

V.N.21 Oxide-Metal Interactions Studied on M@Oxide, Core-Shell Catalysts

Principal Investigator: Raymond J. Gorte
Chemical & Biomolecular Engineering
University of Pennsylvania
311 Towne Building, 220 South 33rd Street
Philadelphia, PA 19104
Phone: 215/898-4439
Email: gorte@seas.upenn.edu

Chen Chen
Chemical & Biomolecular Engineering
University of Pennsylvania
311 Towne Building, 220 South 33rd Street
Philadelphia, PA 19104
Phone: 215/898-4439
Email: chenc5@seas.upenn.edu

Lisandra Arroyo
Chemical & Biomolecular Engineering
University of Pennsylvania
311 Towne Building, 220 South 33rd Street
Philadelphia, PA 19104
Email: lisyarroyo@gmail.com

DOE Program Manager: Raul Miranda
Email: Raul.Miranda@science.doe.gov

Objectives

The primary objective of this work is to develop better catalysts through optimization of metal/metal-oxide interactions. The primary goals of the present work will be: 1) to investigate the catalytic properties of core-shell catalysts prepared by self-assembly methods to determine how the oxide shells affect the activity of metal catalysts, 2) to use these materials to characterize the energetics associated with oxide-metal interfaces in systems of catalytic interest, 3) to characterize the nature of the oxide-metal interface spectroscopically, and 4) to develop a better understanding of the role that oxide-metal interactions have on catalytic properties.

Abstract

Core-shell nanoparticles have been synthesized in organic solutions using self-assembly methods, with Pd or Pt at the core and ceria, zirconia, and titania as the shell. These are then adsorbed in monolayer form onto oxide supports that have been functionalized using silanes to make them hydrophobic. The primary goals of the present work are: 1) to investigate the catalytic properties of core-shell catalysts prepared by self-assembly methods to determine how the oxide shells affect the activity of metal catalysts, 2) to use

these materials to characterize the energetics associated with oxide-metal interfaces in systems of catalytic interest, 3) to characterize the nature of the oxide-metal interface spectroscopically, and 4) to develop a better understanding of the role that oxide-metal interactions have on catalytic properties

Progress Report

Initial studies with Pd@ceria/alumina demonstrated that the activity of this catalyst is a strong function of calcination temperature, with catalysts showing greatly improved activity when heated to above 1073 K. To understand this, we have investigated the properties of a Pd@CeO₂/Si-Al₂O₃ catalyst after calcination at 773 K and after calcination at 1073 K.

Calcining to higher temperatures increased rates for the methane-oxidation reaction over Pd@CeO₂/Si-Al₂O₃ by a factor of more than three for measurements in 0.5% CH₄ and 5% O₂. The effect of increasing calcination temperature on this catalyst was even more dramatic for methane-steam reforming (MSR). The Pd@CeO₂/Si-Al₂O₃ catalyst calcined to 773 K was unstable for MSR, losing almost all of its activity over the period of an hour while the catalyst calcined at 1073 K showed reasonably stable rates. CO adsorption, monitored using volumetric uptakes, and FTIR indicated adsorption on the Pd was suppressed following reduction at 673 K in H₂ when the catalyst had been calcined at only 773 K, but not after 1073 K. Pulse-reactor measurements demonstrated that catalysts calcined at either 773 K or 1073 K were heavily reduced under MSR reaction conditions at 673 K but that the catalyst heated to 1073 K could be reoxidized by H₂O at this temperature, while the 773-K sample could not be. It is suggested that increasing calcination temperature modifies the structure of the ceria shell, which in turn changes the ceria redox properties.

Future Directions

We are continuing our investigations of the Pd@Ceria/alumina catalyst in order to understand why it shows exceptional activity for methane oxidation. We are also beginning similar studies of catalysts prepared with different metal cores and different oxide shells.

Publication list

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