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Controlling the Surface Environment of Heterogeneous Catalysts Using Self-Assembled Monolayers

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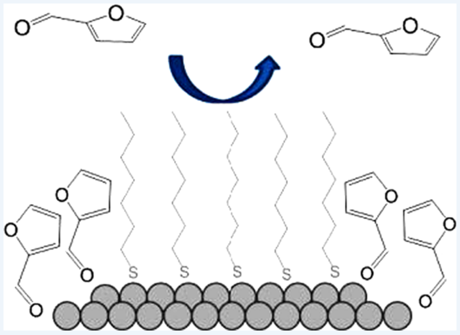

CONSPECTUS: Rationally designing and producing suitable catalysts to promote specific reaction pathways remains a major objective in heterogeneous catalysis. One approach involves using traditional catalytic materials modified with self-assembled monolayers (SAMs) to create a more favorable surface environment for specific product formation. A major advantage of SAM-based modifiers is their tendency to form consistent, highly ordered assembly structures on metal surfaces. In addition, both the attachment chemistry and tail structures can easily be tuned to facilitate specific interactions between reactants and the catalyst. In this Account, we summarize our recent modification approaches for tuning monolayer structure to improve catalytic performance for hydrogenation reactions on palladium and platinum catalysts. Each approach serves to direct selectivity by tuning a particular aspect of the system including the availability of specific active sites (*active-site selection*), intermolecular interactions between the reactants and modifiers (*molecular recognition*), and general steric or crowding effects.

We have demonstrated that the tail moiety can be tuned to control the density of SAM modifiers on the surface. Infrared spectra of adsorbed CO probe molecules reveal that increasing the density of the thiols restricts the availability of contiguous active sites on catalyst terraces while maintaining accessibility to sites located at particle edges and steps. This technique was utilized to direct selectivity for the hydrogenation of furfural. Results obtained from SAM coatings with different surface densities indicated that, for this reaction, formation of the desirable products occurs primarily at particle edges and steps, whereas the undesired pathway occurs on particle terrace sites. As an alternative approach, the tail structure of the SAM precursor can be tuned to promote specific intermolecular interactions between the modifier and reactant in order to position reactant molecules in a desired orientation. This technique was utilized for the hydrogenation of cinnamaldehyde, which contains an aromatic phenyl moiety. By using a phenyl-containing SAM modifier with an appropriate tether length, > 90% selectivity toward reaction of the aldehyde group was achieved. In contrast, employing a modifier where the phenyl moiety was closer to the catalyst surface biased selectivity toward the hydrogenation of the C=C bond due to reorienting the molecule to a more "lying down" conformation. In addition to approaches that target specific interactions between the reactant and modified catalyst, we have demonstrated the use of SAMs to impose a steric or blocking effect, for example, during the hydrogenation of polyunsaturated fatty acids. The SAMs facilitated hydrogenation of polyunsaturated to monounsaturated fatty acids but inhibited further hydrogenation to the completely saturated species due to the sterically hindered, single "kink" shape of the monounsaturated product.

The recent contributions discussed in this Account demonstrate the significant potential for this approach to design improved catalysts and to develop a deeper understanding of mechanistic effects due to the near surface environment.

INTRODUCTION

The rational design of a surface environment tailored for a particular catalytic application requires an intimate understanding of reactive intermediates and the electronic nature of the surface. In order to control these parameters, one approach has been to adjust the properties of catalytic materials using inorganic or organic modifiers. For example, the Lindlar catalyst employs a combination of both organic (quinoline) and inorganic (lead) modifiers on a palladium/$CaCO_3$ catalyst. This catalyst is often used during the hydrogenation of alkynes to enhance selectivity to the alkene without further hydrogenation to the undesirable alkane.[1,2]

Alternatively, nanoparticles with specific sizes, shapes, and crystal faces can be synthesized and provide valuable information in determining the role of catalyst active sites for subsequent use in heterogeneous applications. Organic ligands are commonly used to stabilize these particles during synthesis. Traditionally, the effect of the "leftover" organics has often been ignored, but more recent studies have attempted to characterize the role of these ligands and even tune their properties to improve catalytic performance. In some cases, the presence of the stabilizing ligand has been shown to improve selectivity to desired products.[3,4]

The history of organic modifiers in catalysis is extensive (for related reviews, see 5−8). A number of recent studies investigating the role of polymers,[9] dendrimers,[10,11] and chiral modifiers[12] in heterogeneous systems suggest that catalytic performance is often highly sensitive to the structure of the organic species. With increasing attention being paid to organic

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modifiers, there is growing interest in developing more consistent, highly ordered structures that can provide a systematic approach for mechanistic studies. Toward this end, self-assembled monolayers (SAMs) have recently been used to modify catalysts in a more consistent way. SAMs are organic assemblies composed of molecules containing a headgroup that interacts strongly with a solid surface.[13,14] When exposed to metal surfaces, thiol molecules covalently bind to the metal through a sulfur attachment group producing ordered and stable monolayer films. SAMs provide versatility as a modification platform due to the tunability of their tail-group structure. Moreover, SAM preparation is robust and consistent because monolayer formation is both spontaneous and self-limiting and therefore does not, in theory, depend on the deposition technique.

The successful use of SAMs in controlling selectivity of supported metal catalysts was demonstrated by Marshall et al., where different alkanethiolate coatings were used to dramatically improve the selectivity of the hydrogenation of 1-epoxy-3-butene to 1-epoxybutane.[15] The enhanced selectivity was found to be independent of the tail functionality and attributed to an electronic effect induced by the presence of the sulfur attachment group and selective poisoning of the epoxide moiety.[16] Interestingly, increasing the thiol tail length resulted in improved activity, which was correlated to the higher degree of monolayer order associated with SAMs having longer tails. More recent work in our group has focused on developing several approaches utilizing SAMs to enhance catalytic performance by tuning a particular aspect of the system including the availability of specific active sites (*active-site selection*), intermolecular interactions between the reactants and modifiers (*molecular recognition*), and general steric or crowding effects via the inferred mechanisms illustrated in Figure 1. This Account summarizes our recent progress in conjunction with related developments in the field using SAMs to improve catalytic performance in heterogeneous catalysis.

