RICE UNIVERSITY

Catalytic Oxidation Properties of Palladium-decorated Gold Nanoparticles

by

Zhun Zhao

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

Doctor of Philosophy

APPROVED, THESIS COMMITTEE:

Michael S. Wong, Chair
Professor in Chemical and Biomolecular Engineering, Chemistry, Civil and Environmental Engineering, Materials Science and NanoEngineering

Ramon Gonzalez
Professor in Chemical and Biomolecular Engineering, Bioengineering

Junrong Zheng
Assistant Professor in Chemistry

HOUSTON, TEXAS
September 2014
Abstract

Catalytic oxidation properties of palladium decorated gold nanoparticles
by
Zhun Zhao

Bimetallic palladium gold (PdAu) catalysts have been shown to be superior to monometallic ones in many reactions, but the reasons for the enhancement are not thoroughly understood. In this work, palladium decorated gold nanoparticles (Pd-on-Au NPs) are used as structured model catalysts, allowing for the precise control of both size and metal distribution with Pd surface coverage (sc%). By testing reactions on a range of these catalysts, we hope to gain insight into the active site for a given reaction.

In hydrodechlorination of perchloroethene (PCE), Pd surface coverage was found to be the key factor in catalyst activity, with the optimum at 80 sc%. A complete mechanistic model that coupled mass transfer processes with the surface reactions was further developed, consistent with the observed product profiles.

Carbon supported Pd-on-Au NPs were tested for liquid phase glycerol oxidation for the first time. The best catalyst (80 sc%) had an initial TOF of ~6000 h⁻¹, >10 times more active than Au/C and Pd/C. Catalytic activity, selectivity, activation energy and deactivation rate constant exhibited strong volcano-shaped dependences upon Pd sc%. *Ex situ* XANES results showed no
to little change in surface Pd-O% for Au based catalysts, suggesting the possibility of Au suppressing Pd oxidation during reaction.

*Ex situ* EXAFS results further confirmed the core-shell structures of 60 and 150 sc% Pd-on-Au/C catalysts via Punnett square analysis, and also ascertained no to little change in their oxidation states and coordination numbers post glycerol oxidation. EXAFS observations correlate with kinetics results, and lead to the conclusion that catalysts with a larger amount of 3-D Pd ensembles are more prone to oxidize during glycerol oxidation, making them less resistant to deactivation.

Finally, Pd-on-Au/C catalysts were tested for room temperature formic acid decomposition. *In situ* XAS revealed that core-shell structures of 60, 150 and 300 sc% Pd-on-Au NPs maintained while oxidized Pd species was partially reduced during reaction. Catalyst with higher fraction of 3-D Pd ensembles showed much higher dehydrogenation activity than those with mostly 1-D or 2-D, correlating to the proposed mechanism that the dehydrogenation pathway is favored over metal terrace sites.
I would like to express my deep gratitude to my Ph.D. advisor Prof. Michael Wong. Prof. Wong was the main reason I chose to attend Rice deciding where to pursue my Ph.D. This decision has profoundly shaped both my professional and personal lives. As a respected advisor and educator, Prof. Wong offers sincere encouragement while holding his students to his high standards for research. More than just an advisor, he has become like a trusted friend; he generously shares his life experience and advice as well as taking interest in my personal life. He has been essential to all my progress over the years. Thank you for all the kind effort and consideration. One day a teacher, forever a teacher.

I would like to thank Prof. Ramon Gonzalez for very generously helping me with HPLC, and for being my collaborator and committee member as well. I would like to thank Prof. Junrong Zheng for being my collaborator and committee member. Both have helped significantly with my research through our very insightful discussions. I thank Dr. Kimberly Heck for proof-reading my thesis.

I would like to express my appreciation for Dr. Jeffrey T. Miller, my long term collaborator at Argonne National Laboratory. I thank him not only for generously offering guidance on X-ray absorption spectroscopy but also for sharing his broad knowledge of catalysis. I would also like to acknowledge his previous and current team members at Argonne: Drs. Tianpin Wu, Soma Chattopadhyay, Neng Guo, Neil M. Schweitzer, and Mr. Guanghui Zhang, for their kind help during my onsite experiments at Argonne.
I would like to thank all my current and previous colleagues in the Catalysis and Nanomaterials Laboratory for helping me during my Ph.D. Specifically, I wish to thank Drs. Yu-lun Fang, Huifeng Qian, Jie Yu, Kimberly Heck, Jerimiah Forsythe, Zachary Schaefer, Hitesh G. Bagaria, Sukit Leekumjorn, Sravani Gullapalli, Lori Pretzer, Gautam Kini, Nikolaos Soultanidis, Mr. Juan C. Velazquez, Mr. Varun Shenoy Gangoli, Ms. Li Chen and Mr. Quang Nguyen for their kind help and advice during my experiments and project development. I wish to thank Mr. Pongsak Limpornpipat, Ms. Nicole Lu, Ms. Joni Arentz for helping with experiments. I wish to thank Kai Zhou for help during our collaboration. Finally, I wish to thank visiting scholars Drs. Hao Yu, Weixia Tu, Ho-Jeong Chai, Hao Qian, Shujing Li and Hua Yang for helpful discussions.

I would like to thank all my friends and colleagues at Rice who have given their kind help to me. I thank Drs. Dichuan Li, Jiebo Li, Zhengzheng Feng, and James M. Clomburg for helpful collaborations and discussions. I thank Mr. Yongchao Zeng and Di Du for being great friends.

I would like to thank all my friends and colleagues from universities and institutions outside of Rice. Among them, thank all my undergraduate classmates in Tsinghua University for being such helpful resources. I would especially like to thank my best friend Dr. Siwei Luo, for being so supportive during my Ph.D.

I would like to thank my family and friends in Houston. Countless thanks should go to my aunt Dr. Jinhua Bai and her family in Houston for the great influence she had on me. I thank the Larsons’ for being my host family over these years and showing me how Americans live. I thank Prof. Engang for being a great friend and big brother.

I am very grateful for my family in China: my father, Sancheng Zhao, mother, Xiaoyan Zeng, younger sister, Yu Zhao, for their spiritual and financial support. Without my parents’
nurturing and support I would have never made it to this point in my career, nor would I be the same person I am right now. Financially, they have never asked for repayment nor even asked why. The sacrifices they made will always be in my thoughts; their generosity is something that I will try to embody in future endeavors. Mom and Dad, thank you for everything.

Last but most important, I would like to express my most sincere gratitude to my wife, Ms. Jingjing Bai, and my daughter, Bailey B. Zhao. In retrospect, I count myself very fortunate to have met my wife in 2010, which gave me a renewed sense of purpose. My time in graduate school would have been much darker without her gentle support and understanding. I doubt that I would have been confident and persistent enough to overcome all the hurdles and failures of graduate school to get to where I am today. The birth of our lovely daughter Bailey has not only given me unexpected joy but also a new goal, to pursue a better future for my family. Life is not easy. But with you both, I am more than ready for any challenge that may come. Thank you both for everything!

To my beautiful wife Jingjing Bai and lovely daughter Bailey B. Zhao

Zhun Zhao

September 2014
Table of Contents

Chapter 1 Background and Research Overview 1
  1.1. Introduction to bimetallic catalysts 1
    1.1.1. History 1
    1.1.2. Bimetallic structures 2
    1.1.3. Synthesis 3
  1.2. Synergistic effects 4
    1.2.1. Geometric effect 4
    1.2.2. Electronic effect 5
    1.2.3. Bifunctional effect 7
  1.3. Bimetallic PdAu catalysis 8
  1.4. Oxidation states and activity 12
  1.5. Summary of Pd-on-Au NPs catalysis 15
  1.6. Motivation and research overview 17
  1.7. References 21

Chapter 2 Degrading Perchloroethene at Ambient Conditions Using Pd and Pd-on-Au Reduction Catalysts 30
  2.1. Introduction 30
  2.2. Materials and methods 33
    2.2.1. Synthesis 33
    2.2.2. Characterization 33
    2.2.3. Reaction testing 33
    2.2.4. Reaction data analysis 34
  2.3. Results and discussions 36
    2.3.1. Confirmation of NP sizes 36
2.3.2. Assessing mass transfer effect on rate constants
2.3.3. Catalytic activity
2.3.4. Selectivity differences
2.3.5. Reaction mechanism
2.4. Conclusions
2.5. Symbols and notations
2.6. Supplementary information
2.7. References

Chapter 3 Volcano-shape Glycerol Oxidation Activity of Palladium-decorated Gold Nanoparticles

3.1. Introduction
3.2. Experimental
3.2.1. Catalyst preparation
3.2.1.1. Monometallic NPs
3.2.1.2. Bimetallic Pd-on-Au NPs
3.2.1.3. Carbon supported NPs
3.2.2. Catalyst characterization
3.2.2.1. Transmission Electron Microscopy (TEM)
3.2.2.2. Nitrogen Physisorption Studies
3.2.2.3. X-ray Absorption Spectroscopy (XAS)
3.2.3. Catalytic testing
3.3. Results and discussions
3.3.1. Catalyst structure
3.3.2. Mass transfer resistances analysis
3.3.3. Glycerol oxidation activity of carbon-supported Au NPs and Pd NPs
3.3.4. Glycerol oxidation activity of carbon-supported Pd-on-Au NPs
3.3.5. Glycerol oxidation selectivity
3.3.6. Activation energy and deactivation analysis
3.3.7. Assessment of reaction environment on metal oxidation state through XANES characterization
Chapter 4 EXAFS Characterization of Palladium-on-Gold Catalysts Before and After Glycerol Oxidation

4.1. Introduction

4.2. Experimental
   4.2.1. Materials and Chemicals
   4.2.2. Catalyst Preparation
   4.2.3. Transmission Electron Microscopy (TEM)
   4.2.4. Reaction data analysis
   4.2.5. X-ray Absorption Spectroscopy (XAS)

4.3. Results and Discussion
   4.3.1. 4-nm Au/C catalysts
   4.3.2. 4-nm Pd-on-Au/C (60 sc% and 150 sc%) catalysts
   4.3.3. 4-nm Pd/C catalysts
   4.3.4. Effect of exposure to the reaction solution ("0-hr Rxn" samples)
   4.3.5. Effect of glycerol reaction on NPs ("3-hr reaction")
   4.3.6. Correlation to catalytic activity

4.4. Conclusions

4.5. Supplementary Information

4.6. References

Chapter 5 Room Temperature Formic Acid Decomposition for Hydrogen Generation using Carbon Supported Palladium-on-Gold Nanoparticles

5.1. Introduction

5.2. Experimental
   5.2.1. Materials and Chemicals
   5.2.2. Catalyst Preparation
      5.2.2.1. Au, Pd, and Pd-on-Au NPs sol Preparation
5.2.2.2. C supported Au, Pd and Pd-on-Au NPs Preparation 155
5.2.3. Catalyst Characterization 156
  5.2.3.1. *Ex situ* X-ray Absorption Spectroscopy (XAS) 156
  5.2.3.2. *In situ* X-ray Absorption Spectroscopy (XAS) 157
5.2.4 Catalytic Testing 157
5.2.5 Reaction rate constants 158
  5.2.5.1. Reaction rate constants 158
  5.2.5.2. Metal Dispersion 159
5.3. Results and Discussion 160
  5.3.1. Mass Transfer Analysis 160
  5.3.2. Activity Analysis 162
  5.3.3. CO concentration 164
  5.3.4. Effect of pH 165
  5.3.5. *Ex situ* XAFS structures of as-synthesized catalysts 167
  5.3.6. *In situ* XAS characterization during reaction 170
  5.3.7. Correlation with kinetics results 173
5.4. Conclusions 175
5.5. Supplementary Information 176
5.6. References 177

**Chapter 6 Recommendations for Future Work** 180
6.1. Recommendations for future work 180
  6.1.1. Modulating the catalysis for glycerol oxidation using bimetallic M-on-gold catalysts (M=Pt, Cu, Fe, Ni, Co, Zn) 180
  6.1.2. Synthesizing ultra-small Pd-Au nano-clusters 182
  6.1.3 Low temperature methane direct oxidation to methanol using ultra small Pd-Au nano-clusters 184
6.2. References 186
List of Figures

Figure 1.1. Scheme of four possible mixing patterns: core–shell (a), subcluster segregated (b), homogeneous (c), multi-shell (d). The pictures show cross sections of the clusters. 3

Figure 1.2. Routes for bimetallic nanocatalysts synthesis with controlled shapes: continuous growth, crystallites coalescence, seeded growth and galvanic replacement reaction. 4

Figure 1.3. Scheme of two different binding modes of formate species on metal surface: (a) bridging mode, (b) linear mode. 5

Figure 1.4. STEM-HAADF image of carbon supported Au–Pd NPs catalyst prepared by sol-immobilization. 9

Figure 1.5. Dependence of glycerol oxidation TOF and selectivity to glyceric acid on Pd/Au atomic ratio. 10

Figure 1.6. Concentration profile for Au/C catalyzed glycerol oxidation and liquid chromatography mass spectrum in electronegative ion mode (LC-MS) of glyceric acid formed during glycerol oxidation over Au/C. 12

Figure 1.7. In situ EXAFS spectra (a) and their Fourier transformed data (b) of 5 wt% Pd/Al2O3 under various reaction conditions. 13

Figure 1.8. TOF of Pd/Al2O3 Catalysts for selective aerobic oxidation of crotyl alcohol as a function of Pd cluster size and the total percentage of oxidized Pd. 14

Figure 1.9. (a) the “volcano-shaped” dependence of reaction rate constant of HDC of TCE on Pd surface coverage; (b) model structure of Pd-on-Au NPs. 16

Figure 2.1. TEM images and corresponding particle size histograms of (a) Au NPs, (b) 80 sc% Pd-on-Au NPs, and (c) Pd NPs. Each bar represents the total number of NPs of a particle diameter ±0.25 nm. 36

Figure 2.2. PCE conversion profiles for Pd-on-Au NPs with (a) 0-80 sc%, (b) 80-300 sc%, and for (c) Pd NPs and Pd/Al2O3 catalysts. (d) PCE HDC kcat (blue) and kcat' (red) values plotted (with error bars of ±1 standard deviation) against surface coverage for Pd-on-Au NPs. Reaction 39
conditions: \( C_{\text{Pd}} = 3.94 \times 10^{-5}, \ 1.84 \times 10^{-4}, \text{and} \ 1.45 \times 10^{-3} \) g Pd/L for Pd-on-Au NPs, Pd NPs, and Pd/Al\(_2\)O\(_3\), respectively. 23 °C, atmospheric pressure, H\(_2\) headspace, pH = 7.0, citrate buffer, \( C_{\text{PCE,0}} = 16.6 \) ppm = 0.1 mM.

