Understanding the Role of Reaction Conditions and Zeolite Properties on Interconversion Between Cations and Nanoparticles in Pd/Zeolites

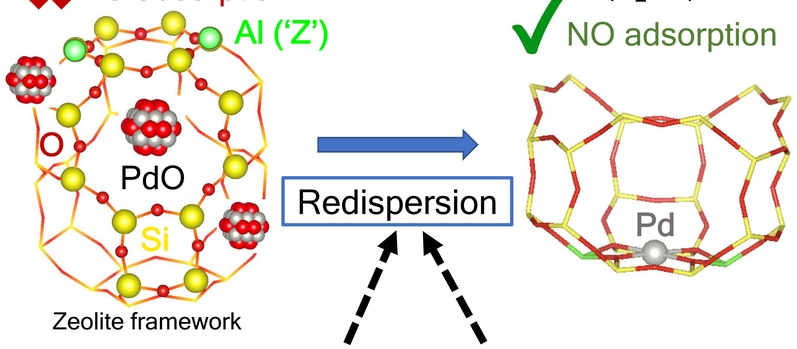
Keka Mandal[1], Trevor Lardinois[2], Chris Paolucci[1], and Rajamani Gounder[2]
1 University of Virginia, 2 Purdue University

Paolucci Group

INTRODUCTION

Pd agglomerates
✖ NO adsorption

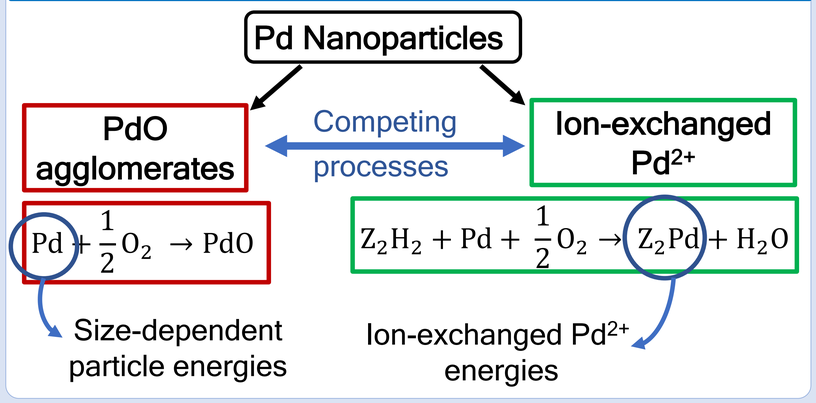
Ion-exchanged Pd^{2+} (Z_2Pd)
✓ NO adsorption



- Smaller Pd particles on Al_2O_3 → greater extent of conversion to mononuclear $Pd(OH)_2$; lower decomposition temperature (< 873 K)
  (Goodman *et al, Nat. Catal.* **2019**, *2* (9), 748-755.)
- Larger Pd particles on Al_2O_3 → need higher O_2 pressures to fully oxidize to PdO
  (Chin *et al J. Phys. Chem. C* **2016**, *120 (3)*,1446-1460.)

OBJECTIVE

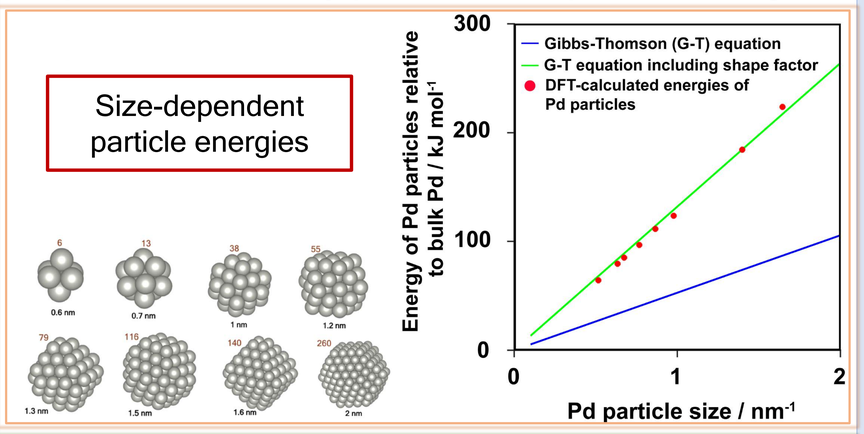
1. Using density functional theory (DFT) calculations and thermodynamic analysis, develop thermodynamic and kinetic models to predict redispersion of Pd agglomerates to ion-exchanged Pd^{2+} as a function of particle size and the reaction environment
2. Validate against experimental data



RESULTS

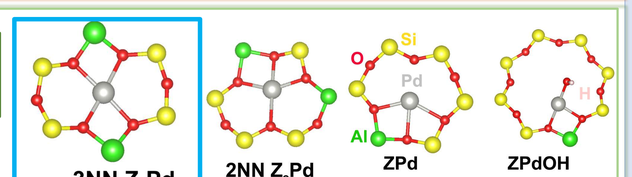
1. Thermodynamic model similar to Gibbs-Thomson Equation accurately predicts nanoparticle energies