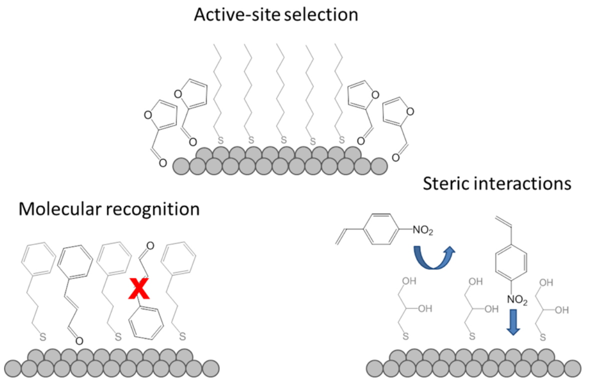

Figure 1. Recent approaches for tuning catalytic particles using SAMs.

ACTIVE-SITE SELECTION

Active-site selection (Figure 1) involves using SAM monolayers that preferentially expose specific types of reactive sites associated with a desirable reaction pathway, while simultaneously blocking sites or groups of sites related to undesirable products. We recently demonstrated that by variation of the steric bulkiness of the tail moiety, the surface density of the thiolate modifiers could be controlled, creating a reliable approach for exposing specific types of reactive sites.[17] 1-Octadecanethiol (C18), a straight-chain alkanethiol with nearest-neighbor spacing of ~5 Å on palladium,[18] was used to produce a densely packed monolayer on 5 wt % Pd/Al_2O_3 catalysts. To create a sparser monolayer, a thiolate with a bulky "caged" tail moiety, 1-adamantanethiol (AT), with an expected nearest-neighbor spacing of ~6.9 Å on Pd, was used. The structures of these SAMs are depicted in Figure 2.

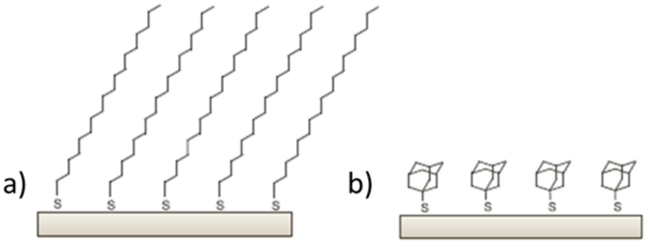

Figure 2. Structure of (a) 1-octadecanethiol (C18) and (b) 1-adamantanethiol (AT), used to control the density of thiolates on 5 wt % Pd/Al_2O_3 catalysts.

CO diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) was used to probe the types of adsorption sites available after SAM modification since CO adsorption features can readily be attributed to binding at specific types of sites. This knowledge is important since there is strong evidence suggesting that there are specific types of sites or groups of sites required in order for a particular pathway to occur.[19] On palladium catalysts, CO primarily binds on top sites, bridging sites, and 3-fold sites. A schematic of the types of adsorption sites expected on fcc (111) planes of palladium is shown in Figure 3.

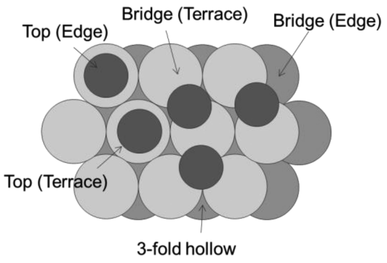

Figure 3. Summary of adsorption sites for CO on palladium catalysts. CO primarily binds on top sites, bridging sites, and 3-fold sites either on terraces or at particle edges and steps.

Results from IR spectroscopy suggested that increasing the density of thiols on the surface generally acts to (1) reduce the *overall* adsorption uptake of carbon monoxide, (2) restrict the availability of contiguous active sites on particle terraces, and (3) leave accessibility to sites located at particle edges and steps largely unaffected. More specifically, C18 SAMs inhibited CO adsorption on top sites on particle terraces, whereas CO was able to bind in these kinds of sites on AT-modified catalysts.

The hydrogenation of ethylene has been studied extensively in the literature, and it has been suggested that the most reactive form involves a π-bound state weakly adsorbed to top sites.[20] With AT- and C18-modified Pd/Al_2O_3 catalysts, ethylene hydrogenation rates were measured to determine the effect of site availability on catalytic activity. Reactions were performed in a gas-phase plug flow reactor at 323 K using a 10:1 hydrogen to reactant feed ratio. Results showed that AT-modified catalysts converted ethylene into ethane a factor of ~17× faster than C18-modified catalysts did, despite having a factor of only ~2× lower thiolate surface coverage. The large differences in reaction rates were consistent with CO DRIFTS studies revealing that top sites on C18 catalysts were only accessible at particle edges and steps whereas AT catalysts also allowed access to top sites on particle terraces. Differences in reactant adsorption energy (dependent on thiol coverage) may also have contributed to the differences in the rate of ethylene conversion. However, adsorption isotherms suggested a difference in adsorption energy of only ~1 kJ/mol between C18 and AT catalysts, implying only a minor dependence of rate on the electronic state of the metal. The proposed adsorption mechanism of ethylene on the SAM-modified catalysts is shown in Figure 4. This study successfully demonstrated the use of SAMs to control the accessibility of specific active sites for a well-studied reaction.

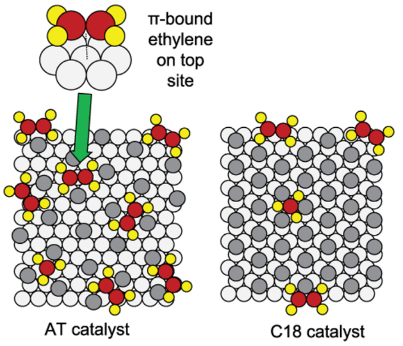

Figure 4. Proposed adsorption mechanism for ethylene on AT and C18 catalysts. On C18 catalysts, ethylene can bind to top sites in a *π*-bound configuration at particle edges and steps. On AT catalysts, ethylene has additional access to top sites on particle terraces. Reprinted with permission from ref 17. Copyright 2013 Elsevier.

For more complex reactant molecules that can readily undergo a number of competing reaction pathways, SAM modification can be utilized to control selectivity by blocking the sites associated with undesirable product formation. On palladium catalysts, the hydrogenation of furfural primarily undergoes an undesirable decarbonylation process producing furan and CO.[21,22] Conversely, the hydrogenation of the aldehyde moiety and subsequent hydrodeoxygenation producing desirable products furfuryl alcohol and methylfuran occurs much less readily on palladium catalysts. Figure 5 summarizes the major reaction pathways for furfural hydrogenation.