Figure 2.3. Reaction profiles of PCE HDC using (a) 60 sc% Pd-on-Au NPs, (c) Pd NPs, and (e) Pd/Al\(_2\)O\(_3\). The concentration-time profiles of reaction products during PCE HDC using (b) 60 sc% Pd-on-Au NPs, (d) Pd NPs, and (f) Pd/Al\(_2\)O\(_3\). Solid lines are best-fit curves (\( R^2 > 0.96 \)) using a modified Langmuir-Hinshelwood kinetic model (Eqn. 1-4, 8), and the dashed blue lines are the measured carbon balances. Reaction conditions: \( C_{\text{Pd}} = 3.94 \times 10^{-5}, \ 1.84 \times 10^{-4}, \text{and} \ 1.45 \times 10^{-3} \) g Pd/L for 60 sc% Pd-on-Au NPs, Pd NPs, and Pd/Al\(_2\)O\(_3\), respectively, 23 °C, 1 atm, H\(_2\) headspace, pH = 7.0, citrate buffer, \( C_{\text{PCE,0}} = 16.6 \) ppm = 0.1 mM. The 60 sc% sample was chosen over the 80 sc% one due to experimental limitations (the reaction was too rapid for the GC measurements to yield smooth concentration-time profiles).

Figure 2.4. (a) Relative amounts of DCE isomers (1,1-DCE, cis-1,2-DCE, and trans-1,2-DCE) at 40% PCE conversion, for Pd-on-Au NPs of various Pd surface coverages (dashed lines mark the selectivity values averaged over the 10-150 sc% range. (b) Comparison of DCE isomer distributions for Pd-on-Au NPs (averaged over the 10-150 sc% range), Pd NPs, and Pd/Al\(_2\)O\(_3\) at 40% PCE conversion.

Figure S2.1. The linear relationships between (a) observed reaction rate constant \( k_{\text{meas}} \) and Pd reactor content, and (b) \( 1/k_{\text{meas}} \) and \( 1/C_{\text{Pd}} \). The red circles mark the default Pd content for the PCE HDC batch reaction studies. The line in panel (a) was fitted with Pd reactor content from 0 to 3.94 \times 10^{-5} \) g Pd/L. Reaction conditions: 60 sc% Pd-on-Au NPs, 23 °C, atmospheric pressure, 800 rpm stir rate, H\(_2\) headspace, pH = 7.0, citrate buffer, \( C_{\text{PCE,0}} = 16.6 \) ppm = 0.1 mM.

Figure 3.1. TEM images of (a) Au NPs, (b) 60 sc% Pd-on-Au NPs, (c) 150 sc% Pd-on-Au NPs, and (d) Pd NPs, and their immobilized forms as (e) Au/C, (f) 60 sc% Pd-on-Au/C, (g) 150 sc% Pd-on-Au/C, and (h) Pd/C.

Figure 3.2. The relationships between (a) observed reaction rate constant \( k_{\text{meas}} \) and catalyst mass concentration, (b) \( 1/k_{\text{meas}} \) and \( 1/(\text{mass of catalyst}) \) at 350, 700, and 1000 rpm stirring rates. The red circles mark the default catalyst charge and stirring rate for the glycerol oxidation reaction. The line in panel (a) was fitted with catalyst mass concentration from 0 to 1.87 \) g/L; the red and black lines in panel (b) were fitted with data points only within linearity (solid points). Reaction conditions: 60 sc% Pd-on-Au/C, 60 °C, 107 mL, 0.1 M glycerol, 0.4 M NaOH, and 120
mL/min O₂.

Figure 3.3. Glycerol oxidation using (a,b) Au/C and (c,d) Pd/C catalysts: (a,c) glycerol concentration and carbon balance, and (b,d) reaction products. Reaction conditions: 0.2 g Au/C or Pd/C, 60 °C, 1000 rpm stirring rate, 107 mL reaction volume, 0.1 M glycerol, 0.4 M NaOH, and 120 mL/min O₂ flow.

Figure 3.4. Reaction profile of glycerol oxidation reaction using 60 sc% Pd-on-Au/C catalyst (a) glycerol and carbon balance, and (b) reaction products. Reaction conditions: 0.2 g 60 sc% Pd-on-Au/C, 60 °C, 1000 rpm stirring rate, 107 mL, 0.1 M glycerol, 0.4 M NaOH, and 120 mL/min O₂ flow.

Figure 3.5. Plots of (a) $k_{cat}$ (b) initial TOF, (c) apparent activation energy, and (d) deactivation constant values with Pd surface coverage. Reaction conditions for (a), (b), and (d): 0.2 g catalyst, 60 °C, 1000 rpm stirring rate, 107 mL, 0.1 M glycerol, 0.4 M NaOH, and 120 mL/min O₂ flow. Reaction temperature range for (c): 40-80 °C.

Figure 3.6. (a) Scheme of glycerol oxidation reaction and its products; Plots of (b) glyceric acid selectivity vs. glycerol conversion and (c,d) selectivity values extrapolated to zero conversion ("initial selectivity") for Au/C, Pd/C, and Pd-on-Au/C catalysts. Reaction conditions: 0.2 g catalyst, 60 °C, 1000 rpm stirring rate, 107 mL, 0.1 M glycerol, 0.4 M NaOH, and 120 mL/min O₂ flow.

Figure 3.7. XANES spectra at the Au L₃ edge for (a) Au/C and Pd-on-Au/C with (b) 60 sc% and (c) 150 sc%; and at the Pd K edge for (d) Pd/C and Pd-on-Au/C with (e) 60 sc% and (f) 150 sc%.

Figure S3.1. Plot of ln(1-x) vs. time for 60 sc% Pd-on-Au/C catalyst. Reaction conditions: 0.2 g 60 sc% Pd-on-Au/C, 60 °C, 1000 rpm, 107 mL, 0.1 M glycerol, 0.4 M NaOH, and 120 mL/min O₂ flow.

Figure S3.2. Glycerol conversion-time profiles for glycerol oxidation reaction with O₂ flowing at 120 mL/min, 300 mL/min, and without O₂ flow (1 atm 150 mL headspace O₂ only). Reaction conditions: 0.2 g 60 sc% Pd-on-Au/C, 60 °C, 1000 rpm, 107 mL, 0.1 M glycerol, and 0.4 M NaOH.

Figure S3.3. pH of reaction medium-time profile for glycerol oxidation reaction. Reaction conditions: 0.2 g 60 sc% Pd-on-Au/C, 60 °C, 1000 rpm, 107 mL, 0.1 M glycerol, 0.4 M NaOH, and 120 mL/min O₂ flow.

Figure S3.4. Plot of ln(1-x) vs. time for (a) Au/C, Pd/C, and 10 sc% to 80 sc% Pd-on-Au/C catalysts, (b) 80 sc% to 300 sc% Pd-on-Au/C catalysts. Solid
lines are the fitted values to the first 2 hr of reaction profiles using 1st order kinetics for each catalyst.

**Figure S3.5.** (a) Conversion-time profiles and (b) selectivity distributions at 30% glycerol conversion for Au/C, Pd/C and 60 sc% Pd-on-Au/C catalysts. Reaction conditions: 0.2 g catalyst, 60 ºC, 1000 rpm, 107 mL, 0.1 M glycerol, 0.4 M NaOH, and 120 mL/min O$_2$ flow.

**Figure S3.6.** Plot of selectivity to (a) tartronic acid or (b) lactic acid vs. conversion of glycerol for Au/C, Pd/C, and Pd-on-Au/C catalysts. Reaction conditions: 0.2 g catalyst, 60 ºC, 1000 rpm stirring rate, 107 mL, 0.1 M glycerol, 0.4 M NaOH, and 120 mL/min O$_2$ flow.

**Figure S3.7.** Plot of natural logarithm of pre-exponential factor ln(A) against apparent activation energy $E_a$.

**Figure 4.1.** TEM images of Au/C sample (a) as synthesized, (b) 0 hr Rxn, (c) 3 hr Rxn.

**Figure 4.2.** TEM images of 60 sc% Pd-on-Au/C sample (a) as synthesized, (b) 0 hr Rxn, (c) 3 hr Rxn.

**Figure 4.3.** (a) XAS-measured CNs for Pd-on-Au NPs with 60 sc% and calculated CNs for alloyed 4 nm PdAu NPs (in parenthesis) with the same metal content (21.4 mol% Pd), total Au CN (11.4), and total Pd CN (10.6); (b) XAS-measured CNs for Pd-on-Au NPs with 150 sc% and calculated CNs for alloyed 4 nm PdAu NPs (in parenthesis) with the same metal content (42.5 mol% Pd), total Au CN (10.9), and total Pd CN (9.7). Experimental CNs were those of NPs after hydrogen reduction at 200 ºC.

**Figure 4.4.** TEM images of Pd/C sample (a) as synthesized, (b) 0 h rxn, (c) 3 h rxn.

**Figure 4.5.** Coordination numbers of (a) Au-Au, (b) Au-Pd, (c) Pd-Pd, (d) Pd-Au and (e) Pd-O scatters (Pd-C(O) scatter for Pd/C) from EXAFS and (f) percentage of Pd-O from XANE for untreated samples of Au/C, 60 sc% and 150 sc% Pd-on-Au/C, and Pd/C catalysts as-synthesized, before (0 hr Rxn) and after glycerol oxidation reaction (3 hr Rxn). "N/A" = no detection of scattering signal or no available number.

**Figure S4.1.** Coordination numbers for (a) Au-Au, (b) Au-Pd, (c) Pd-Pd, and (d) Pd-Au absorbing-scattering pairs for the reduced samples of 4 nm Au/C, 60 sc% and 150 sc% Pd-on-Au/C catalysts before and after reaction. "N/A" = no detection of scattering signal or no available number.
Figure 5.1. The relationships between (a) observed reaction rate constant $k_{\text{meas}}$ and Pd metal concentration, (b) $1/k_{\text{meas}}$ and $1/(\text{Pd metal concentration})$ at 1200 rpm stirring rate. The red circles mark the default catalyst charge for the formic acid decomposition reaction. Reaction conditions: 0.5 g catalyst, 23 °C, 1200 rpm stirring rate, 10 mL, 1 M formic acid.

Figure 5.2. Volume of gas released profile for Au/C, Pd/C, and 30, 60, 150 and 300 sc% Pd-on-Au/C catalysts. Reaction conditions: 0.5 g catalyst, 23 °C, 1200 rpm stirring rate, 10 mL, 1 M formic acid.

Figure 5.3. CO concentration profiles for Au/C, Pd/C, and 30, 60, 150 and 300 sc% Pd-on-Au/C catalysts. Reaction conditions: 0.5 g catalyst, 23 °C, 1200 rpm stirring rate, 10 mL, 1 M formic acid.

Figure 5.4. Formic acid decomposition TOF and pH as a function of HCOOH/(HCOOH + HCOONa) ratio. Reaction conditions: 0.2 g catalyst, 23 °C, 1200 rpm stirring rate, 10 mL, 7.1 M total formate species (HCOOH + HCOONa).

Figure 5.5. XAS spectra at the Pd K edge and the percentage of oxidized Pd for (a, b) 60 sc% Pd-on-Au/C, (c, d) 150 sc% Pd-on-Au/C, (e, f) 300 sc% Pd-on-Au/C and (g, h) Pd/C at 0, 5 and 30 min reaction times.

