

Promotion of Activity and Selectivity by Alkanethiol Monolayers for Pd-Catalyzed Benzyl Alcohol Hydrodeoxygenation

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Introduction

Benzyl alcohol is a significant biomass-derived oxygenate from lignin decomposition, which could be converted to benzaldehyde, toluene and benzene. Unfortunately, poor selectivity toward the desired products is a critical issue in the reactions of aromatic oxygenates, which causes higher separation costs and more pollutant byproducts. Several methods have been employed to improve the selectivity, such as use of bimetallic catalysts and different supports. An alternative strategy is to control ensembles of available surface sites and restrict the various oxygenate conformations on the catalyst surface using alkanethiol self-assembled monolayers¹. In this study, alkanethiols that form monolayers with variable surface densities were employed to restrict the conformation of adsorbed benzyl alcohol on Pd for enhancing hydrodeoxygenation (HDO) selectivity to toluene and reducing decarbonylation (DC) selectivity to benzene. Auger electron spectroscopy (AES) and temperature-programmed desorption (TPD) were employed to confirm thiolate coverage and investigate the thermal chemistry on a Pd crystal.

Materials and Methods

To prepare the SAM-coated Pd/Al₂O₃ sample, 70mg Pd/Al₂O₃ (5 wt%) was placed in a 20mL, 5mM thiol/ethanol solution overnight. For reactor studies, 2mg (uncoated and 1-adamantanethiol-coated cases) or 20mg (octadecanethiol-coated case) of Pd/Al₂O₃ diluted with 25mg Al₂O₃ powder was packed in a gas-phase plug flow reactor, conducted at 423K and atmospheric pressure. Feed and product samples were analyzed by an Agilent Technologies 7890A gas chromatograph equipped with a flame ionization detector. A mixed benzyl alcohol stream (the ratio of benzyl alcohol: H₂: He = 0.0015:0.29:0.71) where the flow rate of benzyl alcohol was 3.8 mmol/min, was fed to the reactor. Temperature programmed desorption (TPD) and Auger electron spectroscopy (AES) were conducted in a stainless steel ultra-high vacuum chamber (~1 x 10⁻¹⁰ Torr) equipped with a quadrupole mass spectrometer from VG Scienta and a cylindrical mirror analyzer for AES (MINICMA, LK Technologies). Pd(111) crystal was obtained from Princeton Scientific and cleaned by cycles of heating in 5x10⁻⁸ Torr O₂ between 500 and 900K and sputtering with Ar⁺ ions under room temperature. Sample cleanliness was confirmed through O₂ TPD and Auger electron spectroscopy.

Results and Discussion

As Figure 1(a) shows, the steady-state selectivity to toluene over the uncoated Pd catalysts was around 35% and the dominant product was benzene. After the 1-admantanethiol (AT) monolayers modification, the HDO selectivity was increased and the DC selectivity was decreased. Remarkably, the activity was also improved; this improvement was attributed to a decrease in catalyst poisoning by the reactant aromatic group. After octadecanethiol (C18) monolayer modification, the toluene selectivity was improved to over 82%, and the production

of benzene was decreased to below the detection limit of the gas chromatograph. However, the activity decreased. Mixed monolayers of AT and C18 were prepared to achieve activity and selectivity that was intermediate to the pure coatings.

In AES results, the higher peak amplitude ratio of S to Pd in the C18 coating indicated that a higher fraction of the surface was covered by C18 and a denser thiol monolayer structure was formed on the catalyst surface than AT coating. Comparing with TPD results from uncoated Pd(111), the significantly smaller benzene and hydrogen features relative to the toluene feature indicated a suppression of the DC pathway in preference of the HDO pathway after AT modification. For the denser C18 coating, the benzene and CO signals disappeared completely along with the hydrogen peak around 440K, showing that DC was totally obstructed on the C18-coated surface. Previous work showed that benzyl alcohol DC occurs through flat-lying adsorbates, while HDO results from more upright conformations on Pd(111) surface². Thus, after AT modification, due to the reduced availability of adjacent active sites, upright benzyl alcohol is expected to become more prevalent, increasing the selectivity to toluene. Interestingly, the barrier to desorption of aromatic products was reduced on the AT-coated surface, consistent with a suppression of poisoning. With the C18 coating, there was essentially no available space on terrace sites for flat-lying benzyl alcohol, which causes toluene to become the main product.

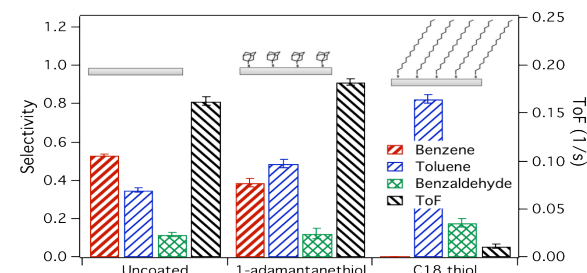


Figure 1. Benzyl alcohol selectivity and turnover frequency for uncoated, AT-coated and C18 thiol-coated Pd/Al₂O₃ at 423 K. The conversion was 40±4% and the mass balance was above 93% in all cases³.

Significance

Although organic monolayers have been shown to improve selectivity in several applications, here we show that they may additionally improve reaction rate by decreasing the selectivity for accumulation of carbonaceous deposits..

References

1. Marshall, S. T.; O'Brien, M.; Oetter, B.; Corpuz, A.; Richards, R. M.; Schwartz, D. K.; Medlin, J. W., *Nature material* **2010**,
2. Pang, S. H.; Román, A. M.; Medlin, J. W., *The Journal of Physical Chemistry C* **2012**, 116 (25), 13654-13660.
3. Lien, C.-H.; Medlin, J. W., *The Journal of Physical Chemistry C* **2014**, 118, 23783-23789.