Single crystal studies of benzyl and furfuryl alcohol, which react through benzaldehyde and furfural intermediates, respectively, suggest that the decarbonylation pathway is predominant when the molecule can adopt a lying-down conformation on the catalyst surface.[22,23] Thus, by restricting the availability of contiguous active sites using a densely packed monolayer, we inhibited the formation of furan to dramatically improve selectivity toward the desired products.[24] Selectivities and rates of formation of each product are shown for 5 and 1 wt % C18, AT, and unmodified Pd/Al_2O_3 catalysts in Figure 6. Hydrogenations were carried out in a gas-phase plug flow reactor at 463 K at a 25:1 molar ratio of H_2 to furfural.

Since the rates of production of furfuryl alcohol and methylfuran were nearly the same on all the catalysts and the availability of step and edge sites was mostly unaffected by the thiol modifiers, it is likely that the production of these species occur preferentially at these sites on palladium. The proposed adsorption mechanism for the reaction using these different SAM modifiers is presented in Figure 7. Overall, the results from hydrogenation of ethylene, furfural, and other reactants such as propionaldehyde show that one mechanism by which SAMs can control reactivity is by selectively blocking certain types of surface sites and that this effect can in part be controlled by designing modifiers that assemble to produce a particular attachment density.

MOLECULAR RECOGNITION

Molecular recognition (Figure 1) involves exploiting noncovalent intermolecular interactions between the surface modifier and reactant molecules to orient the reactant in a desirable way. The ultimate aim of this approach is to create a biomimetic "binding pocket", similar to those found in enzymes, designed to selectively convert reactant molecules to desirable products while maintaining the ease of recoverability of the catalysts. We successfully demonstrated this approach during the hydrogenation of cinnamaldehyde by tuning the structure of the SAM tail to facilitate appropriately positioned aromatic stacking interactions between the reactant and the modifier.[25]

Cinnamaldehyde is an *α*,*β*-unsaturated aldehyde and is of significant industrial importance. Typically, on transition metal catalysts, the major product is formed via hydrogenation of the olefin functionality to produce hydrocinnamaldehyde; however, the more industrially valuable product is cinnamyl alcohol formed from hydrogenation of the aldehyde.[26] Platinum has been shown to be one of the most selective pure metals for producing cinnamyl alcohol and was therefore chosen for these studies. Hydrogenation products are shown in Figure 8.

In order to demonstrate this technique, a variety of SAMs with tail characteristics expected to specifically or nonspecifically interact with the reactant were chosen to determine their effect on selectivity. These modifiers along with corresponding selectivity toward cinnamyl alcohol are shown in together in Figure 9. Reactions were performed in the liquid phase using a semibatch reactor at 323 K.

The results indicated that selectivity could be improved from ~25% on uncoated Pt catalysts to over 95% using the catalyst

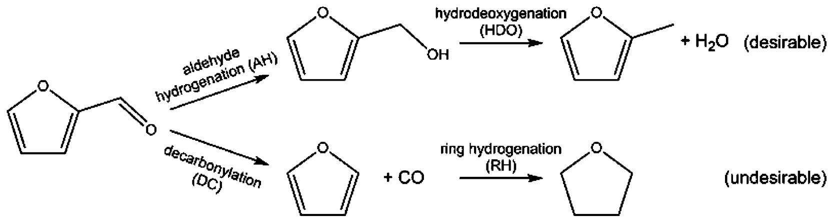

Figure 5. Major reaction pathways for furfural hydrogenation on Pd catalysts. Reprinted from ref 24. Copyright 2013 Nature Publishing Group.

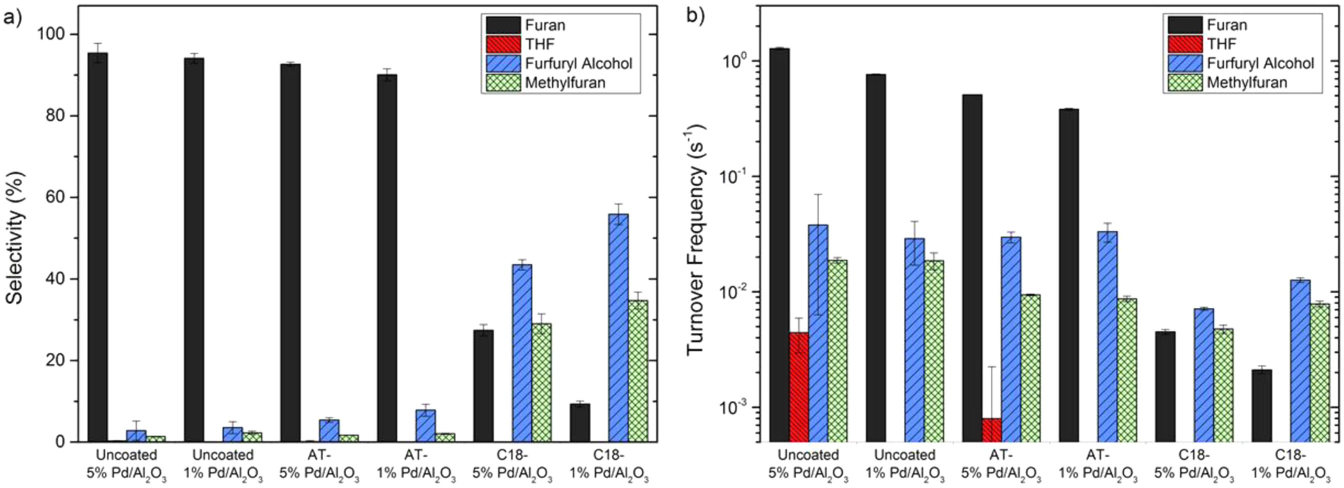

Figure 6. (a) Product selectivity for furfural hydrogenation over uncoated and alkanethiolate SAM coated Pd/Al_2O_3 catalysts. (b) Turnover frequencies are reported as the rate of production normalized by number of surface sites on the uncoated catalyst. Reprinted from ref 24. Copyright 2013 Nature Publishing Group.