Figure S5.1. Chromatography of a typical GC-TCD run. Detection of O2 and N2 was due to the mixture of air during injection.
List of Tables

Table 1.1. Example of bimetallic catalysts for various reactions. 2

Table 2.1. Selected fitted kinetic parameters using modified Langmuir-Hinshelwood kinetics model. 50

Table S2.1. Detailed rate constants of different catalysts. 56

Table S2.2. Calculated metals cost of Pd-on-Au NPs and Pd NPs. 58

Table S2.3. Fitted kinetics parameters using modified Langmuir-Hinshelwood kinetics model. 64

Table 3.1. Initial glycerol/metal mole ratios and catalytic activity results for carbon-immobilized Au, Pd, and Pd-on-Au NPs. Reaction condition: 0.2 g catalyst, 60 °C, 1000 rpm stirring rate, 107 mL, 0.1 M glycerol, 0.4 M NaOH, and 120 mL/min O₂ flow. Each reaction rate constant was the average of three runs. 94

Table S3.1. Comparison of preparation method, metal loading, NP size, TOF, and selectivity to glyceric acid for various catalysts in literature. 113

Table S3.2. Selectivity (normalized to all detected products) and carbon balance (sum of all carbons of detected C₁, C₂ and C₃ compounds divided by initial carbon content of glycerol) for Au/C, Pd/C and Pd-on-Au/C catalysts at 30% glycerol conversion. 116

Table S3.3. List of apparent activation energies (Eₐ), and natural log of pre-exponential factors (ln(A)) for Au/C, Pd/C, and 30 sc%, 60 sc%, 150 sc%, and 300 sc% Pd-on-Au/C catalysts. 118

Table 4.1. EXAFS fit parameters for 4 nm Au/C samples on Au edge. 131

Table 4.2. EXAFS fit parameters for 60 sc% 4 nm Pd-on-Au/C samples on Au and Pd edges. 133
### Table 4.3
EXAFS fit parameters for 150 sc% 4 nm Pd-on-Au/C samples on Au and Pd edges.

### Table 4.4
EXAFS fit parameters for 4 nm Pd/C samples on Pd edge.

### Table 4.5
Glycerol oxidation reaction TOF values for Au/C, Pd/C, and 60 sc% and 150 sc% Pd-on-Au/C. Reaction condition: 0.2 g catalyst, 60 °C, 1000 rpm stirring rate, 107 mL, 0.1 M glycerol, 0.4 M NaOH, and 120 mL/min O₂ flow.

### Table S4.1
Composition of reducing mixture to synthesize 4 nm sized Au NPs.

### Table S4.2
Volumes of PdCl₄²⁻ used to synthesize Pd-on-Au NPs with various Pd surface coverages.

### Table S4.3
Calculated Au and Pd metal contents of Pd-on-Au/C catalysts.

### Table S4.4
Volumes of Au and Pd-on-Au NP sol used to synthesize 1 g of Pd-on-Au/C samples for XAS analysis and their calculated Au and Pd metal contents.

### Table 5.1
Catalytic activity results for carbon-immobilized Au, Pd, and Pd-on-Au NPs. Reaction conditions: 0.5 g catalyst, 23 °C, 1200 rpm stirring rate, 10 mL, 1 M formic acid. Each reaction rate constant was the average of three runs.

### Table 5.2
EXAFS fit parameters for Au/C samples on Au edge. Reaction conditions: 0.2 g catalyst, 23 °C, 0.5 mL, 0.5 M formic acid.

### Table 5.3
EXAFS fit parameters for 60 sc% Pd-on-Au/C samples on Au and Pd edges. Reaction conditions: 0.2 g catalyst, 23 °C, 0.5 mL, 0.5 M formic acid.

### Table 5.4
EXAFS fit parameters for 150 sc% Pd-on-Au/C samples on Au and Pd edges. Reaction conditions: 0.2 g catalyst, 23 °C, 0.5 mL, 0.5 M formic acid.

### Table 5.5
EXAFS fit parameters for 300 sc% Pd-on-Au/C samples on Au and Pd edges. Reaction conditions: 0.2 g catalyst, 23 °C, 0.5 mL, 0.5 M formic acid.

### Table 5.6
EXAFS fit parameters for Pd/C samples on Pd edge. Reaction conditions: 0.2 g catalyst, 23 °C, 0.5 mL, 0.5 M formic acid.
Table 5.7. OPR values of various reaction conditions.

Table S5.1 Comparison among different catalyst materials.
List of Schemes

Scheme 2.1. Proposed reaction pathway of heterogeneously catalyzed PCE HDC, which includes gas-to-liquid transfer as an elementary step. "S" represents catalytic active sites. "k" under the arrows represents corresponding surface reaction rate constant. 48

Scheme S2.1. Derivation of the differential equations describing PCE HDC. 59

Scheme S3.1. Proposed surface reaction of scission of glycerolate and scission of tartronate, and relation to detected species (major products in bold) using Au, Pd, and Pd-on-Au catalysts. Species in dashed boxes and surface intermediates (labeled "ad") were not detected and were inferred to be formed. The blue-colored subscript represents the surface activated species, and the red arrow shows the rate-limiting step of C-H bond cleavage at the beta carbon position to the secondary alcohol group. Reaction products are shown in their acid forms. 117

Scheme 5.1. Set-up for homemade batch reactor by measuring the gas releasing rate from formic acid. 158

Scheme 6.2. Illustration of synthesizing bimetallic M-on-gold catalysts (M = Pt, Cu, Fe, Ni, Co, Zn) 182

Scheme 6.3. Illustration of synthesizing ultra-small Pd-Au nanoclusters. 184

Illustration of direct methane oxidation to methanol. 185
Chapter 1

Background and Research Overview

1.1. Introduction to bimetallic catalysts

1.1.1. History

Bimetallic catalysts are a type of catalytic materials that are comprised of two metal components as active phase. They are often preferred over their monometallic counterparts because of their enhanced activity, selectivity and stability, which are thought to be due to the synergistic effects between the two metals. In the 1960s, Exxon Research and Engineering Company performed considerable research on bimetallic catalysts for hydrocarbon reforming with the contribution of Sinfelt et al. [1-5]. At that time, the major bimetallic systems of interest include Pt-Ru, Ru-Cu, Ni-Cu, Os-Cu, and Pt-Ir [5, 6]. This work led to further research into using bimetallic catalysts for other reactions. Table 1.1 lists examples of bimetallic catalysts studied for selective hydrogenation of unsaturated aldehydes, hydrodehalogenation, hydrodeoxygenation, CO oxidation, synthesis of H$_2$O$_2$, aqueous-phase reforming for H$_2$ production, and alcohol and polyol oxidation [7]. It is noteworthy that for a certain type of reaction many active combinations can
have for the choice of metals, not to mention their variations in particles sizes, morphologies, nano-structures, surface properties and support materials.

**Table 1.1. Example of bimetallic catalysts for various reactions.**

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Bimetal components</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selective hydrogenation of unsaturated aldehydes</td>
<td>Rh-Sn, Pt-Sn, Pd-Sn, Pt-Zn, Pt-Co, Ni-Pt, Pt-W, Ru-Fe, Rh-Cu, Au-In, Pd-Cu, etc.</td>
<td>[8-18]</td>
</tr>
<tr>
<td>Hydrodehalogenation</td>
<td>Pd-Au, Bi-Pd, Pd-Ni, etc.</td>
<td>[19-25]</td>
</tr>
<tr>
<td>Hydrodeoxygenation</td>
<td>Pd–Ni, Pd–Co, Pd–Fe, Ru–Ni, Ru–Co, Ru–Fe, Pt–Ni, Pt–Co, Pt–Fe, etc.</td>
<td>[26-28]</td>
</tr>
<tr>
<td>CO oxidation</td>
<td>M-Pt (M = Ru, Rh, Ir, Pd or Au), etc.</td>
<td>[29, 30]</td>
</tr>
<tr>
<td>Synthesis of H₂O₂</td>
<td>Au-Pd, Au-Pt, etc.</td>
<td>[31-33]</td>
</tr>
<tr>
<td>Aqueous-phase reforming for H₂ production</td>
<td>Pt-Pd, Ru-Rh, Sn-Ni, Pt-Ru, etc.</td>
<td>[34-36]</td>
</tr>
<tr>
<td>Alcohol and polyol oxidation</td>
<td>Au-Pd, Au-Pt, Bi-Pt, Cu-Pt, etc.</td>
<td>[37-41]</td>
</tr>
</tbody>
</table>

1.1.2. Bimetallic structures

Besides particle size, size distribution, and morphology which are the key factors in monometallic catalysis, metal distribution (*i.e.* extent of alloying) is another important factor for bimetallic systems. Possible structures for bimetallic systems (Fig. 2.1) include: core-shell, sub-cluster segregated alloy, homogeneous alloy, and multi-shell. In nature, several factors have been found to affect the metal distribution: relative metal bond strength, surface energy, atomic size, the presence of stabilizing ligands, and electronic/magnetic effects [42]. Those factors can result from different metal types, synthesis methods, and exposure to reaction conditions, etc. However, not all of those mixing patterns are commonly seen due to the above mentioned effects.
for a certain combination of metals. For example, most widely reported structures for PdAu systems are core-shell, inverse core-shell, surface alloy, bulk alloy [21, 43, 44].

![Diagram of mixing patterns](image)

**Figure 1.1** Scheme of four possible mixing patterns: core–shell (a), subcluster segregated (b), homogeneous (c), multi-shell (d). The pictures show cross sections of the clusters. Adapted from [42].

1.1.3. Synthesis

Bimetallic catalysts can be synthesized as the following categorized methods: chemical reduction [45], thermal decomposition [46], electrochemical synthesis, radiolysis [47], and sonochemical synthesis [48]. Among them, chemical reduction is the most widely used method, which can be further subdivided into co-reduction, and sequential reduction of metal precursor salts [7]. Using colloidal chemistry, Xia and co-workers reported the successful synthesis of Pt-Pd bimetallic catalysts with well-controlled structures (alloys, dendrites, core–shells, multi-shells, and supported monolayers) through co-chemical reduction, galvanic replacement, and seed-mediated growth [49]; a summary of such methods is shown in Fig. 2.2 [50]. A good summary and
comparison for the conventional routes for synthesizing bimetallic catalysts is given by Wang and co-workers, which discuss methods such as chemical vapor deposition, incipient wetness impregnation, co-precipitation, deposition–precipitation, liquid-phase synthesis, and aerosol-derived approaches [51].

**Figure 1.2** Routes for bimetallic nanocatalysts synthesis with controlled shapes: continuous growth, crystallites coalescence, seeded growth and galvanic replacement reaction. Adapted from [50].

**1.2. Synergistic effects**

1.2.1. Geometric effect

Electronic, bifunctional and geometric effects have been proposed to explain the widely observed bimetallic enhancement [42, 52-55]. The geometric effect is when atomic ensembles or mixed metal sites are the active phases or where the adsorption process requires an ensemble of more than one atom. In the case of PdAu system, the active sites can be Pd ensembles, Au ensembles or PdAu mixed sites. The geometry of typical bimetallic system can be bulk alloy, surface alloy and core-shell structures, and is determined by the nature of the metals, synthesis methods, and relative metal composition [21]. Tedsree and co-workers concluded a strong dependence of formic acid decomposition on the surface structure of the metal particle [56-58].
In their structure model (Fig. 2.3), formate binds preferentially in a bridging (bidentate) mode onto the large terrace or ensemble sites, which leads to the scission of C-H bond and further to the continuous generation of hydrogen through dehydrogenation route. On surface unsaturated sites (adatoms, corners, steps, kinks), formate binds in linear or multi-linear mode, resulting in formation of CO and poisoning of metal surface [56]. The distribution of two modes is largely controlled by the surface geometry and particle size [59], giving rise to different catalytic activities and selectivities. Another example of geometric effect is the hydrodechlorination of trichloroethene (TCE) over Pd decorated Au NPs. Wong and co-workers experimentally showed that small 2-dimentional (2-D) Pd ensembles are more active than 1-D and 3-D Pd ensembles by controlling Pd surface coverage on Au NPs [19, 21, 60]. DFT calculations revealed that Pd₄/Au structure (representing 2-D Pd) has the lowest TCE adsorption energy than Pd₁/Au (representing 1-D Pd) and Pd₄layer/Au (representing 3-D Pd), and that the best adsorption configuration for the chloroethenes is to bind with a di-σ mode on adjacent Pd atoms [61].

![Figure 1.3](image)

**Figure 1.3** Scheme of two different binding modes of formate species on metal surface: (a) bridging mode, (b) linear mode. Figure adapted from [56].

