Adatom Emission from Nanoparticles: Implications for Ostwald Ripening

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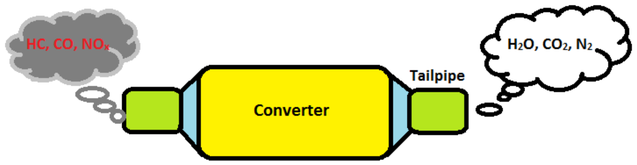
BACKGROUND & MOTIVATION

To achieve clean air in our cities, all modern means of ground transportation make use of catalytic converters. Precious metal-based catalysts such as Pt and Pd are currently used in catalytic converters. To achieve higher fuel efficiency, combustion can be carried out in excess air resulting in a reduction of greenhouse gas (GHG) emissions. Reduction of these emissions has emerged as a major challenge. Most of the pollutants are emitted within the first 30 seconds after starting an engine because the catalyst is cold. The development of catalysts which achieve high activity at low temperatures will improve fuel efficiency and therefore reduce the nation's dependence on foreign fossil fuels.

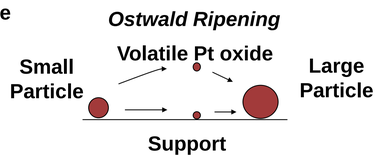


The need to achieve low-T light off leads to increased Pt demand; however, worldwide Pt supplies are limited. A major problem is that catalysts lose activity during use. Pt particles grow in size under oxidizing conditions through Ostwald ripening, which leads to poor stability [1,2]. The addition of Pd has been shown to improve the durability of Pt catalysts [3]. The reasons for the improved durability of Pt-Pd catalysts are not known.

SCOPE: Study the mechanisms by which Pd enhances the stability and catalytic activity of Pt so that novel catalysts can be developed which minimize the use of Pt.

RESEARCH QUESTIONS

- Does the growth of Pt nanoparticles involve volatile Pt oxides or diffusion of adsorbed atoms (adatoms) on the surface?
- Does Pd influence the volatility of Pt?
- What are the mobile species? (Pt, Pd, or both)



APPROACH

In automotive catalysts, the growth of nanoparticles can only be studied post-mortem (after aging). We, therefore, developed a novel approach using model catalysts where it is possible to perform direct measurements of the emission of atoms from nanoparticles. The model catalysts we use allow heat treatment at elevated temperatures under realistic conditions and the opportunity to observe the same nanoparticle before and after treatment.

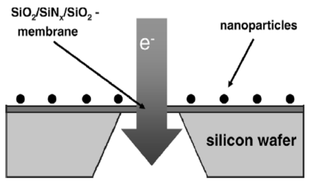
Two different methods have been used

**Statistical approach- used to study thousands of nanoparticles and observe overall phenomena

**Microscopic approach- used to track the behavior of individual nanoparticles

Electron beam evaporation was used to synthesize all samples

- 5 Å of Pt; 5 Å of Pd; 2.5 Å of Pt and 2.5 Å of Pd were deposited on SiO_2 TEM grids [4]
- All samples were reduced in 7% H_2/N_2 at 600°C or higher
- Aging was performed in air at temperatures ranging from 500°C to 800°C



Silicon-based TEM grids allow for high T aging [4]

METHODS

- Volatility of Pt, Pd, and Pt-Pd NPs measured by studying loss of metal on model thin film catalysts
- Tracking of individual nanoparticles allows the study of mechanisms

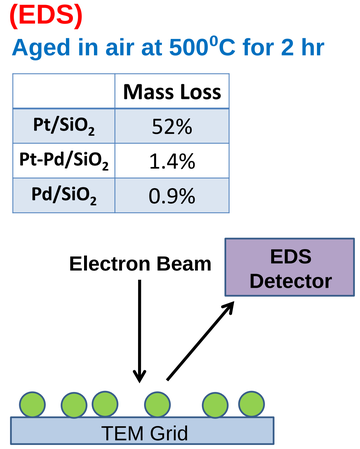
[1]: S.B. Simonsen, I. Chorkendorff, S. Dahl, M. Skoglundh, J. Sehested, and S. Helveg, *Journal of the American Chemical Society*, 2010.
[2]: S.B. Simonsen, I. Chorkendorff, S. Dahl, M. Skoglundh, J. Sehested, and S. Helveg, *Journal of Catalysis*, 2011
[3]: G.W. Graham, H.-W. Jen, O. Ezekoye, R.J. Kudla, W. Chun, X.Q. Pan, and R.W. McCabe, *Catalysis Letters*, 2007
[4]: P. Moodley, J. Loos, J.W. Niemantsverdriet, and P.C. Thüne, *Carbon*, 2009.
[5]: M. Chen and L.D. Schmidt, J. Catal. 56 (1979) 198.
[6]: J.B. Darby, Jr. and K.M. Myles, Metallurgical Transactions ,1972.