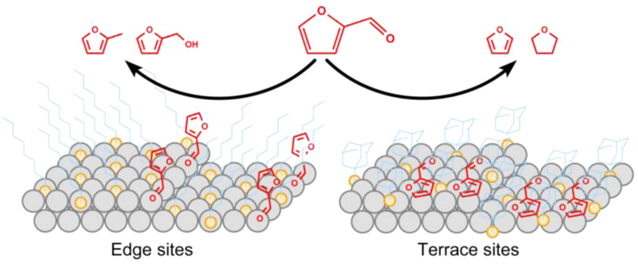

Figure 7. Proposed adsorption mechanism of furfural on C18 and AT modified catalysts. Reprinted from ref 24. Copyright 2013 Nature Publishing Group.

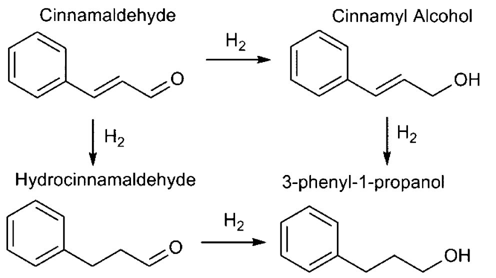

Figure 8. Reaction products during hydrogenation of cinnamaldehyde on Pt/Al_2O_3. Reprinted from ref 25. Copyright 2014 American Chemical Society.

modified with 3-phenylpropanethiol. This modifier contains a phenyl moiety and the same number of carbon atoms as the reactant, cinnamaldehyde, allowing for aromatic stacking interactions between the modifier and surface at an optimal distance for selective conversion of the aldehyde moiety. The proposed adsorption mechanism for this highly selective system is shown in Figure 10. Linear alkanes, not expected to interact specifically with cinnamaldehyde, showed a more modest improvement in selectivity over uncoated catalysts. This nonspecific effect was induced by the presence of the sulfur and was found to be independent of alkanethiol tail length.

Reducing the spacing between the SAM phenyl moiety and the catalyst resulted in lower selectivity for the desired product. It has previously been shown that binding in a horizontal configuration favors olefin hydrogenation while binding vertically favors hydrogenation of the aldehyde.[27] PM-RAIRS studies confirmed that cinnamaldehyde adsorbs in a more upright orientation when a 3-phenyl-1-propanethiol modifier is used compared with uncoated surfaces or SAM-coated catalysts where the phenyl moiety is closer to the surface.

Typically, reaction modifiers improve selectivity at the cost of catalytic reactivity. The relationship between activity and selectivity for the unsaturated alcohol are shown in Figure 11. With cinnamaldehyde, selectivity improvement was accompanied by decreased activity for nearly all of the modifiers tested. However, the most selective catalyst, modified with 3-phenylpropanethiol, did not significantly compromise activity. This was presumably due to its unique mechanism for selectivity improvement. While the overall rate of cinnamaldehyde depletion decreased by ~3×, the rate of cinnamyl alcohol production using 3-phenylpropanthiol-modified catalysts was statistically indistinguishable from rates on the uncoated catalyst, despite the presence of a dense coating of thiolate modifiers.

There are a number of other methods for improving selectivity of α,β-unsaturated aldehydes to the unsaturated alcohol. For example, bimetallic Pt–Co and Pt–Fe catalysts have been shown to produce cinnamyl alcohol with selectivity at and above 95%.[26] In addition, approaches utilize general steric or blocking effects to achieve similarly high selectivities. However, this was the first successful demonstration using specific noncovalent interactions to orient the reactant in such a way as to promote reaction of the aldehyde functionality. While the approach of using noncovalent near surface interactions to control selectivity is in its infancy, it has great potential for mimicking the function of enzymes in an effort to move toward biomimetic catalyst systems.

■ STERIC EFFECTS

The previously discussed approaches involved the use of SAMs to target specific interactions between the reactant and the surface or modifier in order to direct selectivity. Another approach involves using the monolayer to sterically hinder a particular conformation or structure from reaching the catalyst surface (Figure 1). We recently investigated the ability to use

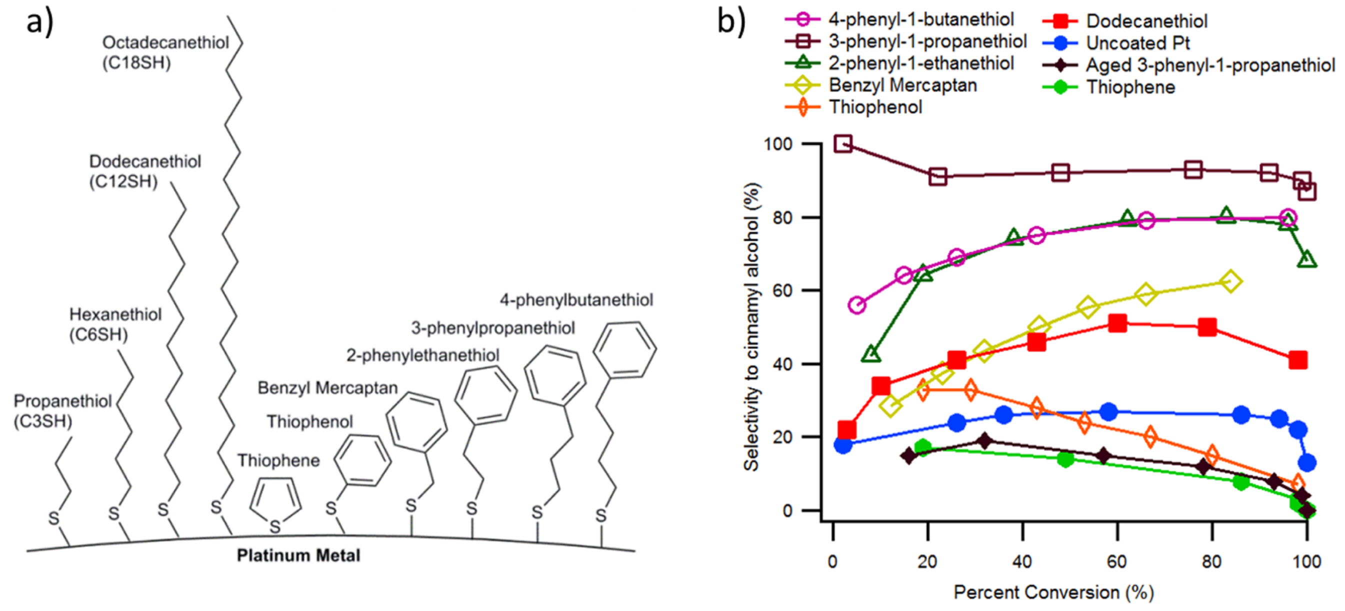

Figure 9. (a) SAMs used for tuning the near surface environment for hydrogenation of cinnamaldehyde. (b) Selectivity to cinnamyl alcohol shown as a function of percent conversion for corresponding modifiers. Reprinted from ref 25. Copyright 2014 American Chemical Society.

