non-specifically improve the selectivity to cinnamyl alcohol, largely through the presence of the sulfur head group, was not as immediately susceptible to aging.

The changes in catalytic properties were supported by DRIFTS experiments (Supplementary Information Fig. S5), which showed that the order of the monolayer decreased significantly with aging in air. These results might also explain some of the losses in selectivity between recycle reactions as the catalysts were exposed to air during the catalyst-recycle procedure. Alkanethiols on flat Pd surfaces have been shown to be stable in air for 2-5 days [26], but undergo oxidation to alkyl sulfonate or sulfate anions. Similarly, alkanethiols on Pt surfaces have been shown to degrade to three distinct sulfur states when stored in air for longer than 7 days [15]. For the alkanethiol modified Pt/Al₂O₃ studied here, these effects appear to be rapid and significant in altering the efficacy of the catalyst.

4. Conclusions

The modification of Pt/Al₂O₃ with thiol SAMs for controlling cinnamaldehyde hydrogenation selectivity has been further characterized, particularly with respect to stability of the catalyst to multiple reaction and regeneration cycles. Recycling of spent catalysts showed a decrease in efficacy for the ligand-specific interaction of a 3-phenyl-1-propanethiol-coated catalyst, but the selectivity improvement was largely regenerated by redepositing a fresh thiol

monolayer on the spent catalyst or by maintaining a fixed concentration of thiol in the reaction mixture. Catalyst aging in air decreased the selectivity of a freshly prepared 3-phenyl-1-propanethiol-coated Pt/Al₂O₃ from greater than 90% to less than 20% when aged for more than two days, consistent with the exquisite sensitivity of the ligand-specific effect to monolayer structure. The work presented here provides an initial insight to the stability of thiol self-assembled monolayer modified supported metal catalysts used for liquid phase hydrogenation. Recycle experiments accompanied by IR characterization show that simple procedures can be used to maintain the efficacy of these modified catalysts over multiple reactions.

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Graphical Abstract

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