Selective Dehydrogenation of Alcohols Using Single Atom Alloy Catalysts

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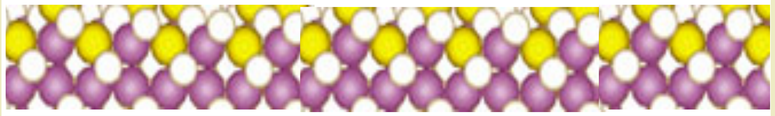
Motivation and Overview

This research aimed to apply the principles of heterogeneous catalysis to the solution of problems in the production of clean energy, specifically catalytic hydrogen production via alcohol dehydrogenation.

Platinum and palladium were alloyed with Cu/SiO_2 catalysts to study the effects of the type and concentration of additive on the activity and selectivity of the catalyst in the dehydrogenation of ethanol to acetaldehydes and hydrogen gas.



Background

Reactants: Methanol and Ethanol

Dehydrogenation *Selective Pathways*

Methanol: $CH_3OH \rightarrow HCOH + H_2$

Ethanol: $CH_3CH_2OH \rightarrow C_2H_4O + H_2$

Non-selective pathways

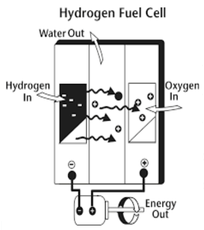
Methanol steam reforming:

$CH_3OH + H_2O \rightarrow CO_2 + 3H_2O$

Water Gas Shift:

$CO + H_2O \rightarrow CO_2 + H_2$

Products: Hydrogen and Aldehydes



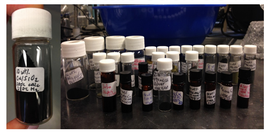
Hydrogen: hydrogen fuel cell (pollution-free energy source), fertilizer, oil refining, oil hydrogenation, electronics

Formaldehyde: building materials, medical preservative, sterilizer, fuel burning appliances

Acetaldehyde: intermediate in the synthesis of other chemicals, acetic acid (vinegar), perfumes, food preservatives, dyes…

Catalyst Synthesis

Catalyst = substance that increases the rate of a chemical reaction without undergoing any permanent chemical change. Decreases the activation energy of the reaction pathway. Copper is *selective.* Rare earth metals such as nickel, platinum, and palladium are *active.*

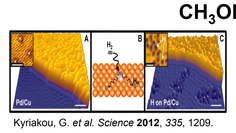


Galvanic Replacement:

$Cu + Pd^{2+} \rightarrow Cu^{2+} + Pd$ ($\Delta E° = +0.575$ V)

$Cu + Pt^{4+} \rightarrow Cu^{2+} + Pt$ ($\Delta E° = +0.4$ V)

Single Atom Alloys:
Pd and Pt act as entrance and exit routes for H2 dissociation and spillover to activate Cu. More CH3OH remains on the surface at higher temperatures, facilitating a greater degree of O-H bond activation



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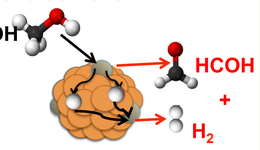
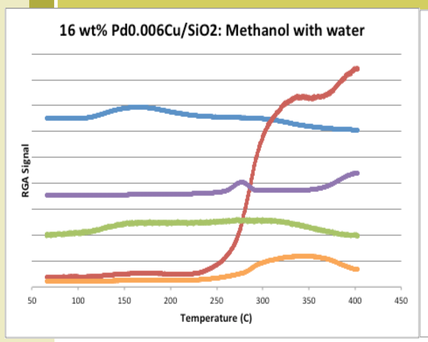
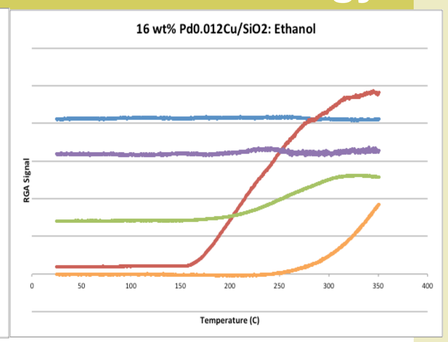
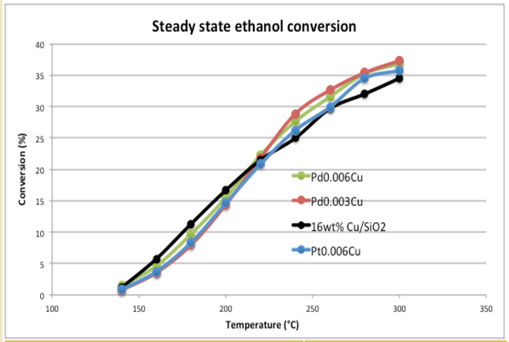


Conversion and Activation Energy





ABOVE: Sample TPSR results for two catalysts. Reactions were carried out in a Micromeritics AutoChem II. Results were visualized using a quadrupole mass spectrometer.