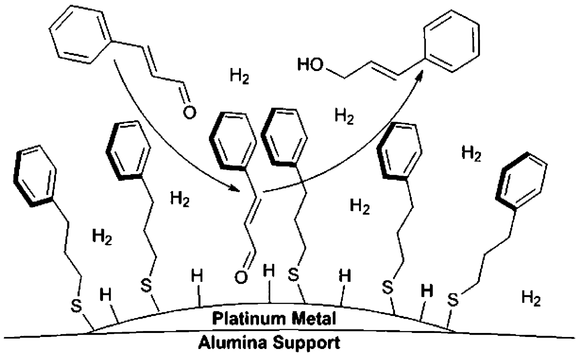

Figure 10. Proposed adsorption mechanism depicting favorable orientation of cinnamaldehyde induced by 3-phenylpropanethiol SAM modifiers. Reprinted from ref 25. Copyright 2014 American Chemical Society.

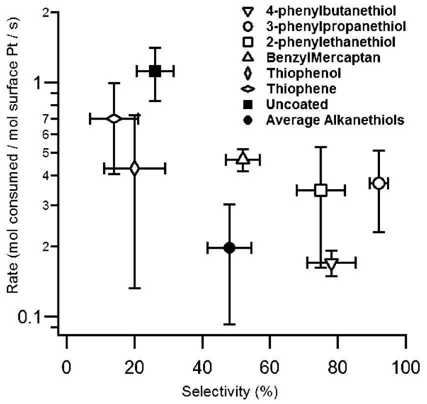

Figure 11. Rate versus selectivity for unsaturated alcohol for both uncoated and SAM coated Pt/Al_2O_3 catalysts. Rates are shown as moles of reactant consumed per mole of surface platinum per second. Alkanethiols C_3SH, C_6SH, $C_{12}SH$, and $C_{18}SH$ were averaged for one data point. Reprinted from ref 25. Copyright 2014 American Chemical Society.

SAMs to prevent further reaction of sterically hindered intermediates during the hydrogenation of polyunsaturated fatty acids.[28] Naturally occurring fatty acids often contain a large degree of unsaturation. Partial reaction toward the monounsaturated product (without undergoing complete hydrogenation) is often important because the fully saturated product has an increased melting temperature detrimental for fuel applications.[29] Thus, it is desirable to design catalysts to partially react polyunsaturated fatty acids to monounsaturated acids. Hydrogenation of unsaturated fatty acids is usually performed in industry using nickel catalysts. However, these catalysts typically require high reaction temperatures, ~450 K, and are operated under high hydrogen pressures, ~16 bar.[30] Using palladium catalysts allows reactions to be performed under much milder conditions (303 K at 6 bar).

Linoleic acid is a polyunsaturated fatty acid containing two carbon−carbon double bonds. On palladium catalysts in a batch system, hydrogenation of linoleic acid produces the fully saturated stearic acid after quickly passing through a monounsaturated intermediate. Using an uncoated palladium catalyst, maximum selectivity toward the monounsaturated product was found to be 64% (at ~10% conversion), which then continuously decreased with further conversion. With an alkanethiol coating, the selectivity for the monounsaturated product was improved to over 80% even at conversions as high as 80%. Selectivity is shown as a function of time for uncoated and dodecanethiol-modified catalysts during the hydrogenation of linoleic acid in Figure 12. Reactions were performed in the liquid phase using a semibatch reactor at 303 K.

In order to probe the mechanism, we measured the rates of hydrogenation for several different unsaturated fatty acids containing different numbers of carbon double bonds over unmodified and alkanethiol modified catalysts. The results, shown in Figure 13, demonstrated that the rate of hydrogenation of monounsaturated fatty acids is decreased significantly compared with that of polyunsaturated fatty acids for SAM-modified catalysts compared with uncoated catalyst.

Figure 13 demonstrates that the presence of the modifier only modestly reduces the hydrogenation rate of the

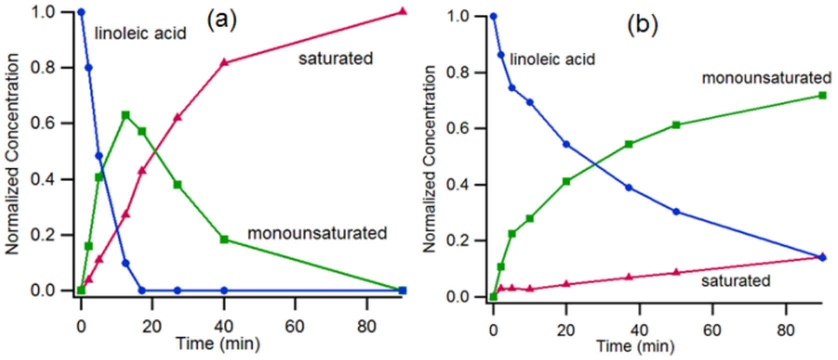

Figure 12. Concentration of reaction species shown as a function of time for the hydrogenation of linoleic acid on (a) uncoated and (b) dodecanethiol coated 5 wt % Pd/Al_2O_3 catalysts where concentrations are normalized to one. Reprinted from ref 28. Copyright 2013 American Chemical Society.

