Journal of Molecular Catalysis A: Chemical 396 (2015) 188–195

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Stability of self-assembled monolayer coated Pt/Al_2O_3 catalysts for liquid phase hydrogenation

Karl R. Kahsar, Daniel K. Schwartz, J. Will Medlin*

Department of Chemical and Biological Engineering, University of Colorado Boulder, Boulder, CO, 80309-0596, United States of America

ARTICLE INFO

Article history:
Received 21 August 2014
Received in revised form 2 October 2014
Accepted 5 October 2014
Available online 14 October 2014

Keywords:
Alkanethiol
Self-assembled monolayer
Unsaturated aldehyde
Hydrogenation
Platinum on alumina

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/Al_2O_3 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/Al_2O_3 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.

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.

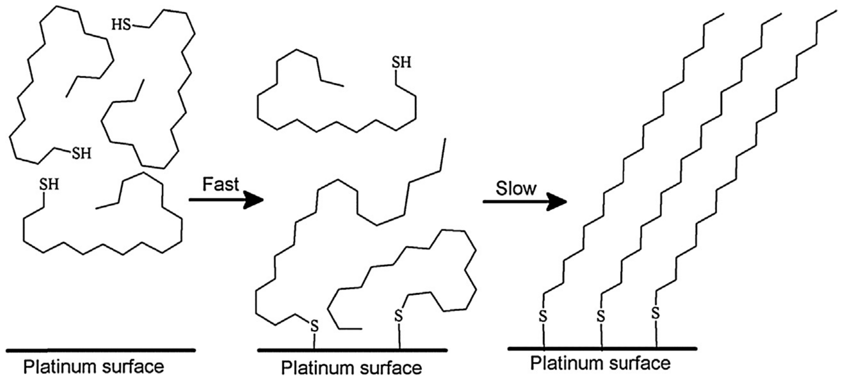
Alkanethiols bind to a metal surface, such as that of a Pt catalyst, in a multistep process to form a SAM, as illustrated in Scheme 1. To prepare thiolate SAMs, the substrate metal is incubated in a dilute solution of typically 1–100 mM of the thiol precursor such that the thiols adsorb and rapidly saturate 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 reorganization step of thiols on the metal surface [14,17].

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

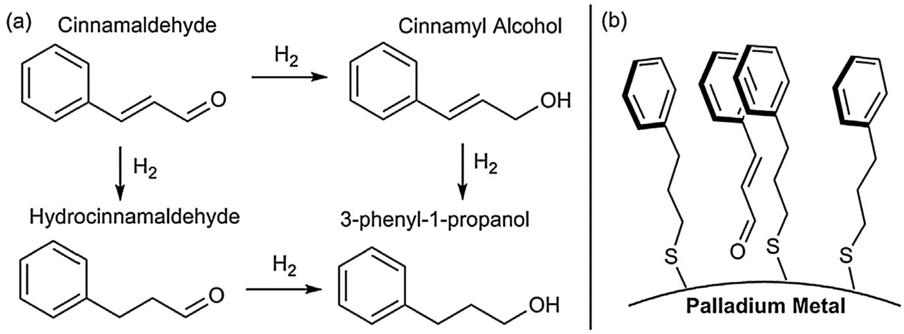
---

* Corresponding author. Tel.: +1 303 492 2418.
E-mail address: Will.Medlin@colorado.edu (J.W. Medlin).

http://dx.doi.org/10.1016/j.molcata.2014.10.004
1381-1169/



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.



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

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.

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/Al_2O_3 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. Gases (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 5 wt% Pt/Al_2O_3 catalyst. The catalysts were oxidized in an 80:20 helium:oxygen mixture at 300 °C for 3 h and then reduced at 200 °C for 2 h 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 (250 mg or less) was added to 40 mL 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 $\sqrt{3}$x$\sqrt{3}$ 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 m^2/g for uncoated 5 wt% Pt/Al_2O_3. Over 12–24 h 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 40 mL of fresh ethanol for 3–12 h 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.