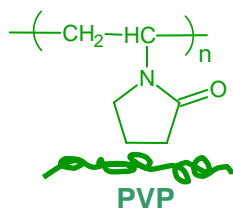


Platinum Nanoparticles of Well-Defined Size and Shape for Model Heterogeneous Catalysis

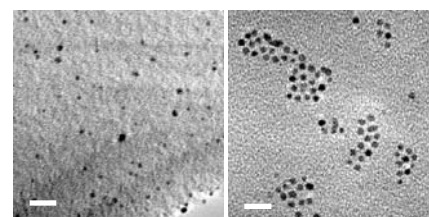
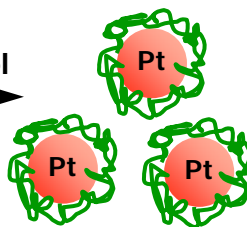
The goal of this project is to design a model catalyst which will be used in a systematic study of the variables that influence reaction selectivity. In order to achieve the overall goal, the following objectives must be satisfied. They include 1) the synthesis of supports, either 3-dimensional mesoporous oxides, or 2-dimensional thin oxide films, 2) the synthesis of metal nanoparticles with tunable size and narrow size distribution, 3) the preparation of catalysts combining the catalytically active metal particles with the support oxide materials, 4) the characterization of the final material with the arsenal of different physical and chemical methods and 5) determine both the role of metal particle size and the role of support on reaction activity and selectivity.

1) Nanoparticle Synthesis

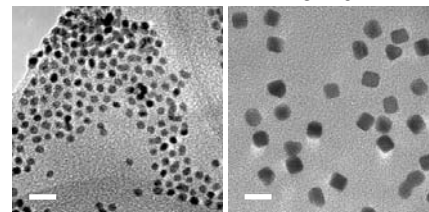
- a. Platinum nanoparticles of varying sizes are synthesized by reducing hexachloroplatinic acid in ethanol or ethylene glycol in the presence of polyvinyl pyrrolidone (PVP) as a stabilizer. By varying the reaction conditions, particles between 1.5 and 8 nm are synthesized.



Alcohol

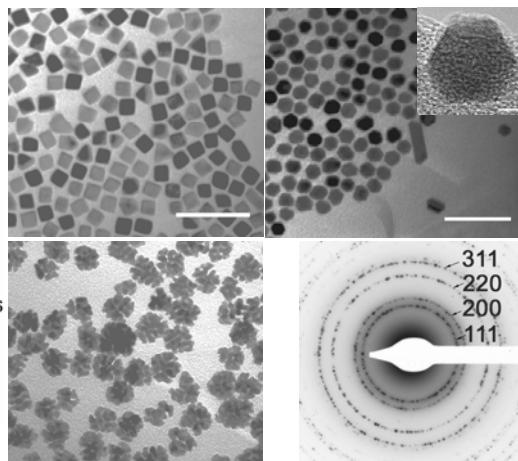
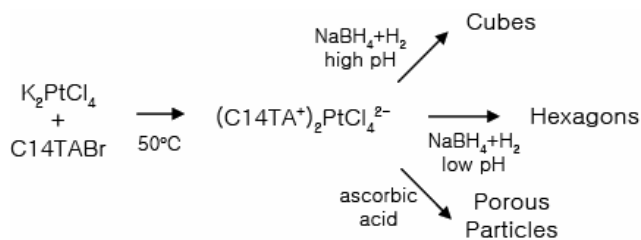


1.7 ± 0.2 nm 2.8 ± 0.2 nm



3.4 ± 0.3 nm 7.2 ± 0.4 nm
scale bar = 10

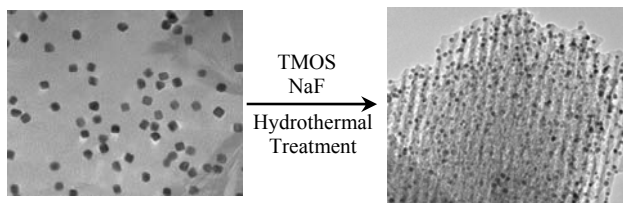
- b. Platinum particles of varying shapes are synthesized by reduction in the presence of cetyltrimethylammonium bromide (CTAB) as a stabilizer. Using this method, cubes, octahedral, and porous particles have been realized.



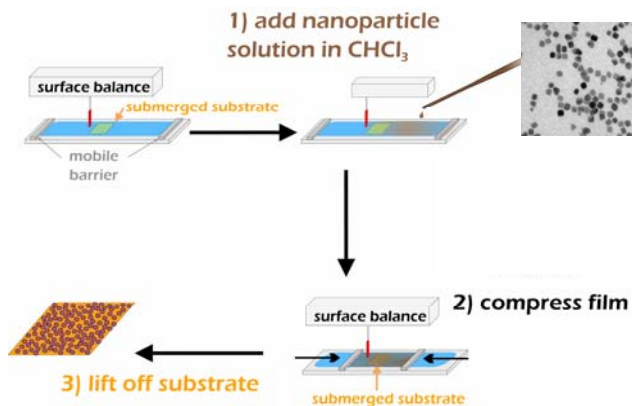
Scale bar = 50 nm

2) Catalyst Synthesis

- a. The current 3-dimensional approach to catalyst synthesis involves the encapsulation of nanoparticles into SBA-15 like mesoporous materials by formation of the oxide in the presence of the nanoparticles. This is accomplished by hydrolysis of tetramethylorthosilicate (TMOS) by NaF.