1.2.2. Electronic effect

The electronic effect is due to the transfer of electron density amongst the two metal components due to metal-metal bonding [62]. Many reaction systems involving bimetallic
catalysts/electrodes have seen a promotional effect due to the electronic effect, such as benzyl alcohol oxidation [37], electrochemical oxidation of formic acid [63] and cyclization of acetylene to benzene [64]. DFT (density functional theory) calculations also substantiate the existence of the electronic effect [65, 66]. The electronic effect often results in change in activation energy (usually lowered) or adsorption energy (strengthened or weakened). For example, activation energies have been analyzed for PdAu bimetallic systems in many reactions, such as formic acid decomposition [67], acetylene hydrogenation [68], thiophene hydrodesulfurization [69], CCl\(_2\)F\(_2\) hydrodechlorination [70], and methane oxidation [71]. In all these cases, the addition of Pd significantly lowered activation energies compared with monometallic Au. As to adsorption energy, Niemantsverdriet and co-workers have found that the presence of Au on clean Ru(001) surface shifted the desorption temperature of a fraction of the adsorbed S by ~90 K with a 28% sub-monolayer Au surface coverage, and that the adsorption energy of S on Au decreased by ~6 kcal/mol [62, 72]. For formic acid decomposition, Tedsree and co-workers concluded that their most active bimetallic catalyst Ag@Pd NPs had the largest work function difference (Fermi levels difference) between two metals over other metals (Rh, Ru, Au, and Pt) as core which leads to the favorable adsorption of formate species in a bridge mode on Pd, allowing for the desired dehydrogenation pathway to continuously occur [56].

Two origins of the electronic effect have been proposed: one ascribes to the lateral strain that the substrate metal has on the surface metal (strain effect), altering (broadening/lowering or narrowing/increasing) the \(d\)-band energy of the primary metal on the surface; the other ascribes to the direct heterometallic bonding interactions (ligand effect) between the two metals which alter the electronic states/structures of the surface metal [56, 73]. These two origins are difficult to decouple as they usually occur simultaneously [56]. It is interesting to note that Strasser and
coworkers designed a series of PtCu bimetallic catalysts and clarified a reactivity–strain relationship for oxygen reduction reaction (ORR) [74]. They concluded that the compressive strain from the Pt shell resulted in a shift of the $d$-band structure of Pt, thus weakening the chemisorption of oxygenated species [74].

1.2.3. Bifunctional effect

The bifunctional effect is where two metals catalyze/promote different reaction steps. Monnier and coworkers studied surface coverage effect of Au on Pd for liquid phase glycerol oxidation reaction. They concluded bifunctional effect is responsible for increased activity where in bimetallic Au-Pd sites, Au can stabilize absorbed glycerolate species and Pd can help with the rate limiting step of dehydrogenation of β-C-H bond to form glyceraldehyde [75]. The bifunctional effect is also thought to be present in CO oxidation over various bimetallic catalysts [76] such as PtRu [73], AuAg [77, 78], and AuCu [79]. For the PtRu catalyst, dissociated and adsorbed oxygen species have lower potentials and is more abundant on Ru, which causes them to have greater reactivity to CO adsorbed on Pt atoms [73]. For a bimetallic AuAg catalyst, DFT calculations showed O$_2$ dissociation in the vicinity of Ag surface atoms has a significantly lower energy barrier, thus contributing to the enhanced CO oxidation rate [76, 80].

For most reaction systems, the geometric effect and/or the electronic effect are thought to be frequently cited as the primary mechanisms of catalytic enhancement of bimetallic catalysts as compared to their monometallic counterparts [81]. Although the ensemble effect is suggested to be more dominant over electronic effect by some researchers [44, 82, 83], it is generally challenging to decouple both effects if they are both present [6]. This is because when the
surface composition of the catalyst is changed, both the electronic structure of the individual surface atoms and the distribution of ensembles will be affected [44].

1.3. Bimetallic PdAu catalysis

Gold, the most noble of all metals, is of interest both fundamentally, for example, CO oxidation by ultra-small Au clusters, and for practical applications, for example room temperature conversion of biomass to fine chemicals and destruction of environmental pollutants. Incorporating Au with another metal, such as Pt, Pd or Bi, often enhances the added metal's activity, selectivity and stability. Palladium-gold (PdAu) catalysts in particular have been extensively studied due to their widely known synergistic effect. The research of PdAu catalysis has been investigated in many fields, such as selective oxidation reactions (alcohol, hydrocarbon, formic acid, etc.) [37, 84-90], environmental pollution control (CO oxidation, hydrodechlorination of chlorinated compounds, and reduction of NO$_2^-$) [22, 60, 91-94], direct synthesis of H$_2$O$_2$ [95-97], and fuel cells [98-100]. In industry, PdAu catalysts have been widely used to produce vinyl acetate monomer (VAM) in fixed bed processes [101, 102].

The oxidation properties of PdAu bimetallic catalysts have been extensively examined in various oxidation reactions, such as alcohol oxidation (e.g. methanol, ethanol, and glycerol), hydrocarbon oxidation (e.g. methane, and decane), CO oxidation, and formic acid oxidation [37, 84-92].

In particular, PdAu catalysts have been extensively studied for glycerol oxidation to fine chemicals. Hutchings and co-workers have shown that activated carbon (AC) supported homogeneous Pd-Au alloys (Fig. 2.4) prepared by sol-immobilization method had significantly enhanced activity in glycerol oxidation compared to monometallic Pd and Au catalysts [38].
Characterized through scanning transmission electron microscopy-high angle annular dark field (STEM-HAADF) (Fig. 2.4), the group found significant Au on the surface of the catalyst particles, which they claimed to explain the enhanced activity and selectivity to glyceric acid [38]. Furthermore, by immobilizing their alloyed Pd-Au nanoparticles of different metal compositions on MgO, the group showed that glycerol oxidation can be achieved under base-free and ambient conditions with glyceric acid being the most selective product [103].

Prati and co-workers have also shown significant improvement in the activity of their PdAu bimetallic systems as compared to monometallic ones [39, 87, 104-110]. They have examined the dependence of activity and selectivity on reaction conditions, such as catalyst amount, temperature, pressure, and amount of NaOH used, as well as optimizing catalyst nanoparticle synthesis by looking at the effect of the order of reduction of the metal salts, reducing and stabilizing agent, particle size, and support [39, 87, 104-108, 111]. Co-reduction of Pd and Au was shown to have higher activity and selectivity to glyceric acid than sequential reduction.
methods [105]. By tuning the metal (Pd, Au, and Pd-Au) particles size from 2 to 16 nm, they observed a progressive decrease of activity and a simultaneous increase in the selectivity to glyceric acid [87]. Moreover, through adjusting the amount of Pd deposited on preformed AC supported Au seeds, they have shown the tunability of catalytic activity in glycerol oxidation with various Pd/Au atomic ratios (Fig. 2.5) [107, 108]. Fig. 2.5 shows that all synthesized bimetallic catalysts were more active than monometallic Pd and Au ones, and their most active composition (TOF = 4400 h⁻¹) occurred with a Pd/Au atomic ratio of 10/90 and a catalyst support loading of 1 wt% metals. They further stated that Au can improve the deactivation resistance of Pd in the PdAu alloy particles with Pd/Au atomic ratios between 80/20 and 40/60 [107, 108].

![Figure 1.5](image)

**Figure 1.5** Dependence of glycerol oxidation TOF and selectivity to glyceric acid on Pd/Au atomic ratio. Figure adapted from [107, 108].

Davis and co-workers synthesized their PdAu bimetallic catalysts by reducing Au onto AC supported Pd NPs with hydrogen. Their AuPd bimetallic catalysts were, interestingly, less active
but more selective to glyceric acid than monometallic Au. Although no enhancement was observed for Pd on Au in terms of activity, Pd was proposed to highly disperse Au as well as to minimize the undesired formation of H$_2$O$_2$ (thought to be responsible for C-C bond cleavage) [112]. It is noteworthy that Davis and co-workers extensively studied the promotional effect of hydroxyl group and concluded that basic conditions were required to deprotonate glycerol to glycerolate before being selectively oxidized over the Au surface [113]. They further showed that the oxygen atoms originating from hydroxyl group rather than molecular oxygen are incorporated into glycerol during its oxidation by Au and Pt (Fig. 2.6) [114]. Fig. 2.6 shows the concentration profile for Au/C catalyzed glycerol oxidation and the mass of glyceric acid formed with two different sources of O$_2$ and H$_2$O. It is clear to see that $^{18}$O$_2$ + H$_2^{16}$O source mostly leads to the formation of glyceric acid with a mass of 105, while $^{16}$O$_2$ + H$_2^{18}$O source leads to the formation of glyceric acid with a mass of 111, 109 and 107, making conclusive the statement that the oxygen in glyceric acid comes from H$_2$O/OH$^-$. 
1.4. Oxidation states and activity

Despite these recent advances in aqueous phase oxidation of glycerol using bimetallic PdAu catalysts, there is currently no research that describes a systematic study of structural-property relationships of PdAu catalysts for glycerol oxidation with both controlled nanoparticle size and metal distribution. However, for alcohol oxidation reactions in general, many studies have addressed the relation between the oxidation state of the Pd catalyst and observed reactivity.

In liquid phase benzyl alcohol oxidation at 50 °C in cyclohexane, Grunwaldt and co-workers found that Pd/Al₂O₃ catalyst with pre-reduced metallic surface Pd was much more active (>50 times) than Pd/Al₂O₃ catalyst with oxidized surface Pd, which had very low activity [115]. From their *in situ* EXAFS spectra and $k^3$-weighted Fourier transformed data (Fig. 2.7), Pd was in the oxidized form under argon/cyclohexane, and benzyl alcohol/O₂/cyclohexane
conditions, correlating to the observed slow catalytic activity. However, after being treated by H$_2$ in cyclohexane at 50 °C, Pd became mostly metallic and exhibited greatly increased activity in benzyl alcohol oxidation. They concluded that these observations match the oxidative dehydrogenation mechanism, that Pd can get over-oxidized when too much O$_2$ is present, and that surface hydrogen species, CO and other in situ generated compounds are not efficiently removed when too little O$_2$ is present [115-117]. These results are supported by Baiker and co-workers who used in situ attenuated total reflectance infrared spectroscopy for benzyl alcohol oxidation in cyclohexane over Pd catalysts which showed that over-oxidized surface Pd atoms are less active [118, 119]. After testing both metallic and oxidized Pd/Al$_2$O$_3$, Iglesia and co-workers also observed for gas-phase oxidation of methanol (40 °C) that PdO clusters were much less active than metallic Pd clusters and that excessive O$_2$ inhibited the reaction [120].

![Figure 1.7 In situ EXAFS spectra (a) and their Fourier transformed data (b) of 5 wt% Pd/Al$_2$O$_3$ under various reaction conditions. Figure adapted from [115].](image)

While metallic Pd has been widely reported to be the active site for many reactions, oxidized Pd, in contrast, has been shown to be more active in several cases. For example, Kaneda
and co-workers tested ~4-nm Pd NPs for cinnamyl alcohol oxidation to cinnamaldehyde (60°C, 1 bar O$_2$ in acetic acid) and concluded that Pd surface oxides were the active sites as opposed to metallic Pd [121]. Lee and co-workers had similar findings for crotyl and cinnamyl alcohol oxidation catalyzed by both Pd/mesoporous-Al$_2$O$_3$ and Pd/amorphous-Al$_2$O$_3$ that oxidized Pd was the active phase. Characterized by operando and ex situ XAS, the group observed that the TOF increases proportionally to the extent of surface Pd oxide (Fig. 2.8) [122-125]. One possible explanation for this phenomenon is that the desorption of chemisorbed aldehydes is favored and promoted over an oxidized surface Pd layer. This is essential for maintaining high catalytic activity during oxidation because the decarbonylation products of those aldehydes (CO and alkylidyne fragments) will irreversibly bind to the metal surface, resulting in deactivation.

**Figure 1.8** TOF of Pd/Al2O3 Catalysts for selective aerobic oxidation of crotyl alcohol as a function of Pd cluster size and the total percentage of oxidized Pd. Figure adapted from [112].

The relationship between metal oxidation states and catalytic acidity is still under debate. For one thing, they can be the cause and consequence for each other. For another, metallic and
oxidized surface Pd atoms are both claimed to be the active sites for aerobic alcohol oxidation. Nevertheless, the types of alcohol and reaction conditions (solvent used, temperature, \( \text{O}_2 \) pressure, and pH) are important factors to consider as well as the reaction mechanism.

1.5. Summary of Pd-on-Au NPs catalysis

Pd-on-Au NPs in this thesis were precisely designed as 4 nm Au core with atomic layer thin Pd coatings corresponding to various Pd surface coverages (sc%). Different from many other PdAu bimetallic systems, Pd-on-Au NPs allow the independent control of both particle size and metal distribution. They have been widely investigated in the application of hydrodechlorination (HDC) of trichloroethene (TCE) in our previous studies [20, 60, 126-130]. The colloidal catalyst has extremely high reaction rate constants for TCE HDC (Fig. 1.9a), with the most active composition exhibiting a first-order rate constant (>1900 L g\(^{-1}\) Pd min\(^{-1}\)) that was >10, >70, and >2000 times higher than monometallic Pd NPs, Pd/Al\(_2\)O\(_3\), and Pd black, respectively [127]. Meanwhile, Pd-on-Au NPs have been shown to have much higher deactivation resistance to chloride and sulfur poisons than monometallic Pd catalysts in the aqueous HDC of TCE [20]. The reactivity of Pd-on-Au NPs changes with the Pd surface coverage such that a “volcano-shaped” dependence of activity over Pd surface coverage was observed for HDC of TCE (Fig. 1a) [127, 128]. A more recent study further showed that the activity of the catalysts for the HDC of TCE was also a function of Au core size, with 7 nm Pd-on-Au NPs being the most active catalyst among those with 3, 7, and 10 nm Au core sizes [60].
Figure 1.9 (a) the “volcano-shaped” dependence of reaction rate constant of HDC of TCE on Pd surface coverage (adapted from [19]); (b) model structure of Pd-on-Au NPs.