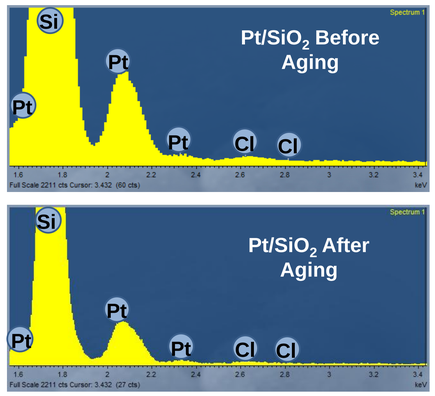
RESULTS

Macroscopic Approach- Energy Dispersive X-ray Spectroscopy (EDS)

Aged in air at 500°C for 2 hr

	Mass Loss
Pt/SiO_2	52%
$Pt-Pd/SiO_2$	1.4%
Pd/SiO_2	0.9%

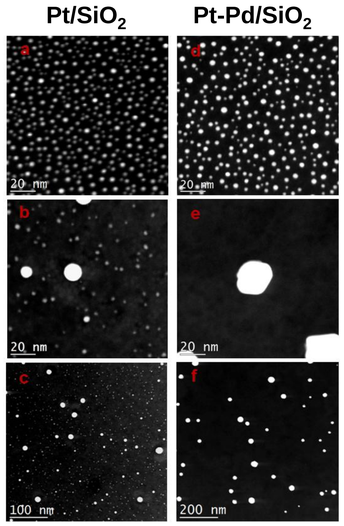




Amount of metal determined by EDS

Macroscopic Approach- Imaging

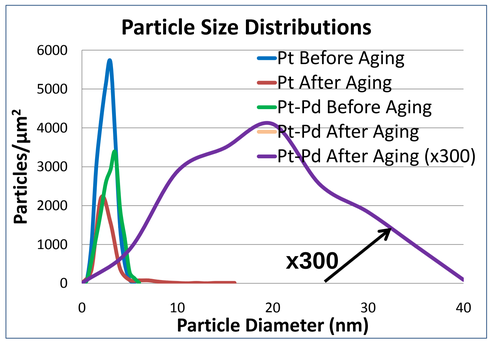
Aged in air at 800°C for 1.5 hr

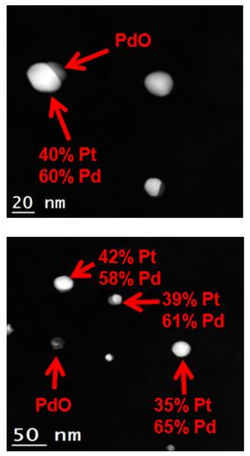


	Pt/SiO_2	$Pt-Pd/SiO_2$
Mass loss	88%	16%

Addition of Pd to Pt led to a dramatic decrease in the emission of Pt; however, the impact on the rates of Ostwald ripening was minimal. This suggests that surface diffusion of adatoms rather than emission to the vapor phase may play a major role in catalyst sintering.

By counting particles to determine the mass loss, we found that addition of Pd led to an 82% decrease in the emission of volatile Pt oxides, confirming the observations made by EDS. The emission of Pt does not correlate with the growth of particle size.





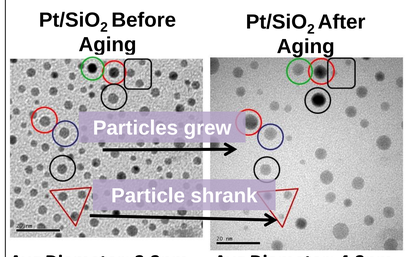
EDS showed that the compositions of individual nanoparticles after aging were very similar to those before aging even though the particle size had grown significantly. These results imply that both Pt and Pd can be transported under oxidizing conditions.