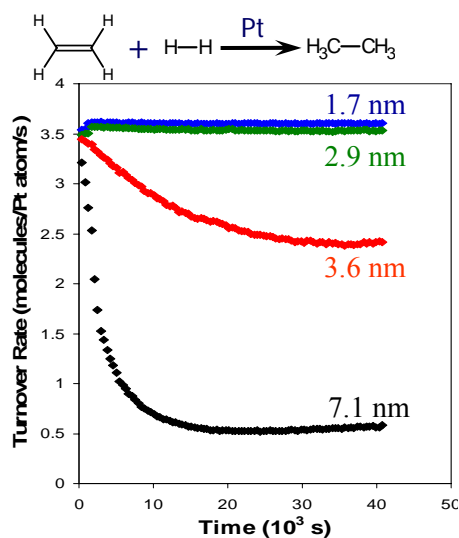


- b. We will shift our focus from 3-dimensional systems to 2-dimensional systems in order to be able to change the oxide on which the particles are deposited. Using a 2-D system also allows us to employ a wide range of surface analytical techniques such as Auger electron spectroscopy and sum frequency generation spectroscopy. These catalysts are synthesized by coating a silicon wafer with the desired oxide by atomic layer deposition (ALD), then depositing the nanoparticles by the Langmuir-Blodgett (LB) technique.

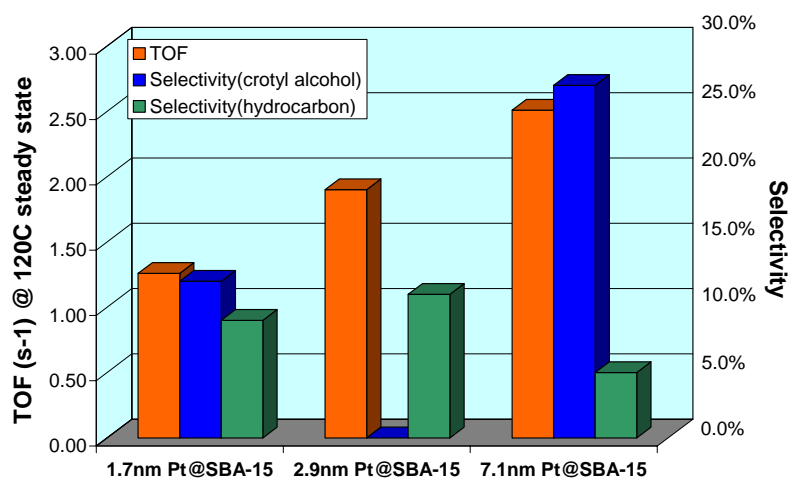
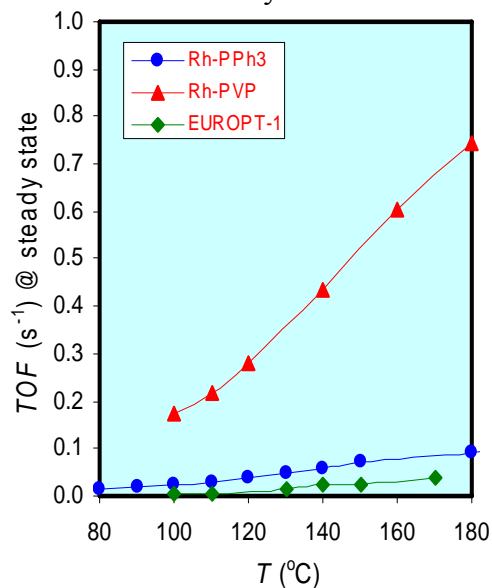


3) Activity and Selectivity for Hydrogenation Reactions by Nanoparticles Supported on SBA-15

- a. Ethylene hydrogenation is a surface insensitive reaction. This makes it a good probe of available surface sites on a catalyst. We find that the initial turnover frequency (TOF) is independent of particle size for platinum catalysts supported on SBA-15, but that larger particles deactivate to a much greater extent than smaller particles.



- b. Crotonaldehyde is the simplest of the α,β -unsaturated aldehydes and is an excellent probe for selective hydrogenation of carbonyl versus vinyl bonds. With platinum particles, we have studied the effect of particle size on activity and selectivity. For rhodium particles, we have studied the effect of capping agent on catalysis.



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