To correlate the nanostructure and the bimetallic synergistic effect, Pd-on-Au NPs have been well characterized through various techniques, such as TEM, XPS, and XAFS [60, 127, 130]. Via XAFS characterization, Pd-on-Au NPs were confirmed to have a core-shell structure where nearly all Pd atoms were located on the surface of an Au-rich core, and only ~20% of them were oxidized, whereas monometallic Pd NPs had 25–35% of its Pd atoms as surface atoms, and nearly all of them were oxidized (Fig. 1.9b) [130]. Au NPs appear to have a capability to keep Pd atoms in the reduced form, generating a set of highly active sites that are not present in monometallic Pd NPs under ambient-temperature reaction conditions [130]. The formation of Pd ensembles was further proposed to explain the dependence of reactivity of HDC of TCE on Pd surface coverage and Au core size [60, 130]. Confirmed by XAFS, at lower Pd surface coverages (<50 sc%) Pd resides on the Au surface mostly as scattered atoms. Adding more Pd atoms will increase the formation of 2-D Pd-Pd ensembles, which are thought to be the most active species for HDC of TCE. When Pd surface coverage moves towards from ~70 sc% to higher values, Pd will start to form 3-D ensembles where the topmost Pd atoms have a higher
tendency of being oxidized and also block the underlying Pd atoms from reactant molecules, resulting in a drop in activity [60].

The successful application of Pd-on-Au NPs in the HDC of TCE and their tunability through Pd surface coverage and Au core size have led to their further applications in some of our recent works, such as HDC of halogenated compounds (perchloroethene, chloroform, and CF₃Clₓ), reduction of oxygenated compounds (nitrite and nitrophenol), and selective oxidation of glycerol [22, 93, 131].

1.6. Motivation and research overview

While Pd-on-Au NPs have been extensively investigated as model catalysts in reductive reactions (hydrodechlorination and hydrodeoxygenation) in our earlier studies, their catalytic oxidation properties are largely unknown. Those properties include: 1. Pd-on-Au NPs’ activity, selectivity and deactivation in oxidation reactions; 2. structural-activity relationships as a function of Pd surface coverages; 3. effect of reaction conditions upon catalyst’s structure, i.e., oxidation states of Pd and Au, metal distribution and particle size. With the motivation to answer these questions, several major studies have been carried out as outlined below. Briefly, Chapter 2 extends our previous understanding in TCE HDC to perchloroethene (PCE) HDC. It serves as the basis for a kinetics analysis (reaction rate constants calculation, mass transfer analysis and correction) and structure-activity analysis for following studies. Chapter 3 provides a comprehensive study using glycerol oxidation as a model reaction to understand the oxidation properties of Pd-on-Au NPs. Chapter 4 further analyzes the effect of reaction conditions on the catalyst’s structure before and after glycerol oxidation. Chapter 5 discusses the Pd-on-Au catalysis of a self-oxidation-reduction reaction - formic acid decomposition and analysis of Pd oxidation state change using in situ XAFS.
Chapter 2 systematically describes the breakdown chemistry of perchloroethene (PCE) based on the catalytic HDC reaction using pure Pd NPs, commercial Pd/Al₂O₃, and Pd-on-Au NP model catalyst. This reaction occurs at room temperature, 1 atm H₂, and in water, which is attractive for groundwater treatment operations. The most active catalyst (80 sc% Pd-on-Au NPs) was shown to have a pseudo-first order rate constant of 4,971 L/g Pd/min, which was 20× and 80× higher than that for Pd NPs and Pd/Al₂O₃. The catalyst's activity exhibits a volcano shape pattern when plotted against the Pd surface coverage, with the most active catalyst having ~80 sc% coverage. Significantly, it appears the volcano-shape structure-property dependence is generalizable from TCE (previous work) to PCE (this work) and possibly to other compounds. A complete mechanistic model of PCE HDC that coupled gas-liquid and liquid-catalyst mass transfer processes with the surface reactions was further developed, consistent with the observed reaction profiles for the three catalysts types. This work has been published as: Z. Zhao, Y.-L. Fang, P. J.J. Alvarez, M. S. Wong, "Degrading perchloroethene at ambient conditions using Pd and Pd-on-Au reduction catalysts" Appl. Catal. B-Environ., 140-141, 468-477 (2013) [22].

Chapter 3 systematically discusses the catalytic activity, selectivity, and deactivation resistance of glycerol oxidation using model carbon supported Pd-on-Au NPs catalysts through first-order glycerol oxidation kinetics and reaction product analyses. Controlling both the size and metal distribution in bimetallic catalysis of glycerol oxidation has long been deemed as an obstacle. This problem can be solved with Pd-on-Au NPs with the observation that the catalytic activity and selectivity of glycerol oxidation can be fine-tuned by the Pd surface coverage on Au. The most robust Pd-on-Au catalyst was more than 10 times (TOF = ~6000 h⁻¹) active than monometallic Pd and Au without any deactivation. With x-ray absorption fine-structure spectroscopy (XAFS), we were able to demonstrate that under reaction conditions (O₂, pH= 13.5,
60 °C), Pd-on-Au NPs maintained their structures while similar exposure of Pd NPs led to oxidation and particle size increases, enabling a mechanistic discussion of the origin of active sites during glycerol oxidation. This chapter provides new molecular insights into glycerol oxidation and shows that Pd-on-Au can serve as a stable and promising structural model for understanding active sites in glycerol and other alcohol oxidation. This work has been published as: Z. Zhao, J. Arentz, L. A. Pretzer, P. Limpornpipat, J. M. Clomburg, R. Gonzalez, N. M. Schweitzer, T. Wu, J. T. Miller, M. S. Wong, "Volcano-shape glycerol oxidation activity of palladium-decorated gold nanoparticles" Chemical Science, 5, 3715-3728 (2014) [131].

Chapter 4 describes the results from ex situ extended x-ray absorption fine structure spectroscopy (EXAFS) in analyzing the structural change (oxidation state and coordination numbers) of Au, Pd and Pd-on-Au catalysts with two Pd surface coverages (sc%) before and after glycerol oxidation reaction (60 °C, 1000 rpm stirring rate, 107 mL, 0.1 M glycerol, 0.4 M NaOH, and 120 mL/min O2 flow). The core-shell structure of 4 nm 60 sc% and 50 sc% Pd-on-Au/C catalysts was confirmed by Punnett square analysis. EXAFS fitting results indicate that while the metal oxidation states of 4 nm Pd-on-Au/C with 60 sc% and 150 sc% and of Au/C were only slightly affected after glycerol oxidation, Pd/C became more oxidized post-reaction. Moreover, Pd/C had a larger particle size post-reaction while 4 nm Pd-on-Au NPs remained unchanged. These results indicate that Au suppresses Pd oxidation, which improves catalytic activity for glycerol oxidation. This work has been submitted to Topics in Catalysis for review.

Chapter 5 discusses the kinetics and structural-activity relationship of room temperature water phase formic acid (HCOOH, FA) decomposition using model Pd-on-Au catalysts. Formic acid decomposition reaction has been extensively used to understand metal surface chemistry due to its molecule simplicity. Kinetics results have showed that 300 sc% Pd-on-Au/C had a
calculated H₂ generation rate of 137 mL/gPd/min and an initial TOF of 123 h⁻¹, much more active than its monometallic counterparts. Au/C was not active at all at room temperature, and although Pd/C and Pd/Al₂O₃ exhibited small activities, they quickly began to deactivate. *In situ* XAS revealed that Pd-on-Au catalysts had their surface oxidized Pd partially reduced and that their structures maintained during reaction. A geometric mechanism was proposed that 3-D Pd ensembles favor the desired dehydrogenation pathway while 1-D and small 2-D Pd ensembles favor the dehydration pathway, indicating a completely different structural-activity relationship from PCE HDC and glycerol oxidation, both of which favor 2-D Pd ensembles.

Chapter 6 proposes several directions for future work, including: modulating the catalysis for glycerol oxidation using bimetallic M-on-gold catalysts (M=Pt, Cu, Fe, Ni, Co, Zn), synthesizing ultra-small Pd-Au nano-clusters, and studying low temperature methane direct oxidation to methanol using ultra small Pd-Au nano-clusters.

In addition to the above mentioned major works, several co-authored works have been published and listed below. Contribution in XAFS characterization of Pd-on-Au NPs with various Au core sizes and Pd surface coverages leads to the co-authored publication: L. A. Pretzer, H. J. Song, Y.-L. Fang, Z. Zhao, N. Guo, T. Wu, I. Arslan, J. T. Miller, M. S. Wong, "Hydrodechlorination catalysis of Pd-on-Au nanoparticles varies with particle size", *J. Catal.*, **298**, 206-217 (2013)[60].


1.7. References


22. Z. Zhao, Y.-L. Fang, P.J.J. Alvarez, and M.S. Wong, Applied Catalysis B: Environmental, 2013. 140-141: 468-477.


Chapter 2

Degrading Perchloroethene at Ambient Conditions Using Pd and Pd-on-Au Reduction Catalysts

2.1. Introduction

In urban or heavily populated areas, the extensive use of perchloroethene (PCE, "perc", or tetrachloroethene) as the predominant dry cleaning solvent since 1935 has led to its widespread contamination at an estimated 27,000 sites (75% of all dry cleaning facilities) in the U.S., impacting a significant number of private and public water supply wells while threatening many other well areas [1, 2]. PCE is a known central nervous system depressant and is classified by the U.S. Environmental Protection Agency (U.S. EPA) to be a likely human carcinogen [3]. Alternative solvents are being phased in [4, 5], but PCE is still used in 75% of the professional cleaners in the U.S. [6].

PCE, mixed with other chlorocarbons like trichloroethene (TCE) and trichloroethane, is also used as a metal degreaser at electronic manufacturing plants and military facilities (many of which are deemed National Priority List Superfund sites) [7, 8]. It is found in at least 771 of the 1430 Superfund sites above its maximum contaminant level (MCL) of 5 μg/L (= 5 ppb = 30 nM)
in drinking water [9, 10]. PCE was also identified by European Environment Agency (EEA) as one of the most frequently detected volatile organic compounds in groundwater aquifers of most Western European countries [11-13]. In China, PCE pollution has been widely regarded as a serious problem in the delta region of rivers (Yangtze, Pearl, etc.) and in 2005 a northern city in China even reported a PCE concentration of 488 ppb in shallow groundwater, almost two orders of magnitude higher than U.S. EPA MCL [14, 15].

Upon its release into the environment, PCE, having a density greater than that of water (1.62 g/mL), can accumulate into dense non-aqueous phase liquid (DNAPL) pools beneath the water table and slowly dissolve (up to the solubility limit of PCE in water at 20 °C of 150 mg/L = 0.91 mM) to form large plumes that persist over long periods of time. Untreated PCE (ranked as 33rd most toxic, prevalent, and accessible substance at Superfund sites [10]) is a problem because natural biotic degradation can transform it into even more harmful substances such as TCE (ranked 16th) and vinyl chloride (VC, ranked 4th) [2, 10, 16, 17].

Methods of managing PCE contaminated groundwater are similar to those of TCE, which include hydraulic control of the plume (to mitigate migration) using ex situ pump-and-treat technologies of air stripping and activated carbon adsorption [18-20]. These physico-chemical methods are imperfect, though, as they only transfer the contaminants from one phase to another and do not destroy them.

Another approach involves in situ treatment of PCE, in which the contaminant is broken down chemically in the subsurface, such as reactive remediation [21-23], thermal treatment [24], and bioremediation [25, 26]. With reactive remediation, PCE can be degraded through either oxidative or reductive means. Oxidative remediation involves injecting a large quantity of an oxidant such as potassium permanganate [22, 27], into known contaminated areas. Reductive
remediation involves the use of a reductant, with the most widely used material being zero-valent iron (ZVI). In granular or powder form, ZVI is commercially available for remediation applications [28-32] and commonly deployed in permeable reactive barriers (PRBs) [33-36]. A newer development is the use of nanoparticulate zero valent iron (NZVI) to penetrate PCE contamination zones after subsurface injection [37-40].

The use of palladium (Pd) catalysts has been well studied for the reductive remediation of TCE and other chlorinated ethenes in water [41-47]. This technique is advantageous over others as palladium converts the chlorinated ethenes via hydrodechlorination (HDC) to non-toxic ethane with high reaction rates and with minimal formation of chlorinated side products. Our group has shown that palladium-coated gold nanoparticles (Pd-on-Au NPs) have much higher TCE HDC catalytic activity and greater resistance to chloride and sulfide deactivation compared to Pd/Al₂O₃ and Pd NPs [45-50]. Comparison of field-test results of different TCE treatment technologies indicated that the cost of treating the same volume of TCE-contaminated water using Pd catalysis was comparable to that of air-stripping and less expensive than granulated carbon adsorption and permeable reactive barrier [51].