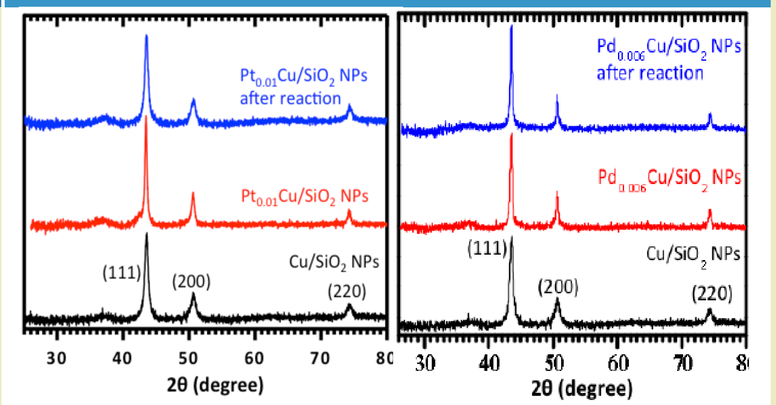


Percent conversion of ethanol to hydrogen at various held temperatures for alloyed catalysts compared to the pure copper catalyst.

Sample (after reduction in H_2-Ar)	Activation energy (J/mol)
16 wt% Cu/SiO_2	75.5
16 wt% $Pd0.003Cu/SiO_2$	70.7
16 wt% $Pd0.006Cu/SiO_2$	67.6
16 wt% $Pt0.006Cu/SiO_2$	65.9
10 wt% $Pt0.012Cu/SiO_2$	58.3

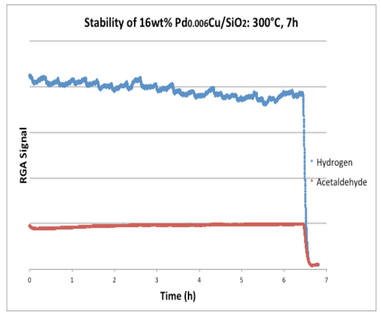
Activation Energy calculated using the slope of an Arrhenius plot

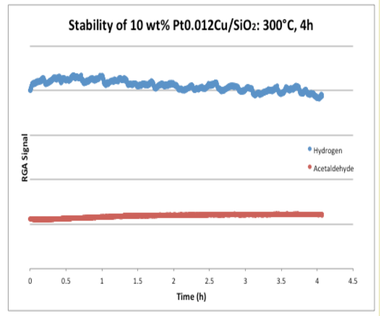
XRD Characterization

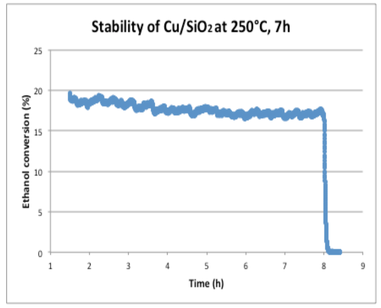


XRD testing showed that the addition of a small amount of Pt (Left) or Pd (Right) does not change the structure of Cu, before and after reaction. Cu particle sizes were 14 nm.

Stability







Stability of PdCu, and PtCu, and pure Cu catalysts are shown, as conversions to hydrogen and acetaldehyde are steady over the course of several hours.

Conclusions

- Palladium samples did not show significant catalytic improvement for the dehydrogenation of ethanol.
- Platinum alloys showed promise. The Pt0.012Cu sample created with an improved method of galvanic replacement resulted in a 22% lower activation energy than that of pure copper.
- Why? Palladium atoms sit on the uncoordinated steps sites where copper is already active for hydrogen desorption. Platinum is also present on copper terraces, which serves to activate those sites as well and provide additional locations for hydrogen desorption.

Future Steps

- TPSR and steady state analysis
  - 8wt% $Pd/Cu\text{-}SiO_2$ and $Pt/Cu\text{-}SiO_2$ catalysts
  - Repeat reactions for error analysis
- Catalyst Characterization: UV-vis analysis – is galvanic replacement successful?
- Parametric conditions: contact time (independent variable: flow rate) – how long does each molecule of ethanol have to be in contact with the catalyst?

References:

1. H. Tierney, A. Baber, J. Kitchin, E. C. Sykes. Hydrogen Dissociation and Spillover on Individual Isolated Palladium Atoms. *Physical Review Letters,* 2009, **103**, 246102.
2. M. Boucher, B. Zugic, G. Cladaras, J. Kammert, M. Marcinkowski, T. Lawton, E. C. Sykes, M. Flytzani-Stephanopoulos. Single atom alloy surface analogs in $Pd_{0.18}Cu_{15}$ nanoparticles for selective hydrogenation reaction. *Phys. Chem. Chem. Phys.,* 2013, **15**, 12187