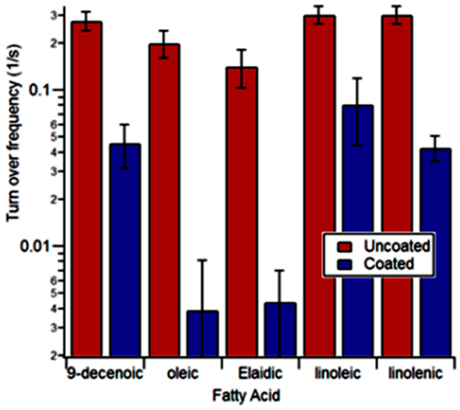

Figure 13. Turnover frequencies for the hydrogenation of oleic acid (*cis*-9-octadecenoic acid), elaidic acid (*trans*-9-octadecenoic acid), linoleic acid (*cis*,*cis*-9,12-octadecadienoic acid), and linolenic acid (*cis*,*cis*,*cis*-9,12,15-octadecatrienoic acid) over alkanethiol coated (average rate of C3, C6, C12, and C18 coatings) and uncoated catalysts. Reprinted from ref 28. Copyright 2013 American Chemical Society.

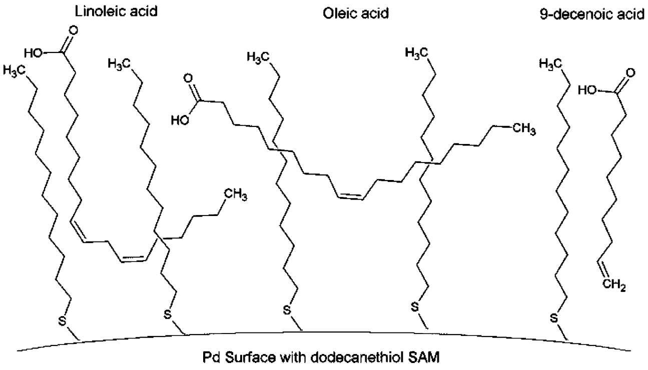

Figure 14. Proposed adsorption mechanism of poly- and monounsaturated fatty acids on alkanethiol modified surfaces. Reprinted from ref 28. Copyright 2013 American Chemical Society.

polyunsaturated species while significantly reducing the ability to hydrogenate the monounsaturated species. These results suggested that polyunsaturated fatty acids, which contain multiple “kinks” have greater access to the catalyst surface than monounsaturated fatty acids. In the proposed adsorption mechanism, the SAMs act to sterically hinder the monounsaturated intermediate from interacting with the surface. This mechanism is depicted in Figure 14.

A number of recent reports using SAMs in the literature have utilized SAMs as modifiers for a similar purpose and attributed selectivity improvements to preventing a particular, often “lying down”, conformation of the reactant molecule. For example, during the hydrogenation of 4-nitrostyrene, two reducible functional groups on either side of a benzene moiety have equal access to the surface in a “lying-down” conformation. Makosch et al. demonstrated that SAM-modification of Pt/TiO_2 catalysts induced a complete change in selectivity from 4-ethylnitrobenzene and 4-ethylaniline on unmodified catalysts to 4-aminostyrene on thioglycerol-modified catalysts. The presence of the monolayer was thought to inhibit the nitrostyrene molecule from lying flat on the catalyst, resulting in preferential interaction of the nitro group.[31] Similarly, Wu et al. recently demonstrated that a sufficiently long-tailed amine capping layer on Pt_3Co nanocatalysts prevented α,β-unsaturated aldehydes from lying flat on the surface, inhibiting direct contact of the C═C bonds with the catalyst.[32] The result was a dramatic enhancement in selectivity to cinnamyl alcohol (desired), which was found to improve with increasing tail length. It has been shown that even small molecules, like ethylene, can be physically blocked from active catalyst sites using bulky diphenyl-modified Pd/TiO_2 catalysts during acetylene hydrogenation.[33]

■ CHALLENGES WITH MONOLAYER-MODIFIED CATALYSTS

A number of challenges remain that will be important to address for the continued development and refinement of this catalyst modification technique. One of the central issues concerns the stability of the organic species, particularly under demanding reaction conditions (high pressures or temperatures or both) over extended periods of time. To examine the effect of harsh reaction conditions on catalytic performance, we recently conducted reactions of C18-coated Pd/Al_2O_3 under furfural hydrogenation conditions (T = 463 K) for ∼15 h.[24] During this time period, the activity of the catalyst decreased slightly (∼5%), but selectivity toward the desired reaction pathway was unchanged. While *performance* was maintained, infrared spectroscopy of the hydrocarbon stretching regime demonstrated some degradation of the organic monolayer over time as evidenced by a reduction in the peak areas and slight shifts in peak position to higher wavenumber. These changes suggested partial desorption and reduced crystallinity of the monolayer. Therefore, this issue may become particularly problematic at high reaction temperatures if selectivity improvements rely on the specific structure of the tail group and subtle interactions between the SAM and reactant.

A number of recent studies have investigated the recyclability of SAM-coated catalysts to gauge the effects on catalytic performance. For example, Cargnello et al. synthesized particles with mixed monolayers containing alkyl, alcohol, and acidic terminations on palladium.[34] The resulting nanoparticles were very stable and showed good recyclability over five reaction cycles for Suzuki cross-coupling reactions. Lu et al. similarly found that dodecanethiolate-modified palladium demonstrated good recyclability for at least six runs for the same reaction.[35]

Another issue often encountered with SAM-modified catalysts is a significant loss in overall catalytic activity upon addition of the SAM, a consequence of the monolayer blocking a large fraction of the active surface area. While the overall rate of consumption of the reactant is often reduced, a number of our recent studies have demonstrated that the actual rate of production of the desired product is nearly[15,24] or completely[25] unaffected by the coating. Ultimately, we would like to move toward improving performance by using the SAM structure to actually enhance desired reaction rates above those on uncoated catalysts. This will most likely involve utilizing a *molecular recognition* approach to enhance performance by favorably influencing reactant orientation or surface affinity. Here, stabilizing interactions in the near-surface environment can hypothetically compensate for the loss of available surface sites in maintaining high reaction rates. Ongoing work in our group is also exploring the use of bimetallic SAM systems as another potential route for enhancing catalytic activity.