Beyond our early observation of Pd-on-Au NPs showing high activity for PCE HDC [47], there are few reports on Pd-based catalysts for PCE degradation in water under ambient conditions. Some reports on Pd catalysts for PCE degradation described results for high-temperature gas-phase conditions [52-54] and for non-aqueous media under ambient conditions [55-57]. Other work discussed the use of Pd-doped NZVI in the in situ destruction of PCE under ambient conditions, in which Pd was the catalyst and iron was the reducing agent [58-61]. In this work, we studied Pd-on-Au NPs for PCE HDC in water using H₂, at room temperature, and at atmospheric pressure. We quantified the catalytic activities of Pd/Al₂O₃, Pd NPs, and Pd-on-Au
NPs, and tested the hypothesis that the NPs exhibited volcano-shape activity dependence for PCE HDC due to the molecular similarity of PCE and TCE. This work has been published as: Z. Zhao, Y.-L. Fang, P. J.J. Alvarez, M. S. Wong, "Degradation of perchloroethene at ambient conditions using Pd and Pd-on-Au reduction catalysts" \textit{Appl. Catal. B-Environ.}, \textbf{140-141}, 468-477 (2013). [62]

2.2. Materials and methods

2.2.1. Synthesis

Briefly, Au NPs (~4 nm) were synthesized via a sodium citrate reduction [46, 63]. Pd-on-Au NPs with Pd surface coverages of 10, 20, 40, 50, 60, 67, 80, 90, 100, 150 and 300 sc% were prepared by reducing specified volumes of a H$_2$PdCl$_4$ solution onto Au NPs by H$_2$ gas. Pd NPs (~4 nm) were synthesized using a similar procedure for Au NP synthesis. The synthesis details are found in Supporting Information. A supported Pd catalyst in the form of Pd/Al$_2$O$_3$ (Sigma-Aldrich, 1 wt\% Pd, average particle size 38-70 μm [43], specific surface area 177 m$^2$/g [45], pore volume 0.20 cm$^3$/g [43]) was also tested as received.

2.2.2. Characterization

The synthesized NPs were imaged using a JEOL 2010 transmission electron microscope (TEM). TEM samples were prepared by depositing NP sol onto a 200-mesh carbon/Formvar TEM grid which was then dried under room temperature. The ImageJ program was used for the size distribution measurements [64]; 250 particles were measured for each sample. Other characterization results can be found in our previous studies [46, 50].

2.2.3. Reaction testing
The batch reactor was prepared by adding 30 mL of a citrate buffer solution to ~140-143 mL of DI water in a 250-mL serum bottle, such that the resulting pH was 7.0. The citrate buffer solution was prepared by dissolving 2.58 g of trisodium citrate (>99.5%, Fisher) into 100 mL DI water and then adjusting the pH to 7.0 using 0.1 M citric acid (prepared separately by dissolving 0.21 g of citric acid (>99.5%, Fisher) into 100 mL of DI water). The bottle was sealed with Teflon tape and a Teflon-coated rubber septum. Hydrogen gas was bubbled through the water for 15 min, filling the headspace. 3 µL of PCE (99.5%, Sigma-Aldrich) and 0.2 µL of pentane (99.7%, Burdick and Jackson) were injected into the reactor as the reactant and internal standard, respectively. The contents were stirred vigorously for 3 hr, sufficient for the sealed batch reactor to reach equilibrium.

Pd-on-Au NP sols (with varying Pd surface coverages) were then charged to the batch reactor, such that the total amount of Pd metal (6.81 µg of Pd metal) was the same. For the Pd-on-Au NP with 0 se% sample, 1 mL of Au NP sol was used. For Pd NPs and Pd/Al₂O₃, 1 mL of Pd NP sol and 1 mL of Pd/Al₂O₃ powder suspension (25 mg/mL) were charged, respectively, corresponding to 31.8 and 250 µg of Pd metal charged. The total liquid amount was set to be 173 mL. The PCE HDC reaction was carried out at room temperature (23 ± 1 °C) under constant magnetic stirring (800 rpm). Each experiment was performed at least twice. The conversion results were averaged and were within ±15%. Headspace gas chromatography was used to monitor the reaction, with catalyst injection marking the start of the reaction (Supporting Information).

2.2.4. Reaction data analysis

GC peaks corresponding to PCE, TCE, ethane, 1,1-DCE, cis-1,2-DCE, trans-1,2-DCE, VC, ethene, n-butane, and butenes (mixture of isomers) were quantified as gas-phase concentrations
in headspace of the reactor. Gas-phase and liquid-phase concentrations were calculated from the total moles of each species injected using Henry's law and the appropriate dimensionless Henry's law constants $H_{cc}$ (= aqueous concentration/gas concentration) for PCE, TCE, ethane, 1,1-DCE, cis-1,2-DCE, trans-1,2-DCE, VC, ethene, n-butane and butenes (0.641, 0.339, 0.0485, 0.999, 0.145, 0.352, 0.999, 0.114, 0.0267, and 0.0340 at 23 °C, respectively) [65-68]. For example, 3 μL of PCE in the 250-mL serum bottle containing 173 mL liquid gives a total mole of 29.3 μmol, a gas-phase concentration of 0.156 mM and a liquid-phase concentration of 0.100 mM (= 16.6 ppm) in the reactor after equilibration. The carbon balance was defined as the total number of carbons of the remaining PCE, products and by-products in the batch reactor, divided by the total number of carbons of the initial PCE amount.

PCE HDC activity was reported for all catalysts assuming first-order reaction kinetics. Reaction rate constants were calculated using $C_{PCE} = C_{PCE,0} \times \exp(-k_{\text{meas}})$ with $C_{PCE,0}$ is initial PCE liquid-phase concentration, $k_{\text{meas}} = k_{\text{cat}} \times C_{\text{Pd}}$, $k_{\text{cat}}$ is the first-order, Pd-normalized rate constant (with units of L/g Pd/min), $C_{\text{Pd}}$ is the Pd content in the reactor, and $t$ is reaction time. For a given catalyst composition, the rate constant $k_{\text{cat}}$ was the average value of three runs ± 1 standard deviation. Another rate constant $k_{\text{cat}'}$ (with units of L/g_{surface Pd}/min) that accounted for surface Pd atom content was calculated from $k_{\text{meas}} = k_{\text{cat}'} \times C_{\text{Pd}'}$, where $C_{\text{Pd}'}$ is the surface Pd content in the reactor. For Pd surface coverages less than 100 sc%, all Pd atoms were assumed to be surface Pd atoms. For Pd surface coverages greater than 100 sc%, the surface Pd content was calculated assuming a magic cluster model of the Pd-on-Au NPs [46, 69-71]. For example, the surface atoms of 150 sc% Pd-on-Au NPs were counted as those Pd atoms in the 9th shell and those Pd atoms in 8th shell that were not covered. Pd dispersion (percentage of Pd atoms as surface atoms) for Pd NPs was calculated to be 25% from the empirically derived relation:
dispersion = \( c/d \), where \( c \) is a constant 1.1 for Pd, and \( d \) is the average particle size (4.4 nm from TEM) [50, 72, 73]. The dispersion for Pd/Al\(_2\)O\(_3\) was 21% [43, 48]. PCE conversion was calculated as \((C_{\text{PCE,0}} - C_{\text{PCE}})/C_{\text{PCE,0}}\). We verified that the \( k_{\text{cat}} \) did not vary at different catalyst charges for the experimental conditions used, which can occur when too much catalyst is used.

2.3. Results and discussion

2.3.1. Confirmation of NP sizes

Typical TEM images for Au NPs, 80 sc% Pd-on-Au NPs, and Pd NPs are shown in Fig. 2.1. The mean diameters (and relative standard deviations) were measured to be 4.1 nm (21%), 4.2 nm (22%), and 4.4 nm (32%) for Au NPs, 80 sc% Pd-on-Au NPs, and Pd NPs, respectively, consistent with our previous studies [46-48, 50].

Figure 2.1. TEM images and corresponding particle size histograms of (a) Au NPs, (b) 80 sc%
Pd-on-Au NPs, and (c) Pd NPs. Each bar represents the total number of NPs of a particle diameter ±0.25 nm.

2.3.2. Assessing mass transfer effect on rate constants

Various amounts of 60 sc% Pd-on-Au NP sol were injected into the batch reactor and the rate constant \( k_{\text{meas}} \) values were recorded. Specifically, 0, 0.233, 0.467, 0.933 and 1.866 mL of sol were charged, such that the corresponding Pd content of the reactor was 0, 0.985×10\(^{-5}\), 1.97×10\(^{-5}\), 3.94×10\(^{-5}\), and 7.88×10\(^{-5}\) g\text{Pd}/L. The \( k_{\text{meas}} \) values varied linearly with \( C_{\text{Pd}} \) from 0 to 3.94×10\(^{-5}\) g\text{Pd}/L, with the slope equal to a \( k_{\text{cat}} \) value of 2413 L/g\text{Pd}/min (Fig. S2.1a). This was within 10% of the \( k_{\text{cat}} \) value determined for 60 sc% Pd-on-Au NPs using the standard catalyst charge of 3.94×10\(^{-5}\) g\text{Pd}/L (2406 L/g\text{Pd}/min, Table S2.1). That the standard catalyst charge was in this linear regime indicated the \( k_{\text{cat}} \) values determined for all other catalytic materials were independent of catalyst amount.

The mass transfer resistances were determined in a manner developed previously for the TCE HDC reaction [49]. Plotting the reciprocal of the non-zero \( k_{\text{meas}} \) and \( C_{\text{Pd}} \) values allowed the gas-liquid and liquid-catalyst surface resistances (1/k\text{gl}\text{a}_{\text{lg}} and 1/k\text{ls}\text{a}_{\text{s}}) and surface reaction rate contribution (1/\( k_{\text{a}} \)) to be determined using the relation 1/\( k_{\text{meas}} \) = \( C_{1} + C_{2} \times 1/C_{\text{Pd}} \) (Fig. S2.1b). The y-intercept \( C_{1} \) related to 1/k\text{gl}\text{a}_{\text{lg}} and the slope \( C_{2} \) related to 1/k\text{ls}\text{a}_{\text{s}} and 1/\( k_{\text{a}} \), where k\text{gl} is the gas-liquid mass transfer coefficient, a\text{gl} is the gas-liquid interface specific areas, k\text{ls} is the liquid-solid mass transfer coefficient, a\text{s} is the particle specific surface areas, and k is the rate constant for surface reaction. The value of 1/k\text{ls}\text{a}_{\text{s}} term was calculated to be 0.00853 min based on the diffusivity of PCE (8.2×10\(^{-6}\) cm\(^2\) s\(^{-1}\) at 25 °C [74]). The 1/k\text{gl}\text{a}_{\text{lg}}, 1/k\text{ls}\text{a}_{\text{s}} and 1/\( k_{\text{a}} \) terms were then determined to be 0.473, 0.00853 and 10.1 min, respectively. Comparison of their values (i.e., 1/\( k_{\text{a}} \) > 1/k\text{gl}\text{a}_{\text{lg}} >> 1/k\text{ls}\text{a}_{\text{s}}) indicated that the liquid-solid mass transfer was the most rapid among
the three processes, and the gas-liquid mass transfer was slow enough to affect observed reaction rate constants. To exclude the gas-liquid mass transfer effect, $k_{\text{cat}}$ should be re-calculated as $k_{\text{cat,corr}}$ using the relation $k_{\text{cat,corr}} = ka/C_{\text{Pd}}$. However, the gas-liquid mass transfer effect was deemed to be small, based on the calculated $k_{\text{cat,corr}}$ (2512 L/gPd/min) being only 4% higher than $k_{\text{cat}}$ (2406 L/gPd/min, Table S2.1). Only for the most active catalyst (80 sc% Pd-on-Au NPs) was the calculated $k_{\text{cat,corr}}$ (5477 L/gPd/min) 10% higher than $k_{\text{cat}}$ (4971 L/gPd/min, Table S2.1). Thus, $k_{\text{cat,corr}}$ values were not calculated for the rest of the catalyst compositions in this study. An analogous experimental mass transfer analysis of the Pd/Al$_2$O$_3$ comparison sample was not carried out. The major structural differences between Pd/Al$_2$O$_3$ and the NPs were the larger particle size and the internal pores of the former, leading to a different liquid-solid mass transfer resistance and a possible intraparticle diffusional effect. The liquid-solid mass transfer resistance was estimated with an earlier method of ours [46] and the intraparticle mass transfer effect was determined from the Thiele modulus and effectiveness factor. Our calculations indicated the liquid-solid mass transfer resistance was small and internal diffusion was a negligible effect (Supplementary Information).