Composition of bimetallic nanoparticles
*before aging: 40% Pt, 60% Pd *after aging: 33% Pt, 67% Pd

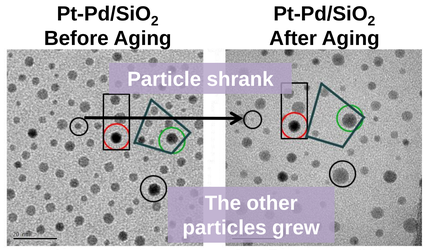
The sample remained metallic under the aging conditions and we saw only a few instances where a PdO phase had segregated from the Pt-Pd alloy.

Microscopic Approach- Set 1

SET 1: Aged in 21% O_2/Ar at 650°C for 15 s



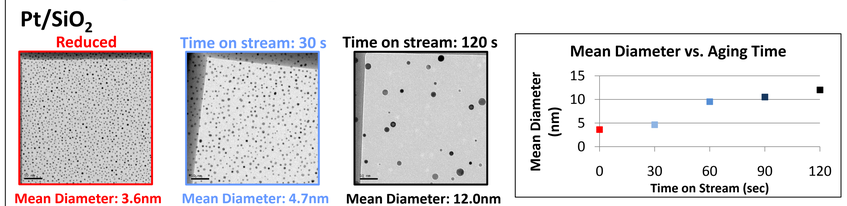
Some particles have shrunk while others have grown. We can therefore conclude that Ostwald ripening is the mechanism for the overall growth in particle size for both Pt and Pt-Pd samples.



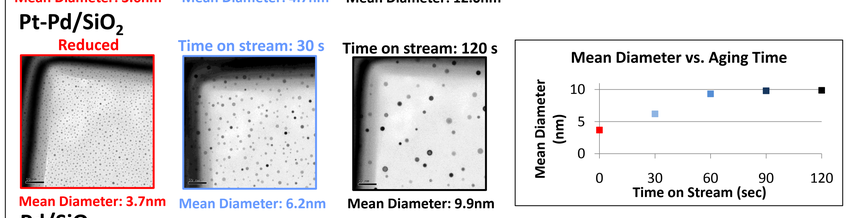
Microscopic Approach- Set 2

SET 2: Aged in 21% O_2/Ar at 650°C for 30, 60, 90, and 120 s

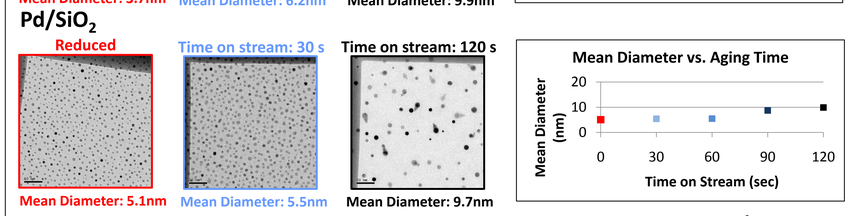
Pt/SiO_2



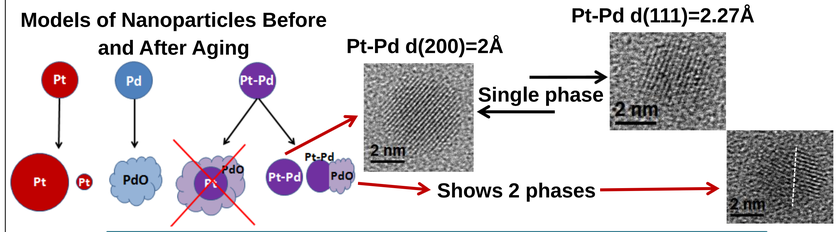
$Pt-Pd/SiO_2$



Pd/SiO_2



Models of Nanoparticles Before and After Aging



SUMMARY & CONCLUSIONS

- The dominant sintering mechanism is Ostwald ripening
- Pt/SiO_2 showed significant mass loss upon aging in air; adding Pd to Pt decreased mass loss by 80%; Pd showed negligible mass loss
- At moderate temperatures, Pd slowed down ripening
- Identical composition of aged nanoparticles, despite significant growth in particle size, suggests similar mobility of Pt and Pd

- Transport of Pt via surface diffusion of adatoms is the dominant mechanism for the growth of nanoparticles

Future work will involve in-situ TEM to observe sintering phenomena at elevated temperature in reactive gas environment. We will also need to investigate the role, if any, of the support. We also have plans to study the oxidation of individual Pt-Pd nanoparticles.

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