Size-dependent particle energies



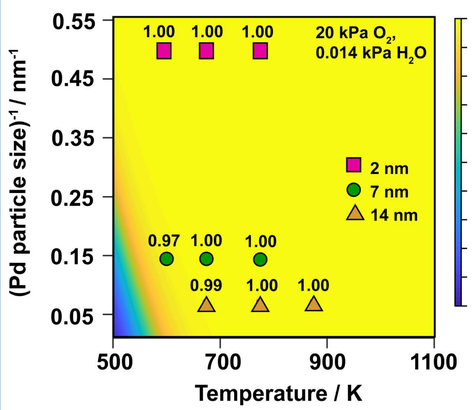
Ion-exchanged Pd^{2+} energies

(Mandal *et al ACS Catal.* **2020**, *10*, 12801-12818)



(NN - nearest neighbor)

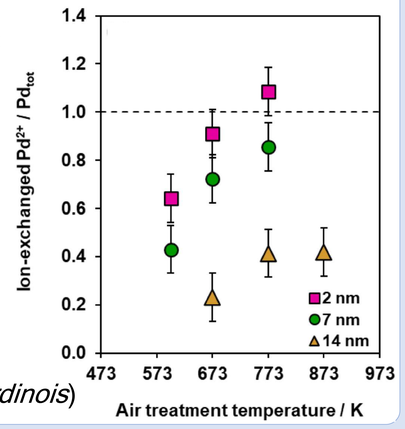
2. Formation of Z_2Pd thermodynamically favorable at the experimental air treatment conditions



Thermodynamic model → all particles completely ion-exchange

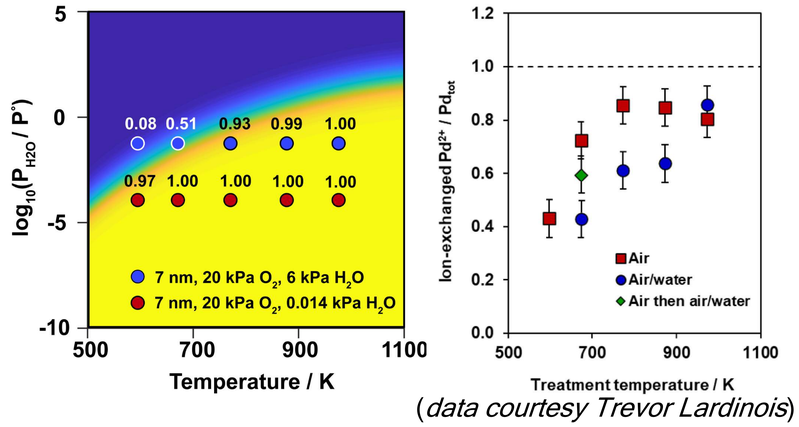
Experimental data→ Ion-exchange increases with temperature, decreases with increase in particle size

Kinetic barriers limit ion-exchange.



(*data courtesy Trevor Lardinois*)

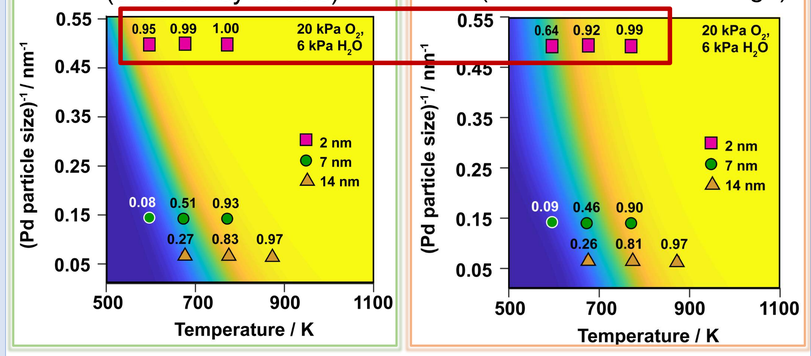
3. Increased H_2O pressure promotes PdO agglomeration



(*data courtesy Trevor Lardinois*)

Thermodynamic predictions and experimental data show H_2O has an inhibiting effect on ion-exchange.

4. Effect of Particle Size Distribution (PSD) prominent for smaller particles



CONCLUSIONS

- ✓ Experimentally observed conversion of large Pd particles to ion-exchanged Pd^{2+} < thermodynamic predictions → kinetic barriers
- ✓ Increase in H_2O pressure promotes PdO agglomeration →critical to PNA deactivation
- ✓ Isothermal redispersion experiments with/ without H_2O exhibit same rates → H_2O affects thermodynamics, not kinetics

FUTURE WORK

- Identify Pd redispersion mechanism
- Model the kinetics of Pd redispersion

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