2.3.3. Catalytic activity

Pd-on-Au NPs with Pd surface coverages ranging from 0 to 300 sc%, Pd NPs, and supported Pd catalysts were tested for PCE HDC reaction ($\text{Cl}_2\text{C}=\text{CCl}_2 + 5\text{H}_2 \rightarrow \text{H}_3\text{C}-\text{CH}_3 + 4\text{HCl}$). All materials were active for the reaction, except for control Pd-on-Au NPs with 0 sc%, i.e., Au-only NPs (Fig. 2.2, Table S2.1). The total Pd content in the batch reactor was kept the same for Pd-on-Au NPs regardless of Pd surface coverage, and so the differences in rate constants were clearly due to the different states of Pd metal on the Au surface. PCE conversion increased with
increasing Pd surface coverage, up to 80 sc% (Fig. 2.2a). The PCE conversion decreased for NPs with surface coverages that exceeded 80 sc%, to the point where Pd-on-Au NPs with 300 sc% (which had 42.4 wt% Pd of total metal content) was less active than Pd-on-Au NPs with 20 sc% (which had 4.7 wt% Pd of metal content) (Fig. 2.2b). The 80 sc% Pd-on-Au NP sample was more active than Pd NPs (which contained ~5× more Pd) and Pd/Al₂O₃ (which contained ~37× more Pd) (Fig. 2.2c). While the conversion-time profiles for some samples did not have a clear exponential time dependence, the assumption of first-order kinetics was sufficient to show clear activity trends with Pd surface coverage.

Figure 2.2. PCE conversion profiles for Pd-on-Au NPs with (a) 0-80 sc%, (b) 80-300 sc%, and for (c) Pd NPs and Pd/Al₂O₃ catalysts. (d) PCE HDC k_{cat} (blue) and k_{cat}' (red) values plotted
(with error bars of ±1 standard deviation) against surface coverage for Pd-on-Au NPs. Reaction conditions: $C_{\text{Pd}} = 3.94 \times 10^{-5}$, $1.84 \times 10^{-4}$, and $1.45 \times 10^{-3} \text{ g}_{\text{Pd}}/\text{L}$ for Pd-on-Au NPs, Pd NPs, and Pd/Al$_2$O$_3$, respectively. 23 °C, atmospheric pressure, H$_2$ headspace, pH = 7.0, citrate buffer, $C_{\text{PCE,0}} = 16.6 \text{ ppm} = 0.1 \text{ mM}$.

The Pd-on-Au NPs had a volcano-shape dependence on surface coverage, with the maximum activity corresponding to 80 sc% (Fig. 2.2d). They were much more active than Pd NPs and Pd/Al$_2$O$_3$ on a per-gram Pd basis (238 and 60 L/g$_{\text{Pd}}$/min). Accounting for only surface Pd atoms, the reaction rate constants for samples with >100 sc% had comparable values (~2600-2633 L/g$_{\text{surfacePd}}$/min). Presumably overcoated with Pd metal, these NPs were several times more active than Pd NPs and Pd/Al$_2$O$_3$, which had corresponding rate constants of 952 and 167 L/g$_{\text{surfacePd}}$/min. This difference in catalytic activity may be the result of Au electronic effects imposed upon the outermost Pd atoms [46]. Such electronic promotional effects have been observed in many other reaction systems involving bimetallic PdAu catalysts or electrodes, such as cyclization of acetylene to benzene [75], electrochemical oxidation of formic acid [76] and benzyl alcohol oxidation [77] and substantiated by DFT (density functional theory) calculations [78, 79].

The volcano-shape feature for the PCE HDC reaction was similar to that for TCE HDC, suggesting a similar dependence on the Pd-on-Au catalyst nanostructure. In our structural model of Pd-on-Au NPs developed for the latter reaction [50, 80], the Pd is in the form of isolated atoms and few small two-dimensional ensembles at the lowest surface coverages, correlating to the lower catalytic activity per-Pd-atom. The per-Pd-atom catalytic activity increases at higher surface coverages, indicative of more active two-dimensional Pd ensembles; it decreases beyond ~60-70 sc%, which is now attributed to the emergence of less active, three-dimensional Pd ensembles [80].
A notable difference was the PCE HDC volcano peak being located at a higher surface coverage (~80 sc%) than the ~60-70 sc% peak for TCE HDC. This difference was statistically real because the 80 sc% value had an uncertainty of 0.8 sc% (one standard deviation based on error propagation analysis, Supplementary Information) and the 70 sc% value has an uncertainty of 2.6 sc% (one standard deviation based on inductively coupled plasma-optical emission spectroscopy results of 70 sc% 3 nm Pd-on-Au NPs from a previous study [80]). The structure for Pd-on-Au NPs at any Pd surface coverage is the same for either reaction, and so this peak offset indicated the active site that gave the highest activity for PCE HDC differed slightly from the active site that gave the highest activity for TCE HDC.

To provide a sense of the materials costs of the most active Pd-on-Au NP catalyst and Pd NPs, we calculated the amount of Pd and Au needed to degrade PCE (dissolved in water) from 100 ppm to 5 ppb for the same reaction time (Table S2.2). With January 2013 spot prices of palladium (~710 US$/oz) and gold (~1670 US$/oz), Pd-on-Au NPs were ~1.6× less expensive than Pd NPs. A practical water treatment technology requires flow conditions, and so a supported version of the bimetallic would be needed. We performed a similar cost analysis using flow performance results for the TCE HDC reaction in comparing the cost of ion-exchange resin supported Pd-on-Au NPs and commercial Pd/Al$_2$O$_3$, and we concluded that the former material cost ~18× times less than the latter [47]. Further refinement of the cost analysis requires additional information about catalyst performance in field tests (accounting for mass transfer effects, deactivation resistance, and regenerability), capital costs, and operational costs.

### 2.3.4. Selectivity differences
The products formed from PCE HDC were plotted with time for 60 sc% Pd-on-Au NP, Pd NP, and Pd/Al$_2$O$_3$ samples (Fig. 2.3). Much more Pd metal was charged for the Pd/Al$_2$O$_3$ case (Table S2.1), resulting in the faster PCE conversion compared to the other two cases. Carbon balance at all time points for the three catalysts was 100 ± 5%.
Figure 2.3. Reaction profiles of PCE HDC using (a) 60 sc% Pd-on-Au NPs, (c) Pd NPs, and (e) Pd/Al₂O₃. The concentration-time profiles of reaction products during PCE HDC using (b) 60 sc% Pd-on-Au NPs, (d) Pd NPs, and (f) Pd/Al₂O₃. Solid lines are best-fit curves (R² > 0.96) using a modified Langmuir-Hinshelwood kinetic model (Eqn. 1-4, 8), and the dashed blue lines are the measured carbon balances. Reaction conditions: C_Pd = 3.94 × 10⁻⁵, 1.84 × 10⁻⁴, and 1.45 × 10⁻³ g/Pd/L for 60 sc% Pd-on-Au NPs, Pd NPs, and Pd/Al₂O₃, respectively, 23 °C, 1 atm, H₂ headspace, pH = 7.0, citrate buffer, C_{PCE,0} = 16.6 ppm = 0.1 mM. The 60 sc% sample was chosen...
over the 80 sc% one due to experimental limitations (the reaction was too rapid for the GC measurements to yield smooth concentration-time profiles).

PCE nearly reached full conversion in less than 1 hr with Pd-on-Au NPs (Fig. 2.3a). At the end of the reaction, 94.6% of the product formed was ethane. Byproducts included n-butane (2.1%) and butenes (3.3%) (Fig. 2.3b). At intermediate reaction times, TCE, all three DCE isomers, and VC were detected, with concentrations peaking at ~5 min into the reaction. No ethene was detected at any time. These trends held true for Pd-on-Au NPs with <100 sc% and also for Pd-on-Au NPs ≥100 sc%.

PCE reached ~86% conversion after 2 hr with Pd NPs (Fig. 2.3c). The majority of the product formed at the end of the reaction was ethane (87.5%) with n-butane (3.2%) and butenes (5.8%) also detected. TCE, all three DCE isomers, and VC were also detected at intermediate reaction times, and they existed with small amounts (3.5% in total) at the end of the reaction due to slow reaction rate of Pd NPs. The peaking times observed for these intermediate species are different for Pd NPs, with TCE and cis-1,2-DCE being at ~30 min, and trans-1,2-DCE, 1,1-DCE and VC being at ~60-70 min. Ethene was detected in trace amounts throughout the reaction.

With 36.8× more Pd charged than the 60 sc% case, PCE reached 92% conversion at 28 min with Pd/Al₂O₃. Ethane had a mole percentage of 99%, with the rest 1% being n-butane. At intermediate reaction times, TCE, cis-1,2-DCE and 1,1-DCE were the only chlorinated ethenes detected. Similar to Pd NPs, TCE and cis-1,2-DCE for Pd/Al₂O₃ peaked at approximately the same time (~2 min), while trans-1,2-DCE spiked at a later time (~6 min).

At intermediate PCE conversions (e.g., 40%), the distribution among the three DCE isomers interestingly differed among the 3 catalyst types (Fig. 2.4). The relative amounts for Pd-on-Au NPs were roughly 53% cis-1,2-DCE, 44% 1,1-DCE, and 3% trans-1,2-DCE at 40% PCE.
conversion, over a wide range of surface coverages. The DCE isomer distributions had a weak
dependence on Pd surface coverage, with cis-1,2-DCE amount slightly decreased with increasing
Pd surface coverage and 1,1-DCE amount slightly increased. For 300 sc% Pd-on-Au NPs, the
cis-1,2-DCE amount (45%) was slightly smaller than the 1,1-DCE amount (53%). The selectivity
to the three DCE isomers at 40% PCE conversion was 4.3% for 60 sc% Pd-on-Au NPs.

Figure 2.4. (a) Relative amounts of DCE isomers (1,1-DCE, cis-1,2-DCE, and trans-1,2-DCE)
at 40% PCE conversion, for Pd-on-Au NPs of various Pd surface coverages (dashed lines mark
the selectivity values averaged over the 10-150 sc% range. (b) Comparison of DCE isomer
distributions for Pd-on-Au NPs (averaged over the 10-150 sc% range), Pd NPs, and Pd/Al₂O₃ at
40% PCE conversion.

The selectivity to the DCE isomers at 40% PCE conversion for Pd NPs and Pd/Al₂O₃ was
7.5% and 1.5%, respectively. Compared to the Pd-on-Au NP case, relatively more trans-1,2-
DCE (16%) and less 1,1-DCE (25%) were formed with Pd NPs. With Pd/Al₂O₃, cis-1,2-DCE
(72%) and 1,1-DCE (28%) were formed but no trans-1,2-DCE was formed (Fig. 2.4b). As a
comparison, the thermodynamic equilibrium amounts of the 3 isomers at 25 °C are 40% cis-1,2-
DCE, 43% 1,1-DCE, and 17% trans-1,2-DCE (calculated from their respective standard Gibbs free energy of formation, 24.16, 24.33, and 26.54 kJ/mol [81]).

A recent DFT study by Andersin and Honkala found that the three DCE isomers had different adsorption energies on Pd-on-Au and Pd(111) surfaces [82]. trans-1,2-DCE was calculated to have a larger free energy of adsorption (-1.18 eV on 7-Pd-atom ensembles on a gold slab, Pd$_{7}$/Au) than either 1,1-DCE and cis-1,2-DCE (-1.10 eV for both). If one considers the relation between the Gibbs free energy of adsorption and adsorption equilibrium constant ($K_{ads} = \exp[-\Delta G_{ads}/kT]$), the larger the adsorption energy is, the "stickier" the adsorbed species is to the surface. Thus, trans-1,2-DCE adsorbs more strongly than cis-1,2-DCE and 1,1-DCE, resulting in its lower solution-phase concentration (consistent with the experimental data). Also contributing to this lower concentration is the higher reactivity of trans-1,2-DCE for HDC (2303 L/gPd/min), compared to cis-1,2-DCE (1813 L/gPd/min) and 1,1-DCE (1519 L/gPd/min) under similar experimental conditions [47].

The same adsorption explanation extended somewhat to Pd(111) surfaces. trans-1,2-DCE, 1,1-DCE and cis-1,2-DCE had calculated adsorption energies of -0.75, -0.69, and -0.65 eV, respectively, on Pd(111) [82], which superficially correlated with the solution-phase concentration trend of trans-1,2-DCE < 1,1-DCE < cis-1,2-DCE. The large difference in trans-1,2-DCE concentration between the Pd NP and Pd/Al$_2$O$_3$ cases was not accounted for, due in part to Pd(111) being a poor structural model of nanoparticulate Pd.

2.3.5. Reaction mechanism

PCE HDC led to the formation and subsequent degradation of TCE, DCE isomers, and VC, similar to TCE HDC. For the TCE HDC reaction, DCE's and ethene formed in small amounts
and then degraded to non-detectable levels; ethane was the dominant product, with butane/butenes as the minor side-products (<3%) at the end of the reaction [46, 47, 80, 83]. The concentration-time profiles (Fig. 2.3) of the partially dechlorinated products, C₂ compounds, and C₄ compounds suggested the following general PCE HDC reaction pathway: after dissolving into water, PCE dechlorinates and hydrogenates one Cl group at a time, eventually forming ethene which hydrogenates into ethane (Scheme 2.1). Carbon-coupling of ethene surface species led to butene/butane formation. These C₄ products were detected with Pd-on-Au NPs and Pd NPs in previous studies on TCE HDC [46, 80, 83]. Observed through surface enhanced Raman spectroscopy was C₄ species chemisorbed on a Pd-on-Au surface, which formed during 1,1-DCE HDC reaction [84]. Lowry and Reinhard reported the formation of C₄-C₆ products (1-butene, n-butane, cis-2-butene, trans-2-butene, and 2-hexene) with Pd/Al₂O₃ during TCE HDC [85].
Scheme 2.1. Proposed reaction pathway of heterogeneously catalyzed PCE HDC, which includes gas-to-liquid transfer as an elementary step. "S" represents catalytic active sites. "k" under the arrows represents corresponding surface reaction rate constant.