Aside from stability and performance, one of the practical issues remaining is the lack of characterization of more complex SAM−particle systems. Linear alkanethiol SAMs have been extensively studied and characterized primarily under static conditions on flat Au surfaces; however, catalytic systems are often much more dynamic. Current investigations have been utilizing more complex SAM structures on different types of metals. In addition, particle curvature introduces additional complexity, which can be difficult to characterize but is now becoming more actively pursued.[36−38] Without a comprehensive picture of the surface environment for each system, the description of what constitutes the particular "active site" becomes somewhat more obfuscated. Toward this point, a common measure used to describe activities of traditional catalysts is the turnover frequency, or the rate of conversion of a molecule per second per site. Restricting the available sites adds ambiguity as to how to most appropriately determine and report the total number of active sites and consequently turnover frequencies for these systems. Studies aimed at quantitatively determining adsorbate concentrations and orientation on both uncoated and coated surface would improve descriptions of these kinds of systems. This information would significantly aid in determining the relationships between reactant adsorption behavior and corresponding reaction pathways.While the effects of the SAMs inferred here have been attributed to specific, unique mechanisms, it is likely that there are other factors at play that can complicate these interpretations. Dynamic effects like surface restructuring, subsurface hydrogen, and changes in the electronic nature of the surface due to the sulfur may contribute to changes observed in catalytic performance. Future work in our group aims to address these kinds of effects to determine how they may be contributing to changes in catalytic performance.

■ CONCLUSIONS

SAMs are becoming increasingly popular as catalyst modifiers in heterogeneous catalysis because they offer a versatile and convenient approach for modifying metal particles to tune their catalytic properties. Recently in our group, we have demonstrated the successful use of SAMs to enhance selectivity using three unique approaches: (1) active-site selection, (2) molecular recognition, and (3) steric interactions. While these and related studies have demonstrated successful utilization of these modifiers, much is yet unknown in the field about the explicit effect of the SAM on reaction mechanisms. In addition, efforts toward improving monolayer integrity over time and at elevated temperatures and pressures will be important in order to develop this modification technique into competitive, state of the art materials. The recent contributions summarized here demonstrate the significant potential for this approach and the need to develop a deeper understanding of mechanistic effects due to the presence of the monolayer.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

Biographies

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■ REFERENCES

(1) Lindlar, H. Ein neuer katalysator fur selective hydrierungen. *Helv. Chim. Acta* **1952**, *35*, 446−456.

(2) Garcia-Mota, M.; Gomez-Diaz, J.; Novell-Leruth, G.; Vargas-Fuentes, C.; Bellarosa, L.; Bridier, B.; Perez-Ramirez, J.; Lopez, N. A density functional theory study of the 'mythic' Lindlar hydrogenation catalyst. *Theor. Chem. Acc.* **2011**, *128*, 663−673.

(3) Chen, K.; Wu, H.; Hua, Q.; Chang, S.; Huang, W. Enhancing catalytic selectivity of supported metal nanoparticles with capping ligands. *Phys. Chem. Chem. Phys.* **2013**, *15*, 2273−2277.

(4) Kwon, S. G.; Krylova, G.; Sumer, A.; Schwartz, M. M.; Bunel, E. E.; Marshall, C. L.; Chattopadhyay, S.; Lee, B.; Jellinek, J.; Shevchenko, E. V. Capping ligands as selectivity switchers in hydrogenation reactions. *Nano Lett.* **2012**, *12*, 5382−5388.

(5) Mallat, T.; Baiker, A. Selectivity enhancement in heterogeneous catalysis induced by reaction modifiers. *Appl. Catal., A* **2000**, *200*, 3−22.

(6) Mallat, T.; Orglmeister, E.; Baiker, A. Asymmetric catalysis at chiral metal surfaces. *Chem. Rev.* **2007**, *107*, 4863−4890.

(7) Pieters, G.; Prins, L. J. Catalytic self-assembled monolayers on gold nanoparticles. *New J. Chem.* **2012**, *36*, 1931−1939.

(8) Niu, Y. H.; Crooks, R. M. Dendrimer-encapsulated metal nanoparticles and their applications to catalysis. *C. R. Chim* **2003**, *6*, 1049−1059.

(9) Feng, B.; Hou, Z. S.; Yang, H. M.; Wang, X. R.; Hu, Y.; Li, H.; Qiao, Y. X.; Zhao, X. G.; Huang, Q. F. Functionalized poly(ethylene glycol)-stabilized water-soluble palladium nanoparticles: property/activity relationship for the aerobic alcohol oxidation in water. *Langmuir* **2010**, *26*, 2505−2513.

(10) Gross, E.; Liu, J. H. C.; Toste, F. D.; Somorjai, G. A. Control of selectivity in heterogeneous catalysis by tuning nanoparticle properties and reactor residence time. *Nat. Chem.* **2012**, *4*, 947−952.

(11) Oh, S. K.; Niu, Y. H.; Crooks, R. M. Size-selective catalytic activity of Pd nanoparticles encapsulated within end-group functionalized dendrimers. *Langmuir* **2005**, *21*, 10209−10213.

(12) Han, D. F.; Li, X. H.; Zhang, H. D.; Liu, Z. M.; Li, J.; Li, C. Heterogeneous asymmetric hydroformylation of olefins on chirally modified Rh/SiO2 catalysts. *J. Catal.* **2006**, *243*, 318−328.

(13) Schwartz, D. K. Mechanisms and kinetics of self-assembled monolayer formation. *Annu. Rev. Phys. Chem.* **2001**, *52*, 107−137.

(14) Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. Self-assembled monolayers of thiolates on metals as a form of nanotechnology. *Chem. Rev.* **2005**, *105*, 1103−1169.

(15) Marshall, S. T.; O'Brien, M.; Oetter, B.; Corpuz, A.; Richards, R. M.; Schwartz, D. K.; Medlin, J. W. Controlled selectivity for palladium catalysts using self-assembled monolayers. *Nat. Mater.* **2010**, *9*, 853−858.

(16) Marshall, S. T.; Schwartz, D. K.; Medlin, J. W. Adsorption of oxygenates on alkanethiol-functionalized Pd(111) surfaces: Mechanistic insights into the role of self-assembled monolayers on catalysis. *Langmuir* **2011**, *27*, 6731−6737.

(17) Schoenbaum, C. A.; Schwartz, D. K.; Medlin, J. W. Controlling surface crowding on a Pd catalyst with thiolate self-assembled monolayers. *J. Catal.* **2013**, *303*, 92−99.

