Functionalization of Alloy Metal Nanoparticles for Enhanced Transport and Catalysis in Membranes
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Benny D Freeman, Michael F Becker, Graeme Henkelman, John W Keto, Desiderio Kovar

The University of Texas at Austin

Introduction

- 150 million tons of light olefins (ethylene and propylene) are produced each year [1]
- 1.4E14 BTU/yr used on separation [2]
- Current separation technology is hugely energy inefficient
- Nanocomposite membranes are promising technology because no phase change required for separation

[1] Ren et al., *Energy*, 33, 2008, 817-833
[2] Eldridge, *Ind. Eng. Chem. Res.* 1993, 32,2208-2212

Research Areas

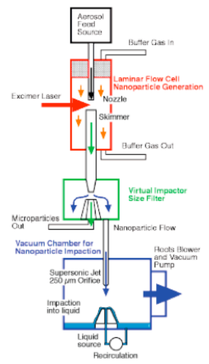
- Nanoparticle (NP) Synthesis and Characterization using Laser Ablation of Microparticle Aerosol (LAMA) process
- Characterization and Optimization of Transport Properties for Nanocomposite Membrane
- Kinetic Monte Carlo Modeling of Transport and DFT Modeling of Binding Geometries
- Educational Outreach

Nanoparticle Synthesis

•Nanoparticles Synthesized by LAMA

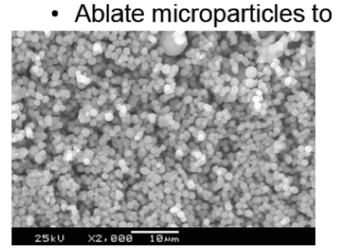
•LAMA Process directly deposits NPs into liquid polymer

•Nanoparticle synthesis does not require capping particles

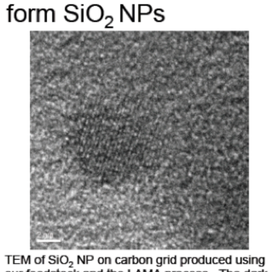


Silica Nanoparticles

- Hydrolyze Tetraethyl Ortho-Silicate to form uniform SiO_2 microparticles
- Ablate microparticles to form SiO_2 NPs



SEM of SiO_2 microparticles produced in our laboratory for use as feedstock for the LAMA process.



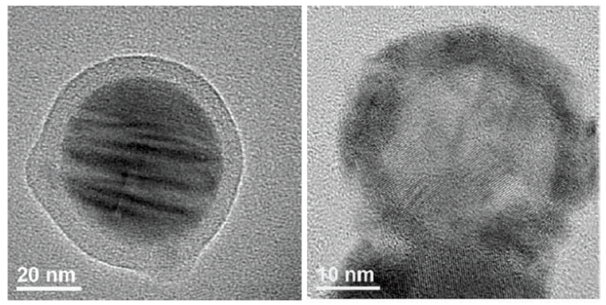
TEM of SiO_2 NP on carbon grid produced using our feedstock and the LAMA process. The dark area is the particle with the lines showing the crystal lattice

Core-Shell Nanoparticles

NP consisting of separate core and shell materials

- Synthesize core NP normally in LAMA process
- Feed core NP and shell Microparticles simultaneously through LAMA
  - Can produce continuous shell on NP core
  - Can produce shell of nano-islands on NP core

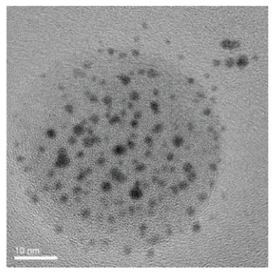
CdSe/ZnS Core-Shell NPs



HRTEM micrograph of core/shell NPs. The left image shows a CdSe core with ZnS shell. The right image shows a ZnS core with CdSe. [3]

[3] Gallardo et al. *Applied Physics A*, accepted 2008

Au/SiO_2 Core-Shell NPs



HRTEM micrograph of core/shell nanoparticles. The larger gray sphere is SiO_2 and the dark spots Au nano-islands .

Nanoparticles to Improve Transport

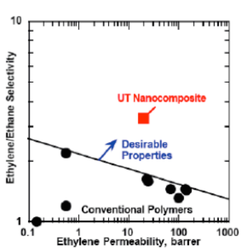
To be economically viable, gas separations membranes must exhibit high flux (permeability) and high purity (selectivity) of the desired component

- Want to increase permeability of olefin with respect to permeability of paraffin
- Include some species-selective "carrier" (silver NP) in membrane matrix
- Increased solubility of olefin over paraffin compared to neat film gives improved membrane performance [4]

[4] Nobel et al., "Rev. of FT Mem.", in *Mat. Sci of Mem.*, Yampolskii, Pinnau, and Freeman (Eds), 2006

Nanocomposite Membrane Performance

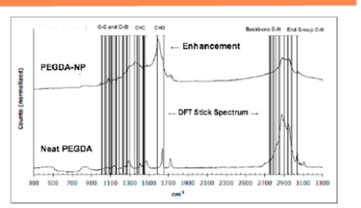
The nanocomposite membrane exhibited increased selectivity for olefins while maintaining olefin permeability compared to neat polymer matrix

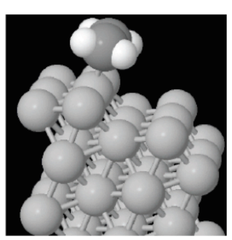


Ethylene-ethane separation properties in conventional polymers and in XLPEO doped with 0.05 vol. % LAMA Ag NPs at 35°C. The AgNPs were nominally 8 nm dia. Permeability coefficients were determined at an upstream pressure of 4.4 atm.

Raman Spectra and DFT Analysis

- Surface enhancement of PEGDA on NP flocs observed
- DFT vibrational spectra used to determine binding of PEGDA on a silver surface

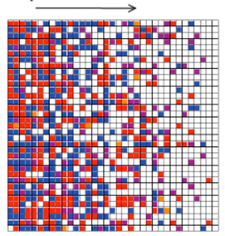


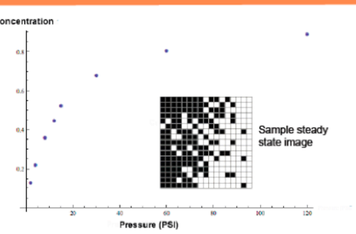


- DFT energetics are also used to investigate the binding of olefins on silver NP surfaces
- Investigating the potential effect of subsurface oxygen on olefin binding to silver-(111) NP facets

Kinetic Monte Carlo Modeling

- Developed a lattice kinetic Monte Carlo simulation based on physical parameters from experimental data
- Particles diffuse through membrane from gas source to output



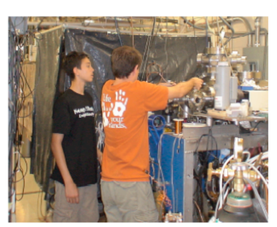


- Arrhenius hopping rates are based upon binding energies
- Tuning pressure, NP loading, and olefin-to-NP binding energy allows us to predict conditions for optimal olefin/paraffin selectivity

Outreach Activities

Texas School for the Deaf (TSD)
- Sponsor meetings for Science Club at TSD
- Recruited TSD student as summer research intern

Austin Children's Museum (ACM)
- Science Sundays program
- Field trips from ACM summer science camps



A graduate student trains Summer Research Intern Cody Kornkven on the LAMA apparatus

For more information contact Benny D Freeman freeman@che.utexas.edu