(18) Love, J. C.; Wolfe, D. B.; Haasch, R.; Chabinyc, M. L.; Paul, K. E.; Whitesides, G. M.; Nuzzo, R. G. Formation and structure of self-assembled monolayers of alkanethiolates on palladium. *J. Am. Chem. Soc.* **2003**, *125*, 2597−2609.

(19) Nørskov, J. K.; Bligaard, T.; Hvolbæk, B.; Abild-Pedersen, F.; Chorkendorff, I.; Christensen, C. H. The nature of the active site in heterogeneous metal catalysis. *Chem. Soc. Rev.* **2008**, *37*, 2163−2171.

(20) Cremer, P. S.; Su, X. C.; Shen, Y. R.; Somorjai, G. A. Ethylene hydrogenation on Pt(111) monitored in situ at high pressures using sum frequency generation. *J. Am. Chem. Soc.* **1996**, *118*, 2942−2949.

(21) Sitthisa, S.; Pham, T.; Prasomsri, T.; Sooknoi, T.; Mallinson, R. G.; Resasco, D. E. Conversion of furfural and 2-methylpentanal on Pd/SiO2 and Pd-Cu/SiO2 catalysts. *J. Catal.* **2011**, *280*, 17−27.

(22) Pang, S. H.; Medlin, J. W. Adsorption and reaction of furfural and furfuryl alcohol on Pd(111): Unique reaction pathways for multifunctional reagents. *ACS Catal.* **2011**, *1*, 1272−1283.

(23) Pang, S. H.; Roman, A. M.; Medlin, J. W. Adsorption orientation-induced selectivity control of reactions of benzyl alcohol on Pd(111). *J. Phys. Chem. C* **2012**, *116*, 13654−13660.

(24) Pang, S. H.; Schoenbaum, C. A.; Schwartz, D. K.; Medlin, J. W. Directing reaction pathways by catalyst active-site selection using self-assembled monolayers. *Nat. Commun.* **2013**, *4*, No. 2448.

(25) Kahsar, K. R.; Schwartz, D. K.; Medlin, J. W. Control of metal catalyst selectivity through specific noncovalent molecular interactions. *J. Am. Chem. Soc.* **2014**, *136*, 520−526.

(26) Gallezot, P.; Richard, D. Selective hydrogenation of *α,β*-unsaturated aldehydes. *Catal. Rev.: Sci. Eng.* **1998**, *40*, 81−126.

(27) Medlin, J. W. Understanding and controlling reactivity of unsaturated oxygenates and polyols on metal catalysts. *ACS Catal.* **2011**, *1*, 1284−1297.

(28) Kahsar, K. R.; Schwartz, D. K.; Medlin, J. W. Selective hydrogenation of polyunsaturated fatty acids using alkanethiol self-assembled monolayer-coated Pd/Al_2O_3 catalysts. *ACS Catal.* **2013**, *3*, 2041−2044.

(29) Moster, B. R.; Haas, M. J.; Winkler, J. K.; Jackson, M. A.; Erhan, S. Z.; List, G. R. Evaluation of partially hydrogenated methyl esters of soybean oil as biodiesel. *Eur. J. Lipid Sci. Technol.* **2007**, *109*, 17−24.

(30) Jovanovic, D.; Radovic, R.; Mares, L.; Stankovic, M.; Markovic, B. Nickel hydrogenation catalyst for tallow hydrogenation and for the selective hydrogenation of sunflower seed oil and soybean oil. *Catal. Today* **1998**, *43*, 21−28.

(31) Makosch, M.; Lin, W. I.; Bumbalek, V.; Sa, J.; Medlin, J. W.; Hungerbuhler, K.; van Bokhoven, J. A. Organic thiol modified Pt/TiO_2 catalysts to control chemoselective hydrogenation of substituted nitroarenes. *ACS Catal.* **2012**, *2*, 2079−2081.

(32) Wu, B. H.; Huang, H. Q.; Yang, J.; Zheng, N. F.; Fu, G. Selective hydrogenation of alpha,beta-unsaturated aldehydes catalyzed by amine-capped platinum-cobalt nanocrystals. *Angew. Chem., Int. Ed.* **2012**, *51*, 3440−3443.

(33) McKenna, F. M.; Anderson, J. A. Selectivity enhancement in acetylene hydrogenation over diphenyl sulphide-modified Pd/TiO2 catalysts. *J. Catal.* **2011**, *281*, 231−240.

(34) Cargnello, M.; Wieder, N. L.; Canton, P.; Montini, T.; Giambastiani, G.; Benedetti, A.; Gorte, R. J.; Fornasiero, P. A versatile approach to the synthesis of functionalized thiol-protected palladium nanoparticles. *Chem. Mater.* **2011**, *23*, 3961−3969.

(35) Lu, F.; Ruiz, J.; Astruc, D. Palladium-dodecanethiolate nanoparticles as stable and recyclable catalysts for the Suzuki-Miyaura reaction of aryl halides under ambient conditions. *Tetrahedron Lett.* **2004**, *45*, 9443−9445.

(36) Corthey, G.; Rubert, A. A.; Picone, A. L.; Casillas, G.; Giovanetti, L. J.; Ramallo-Lopez, J. M.; Zelaya, E.; Benitez, G. A.; Requejo, F. G.; Jose-Yacaman, M.; Salvarezza, R. C.; Fonticelli, M. H. New insights into the chemistry of thiolate-protected palladium nanoparticles. *J. Phys. Chem. C* **2012**, *116*, 9830−9837.

(37) Zheng, Y. B.; Payton, J. L.; Song, T.-B.; Pathem, B. K.; Zhao, Y.; Ma, H.; Yang, Y.; Jensen, L.; Jen, A. K.; Weiss, P. S. Surface-enhanced raman spectroscopy to probe photoreaction pathways and kinetics of isolated reactants on surfaces: Flat versus curved substrates. *Nano Lett.* **2012**, *12*, 5362−5368.

(38) Jimenez, A.; Sarsa, A.; Blazquez, M.; Pineda, T. A molecular dynamics study of the surfactant surface density of alkanethiol self-assembled monolayers on gold nanoparticles as a function of the radius. *J. Phys. Chem. C* **2010**, *114*, 21309−21314.