A modified Langmuir-Hinshelwood kinetic model was developed by assuming that the gas-to-liquid mass transfer and the reversible chemisorption of surface species for the various compounds to be in quasi-equilibrium (Scheme S2.1). This modeling approach implies that all
surface reactions are rate-limiting and does not require a reaction step to be identified as rate-limiting [86-88].

A set of differential equations (Eqn. 1-8) implicitly describing concentration-time profiles for the ten possible chemical species are as follows:

$$\frac{d[PCE]}{dt} = -\beta \times k_{PCE}[PCE]$$ ................................................................. (1)

$$\frac{d[TCE]}{dt} = \beta \times \left( k_{PCE} \frac{K_{PCE}}{K_{TCE}}[PCE] - \sum_i k_{TCE}[TCE]_i \right)$$ .................................................. (2)

$$\frac{d[DCE]}{dt} = \beta \times \left( k_{TCE} \frac{K_{TCE}}{K_{DCE}}[TCE] - k_{DCE}[DCE]_i \right) \quad (i=1,1\)-DCE, trans-1,2-DCE, cis-1,2-DCE)..... (3)

$$\frac{d[VC]}{dt} = \beta \times \left( \sum_i k_{DCE} \frac{K_{DCE}}{K_{VC}}[DCE]_i - k_{VC}[VC] \right)$$ ................................................................. (4)

$$\frac{d[ethene]}{dt} = \beta \times \frac{K_{VC}}{K_{ethene}} k_{VC}[VC] - \beta^2 \times k_{ethene}[ethene] - 2\alpha[S]_{total}K_{ethene}k_{ethene2}[ethene]^2$$ ................. (5)

$$\frac{d[butene]}{dt} = \alpha[S]_{total} \times \frac{K_{ethene}^2}{K_{butene}} k_{ethene2}[ethene]^2 - \beta \times k_{butene}[butene]$$ .............................................. (6)

$$\frac{d[butane]}{dt} = \beta \times \frac{K_{butene}}{K_{butane}} k_{butene}[butene]$$ .................................................................. (7)

$$\frac{d[ethane]}{dt} = \beta \times \frac{K_{VC}}{K_{ethane}} k_{VC}[VC]$$ ............................................................................. (8)

where $\alpha = \frac{1}{1+\sqrt{K_{H_2}[H_2]_0}}$, $\beta = \sqrt{K_{H_2}[H_2]_0} \alpha[S]_{total}$
The numerical solutions to the differential equations were least-squares fit to the concentration-time profiles using Matlab (solid lines of Fig. 2.3; Matlab code provided in Supplementary Information). The coefficient of determination R² was >0.96, indicating a very good fit between the data and fitted curves. Species with zero or trace concentrations, such as ethene, butanes, and butane, were not included, to minimize fitting error. The fitted parameters for each catalyst type are listed in Table S2.3. The relative standard error for most fitted parameters was <10% (except for those associated with VC, which was ~35%).

Table 2.1. Selected fitted kinetic parameters using modified Langmuir-Hinshelwood kinetics model

<table>
<thead>
<tr>
<th>Species</th>
<th>Fitted kinetic parameters</th>
<th>60 sc% Pd-on-Au NPs</th>
<th>Pd NPs</th>
<th>Pd/Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCE</td>
<td>βkₚ₊ₑ</td>
<td>0.082 ± 0.006</td>
<td>0.015 ± 0.001</td>
<td>0.093 ± 0.007</td>
</tr>
<tr>
<td>TCE</td>
<td>Kₚₑ/Kₜₑ</td>
<td>0.29 ± 0.02</td>
<td>0.0034 ± 0.0003</td>
<td>0.019 ± 0.002</td>
</tr>
<tr>
<td></td>
<td>β∑kₜₑ</td>
<td>0.51 ± 0.03</td>
<td>0.075 ± 0.007</td>
<td>1.5 ± 0.12</td>
</tr>
<tr>
<td>DCE’s</td>
<td>β∑k₅ₑ</td>
<td>1.5 ± 0.14</td>
<td>0.14 ± 0.01</td>
<td>1.5 ± 0.14</td>
</tr>
<tr>
<td>VC</td>
<td>βkᵥₑ</td>
<td>0.90 ± 0.3</td>
<td>0.11 ± 0.04</td>
<td>Not fitted</td>
</tr>
</tbody>
</table>

Table 2.1 lists selected fitted parameters for which conclusions can be drawn. The relation, \( \sum k_{DCE_i} \) (the sum of reaction rate constants of all DCE’s degrading to VC) \( \geq \sum k_{TCE_i} \) (the sum of reaction rate constants of TCE degradation to all DCE isomers) > \( k_{PCE} \) (the rate constant of PCE degradation to TCE), held for all three catalyst types. The concentration profiles of Fig. 2.3 thus show the first step in the PCE HDC surface reaction pathway (the reductive replacement of Cl with H group) to be the slowest, using any of the catalysts tested. With the first Cl group removed from PCE, it becomes progressively faster to remove the subsequent Cl groups. This
trend is consistent with other reports that compare the relative reactivities of chlorinated ethenes [44, 47]. Not following this trend is the rate constant of VC degradation to ethene \( k_{VC} \), which was smaller than \( \sum_{i} k_{DCE} \) for Pd-on-Au NPs and Pd NPs. This was probably due to the small amounts of VC detected and to concentration-time profiles of some chemical species (produced after VC degradation, Fig. 2.3) not being included when solving the differential equations. The concentration of VC for the Pd/Al\(_2\)O\(_3\) case was too low to be detected, and not included in the fitting analysis.

2.4. Conclusions

PCE is a prevalent and hazardous groundwater contaminant similar to TCE, but its removal – especially through reduction catalysis – has not been studied as thoroughly. PCE and TCE are chemically related, and this study reveals significant differences in their catalytic conversion through HDC chemistry. Pd-on-Au NPs, Pd NPs, and Pd/Al\(_2\)O\(_3\) successfully catalyze the HDC reaction of PCE in water, at room temperature, and at atmospheric pressure. The catalytic activity of Pd-on-Au NPs varies in a highly controllable manner with Pd surface coverage, with the most active composition having \(~80\) sc%. The volcano shape activity curve resembles the curve of TCE HDC except the latter has peak activity at 60-70 sc%, indicating the Pd-on-Au nanostructure can catalytically distinguish between the two closely related chlorinated ethene species. The appearance and sequential degradation of TCE, DCE isomers, VC, and ethene are evidence that the stepwise dechlorination of each chlorine group occurred for all catalysts tested. The relative amounts of detected DCE isomers differ among the 3 catalyst types, which is attributed to differences in adsorption affinities and reactivities of each isomer to the metal surface. Ethane is predominantly produced at the end of reaction, with the balance being n-
butane and butenes. For PCE conversions > 85%, ethane selectivity is ~95%, ~88%, and 99% for Pd-on-Au NPs, Pd NPs, and Pd/Al₂O₃, respectively. A Langmuir-Hinshelwood kinetics model without determining a rate-limiting step *a priori* is developed, yielding concentration-time profiles that reasonably match experimental data and yielding relative rate constants that indicate PCE becomes increasingly reactive as it dechlorinates stepwise. This work demonstrates the much higher catalytic activity of Pd-on-Au NPs over Pd-only catalysts, showcasing a new approach in reduction catalysis to PCE contamination.

### 2.5. Symbols and Notations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>a&lt;sub&gt;gl&lt;/sub&gt;, a&lt;sub&gt;s&lt;/sub&gt;</td>
<td>Specific areas for gas-liquid interface and NP catalyst solid surface in overall batch reactor liquid volume</td>
</tr>
<tr>
<td>a&lt;sub&gt;s-ex&lt;/sub&gt;, a&lt;sub&gt;i&lt;/sub&gt;</td>
<td>Specific areas for external and internal surface for Pd/Al₂O₃ in overall batch reactor liquid volume</td>
</tr>
<tr>
<td>k&lt;sub&gt;gl&lt;/sub&gt;, k&lt;sub&gt;ls&lt;/sub&gt;, k&lt;sub&gt;i&lt;/sub&gt;</td>
<td>Mass transfer coefficients for gas-liquid, liquid-solid, and intraparticle processes</td>
</tr>
<tr>
<td>k, k&lt;sub&gt;meas&lt;/sub&gt;</td>
<td>Rate constant for overall surface reaction, and observed rate constant for overall reaction</td>
</tr>
<tr>
<td>k&lt;sub&gt;cat&lt;/sub&gt;, k&lt;sub&gt;cat'&lt;/sub&gt;, k&lt;sub&gt;cat,corr&lt;/sub&gt;</td>
<td>Apparent rate constant normalized with total Pd content, rate constant normalized with surface Pd content and mass transfer-corrected rate constant</td>
</tr>
<tr>
<td>C&lt;sub&gt;Pd&lt;/sub&gt;, C&lt;sub&gt;Pd'&lt;/sub&gt;</td>
<td>Pd metal content and surface Pd metal content in the reactor</td>
</tr>
<tr>
<td>C&lt;sub&gt;PCE&lt;/sub&gt;, C&lt;sub&gt;PCE,0&lt;/sub&gt;</td>
<td>PCE liquid-phase concentration and initial PCE liquid-phase concentration</td>
</tr>
<tr>
<td>C&lt;sub&gt;1&lt;/sub&gt;, C&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Y-intercept and slope of 1/k&lt;sub&gt;meas&lt;/sub&gt; – 1/C&lt;sub&gt;Pd&lt;/sub&gt; plot</td>
</tr>
</tbody>
</table>
| k<sub>PCE</sub>, k<sub>TCE</sub>, k<sub>DCEi</sub>, k<sub>VC</sub>, k<sub>ethene1</sub>, k<sub>ethene2</sub>, k<sub>butene</sub> | Surface reaction rate constants for elementary reaction step from PCE to TCE, from TCE to one DCE isomer, from one DCE isomer to
VC, from VC to ethene, from ethene to ethane, from ethene to butene, and from butene to butane

K with subscript: Surface adsorption-desorption equilibrium constant for a given compound

[PCE]: Liquid phase concentration for PCE

[S]_{total}: Total concentration of active sites

2.6. Supplementary Information

**Detailed NP synthesis method:** To synthesize the ~4 nm Au NPs, a gold salt solution was prepared by adding 0.20 mL of 5 wt% HAuCl₄ (0.126 M; prepared by dissolving 5 g of HAuCl₄·3H₂O (>99%, Sigma-Aldrich) in 100 mL of H₂O) into 80.8 mL of deionized (DI) water (>18 MΩ-cm, Barnstead NANOpure Diamond) and heating to 60 °C while stirring. A second solution was prepared by dissolving 0.040 g sodium citrate (>99.5%, Fisher), 0.018 g potassium carbonate (>99.5%, Sigma–Aldrich), and 0.05 g tannic acid (>99.5%, Sigma–Aldrich) into 20 mL of DI water and heating to 60 °C also. The formation of Au NPs was apparent upon addition of the second solution to the first, by the immediate emergence of the reddish-brown color. The mixed solution was then heated to a boil for 2 min before removal from the heat source. Au NPs in the final fluid (dark brown-red color) were verified to be ~4 nm in diameter, according to TEM. The concentration was calculated to be 1.07×10^{14} NP/mL, based on 100% reduction of the Au salt [49].

In the preparation of bimetallic Pd-on-Au NP catalysts, specified volumes of a H₂PdCl₄ solution (2.49 mM; prepared by dissolving 42.2 mg PdCl₂ (99.99%, Sigma-Aldrich) in 95 ml DI water containing 500 µL HCl solution (1 M, Fisher Scientific)), were added to an aliquot of the Au NP sol. Specifically, Pd-on-Au NPs with Pd surface coverages of 10, 20, 40, 50, 60, 67, 80,
90, 100, 150 and 300 sc% were prepared by adding 9, 18, 36, 45, 55, 61, 73, 82, 91, 102, 148 and 347 μL of the Pd salt solution, respectively, to 2 mL of the Au NPs. The precursor amounts were calculated by assuming the Au NPs to be a magic cluster of 7 shells and the Pd coating to comprise the 8th shell [46, 69-71]. A Pd surface coverage of 100% ("100 sc%") corresponded to the complete filling of this 8th shell by Pd atoms, i.e., 100 sc% Pd-on-Au NPs. The solution was mixed for one min using a vortex mixer (Mini Vortexer, Fisher) and bubbled with H₂ gas (99.99%, Matheson) at a flow rate of ~200 mL/min for 2 min, causing the Pd salt to reduce onto the Au NP surface, forming the Pd-on-Au NPs.

Pd NPs were prepared using the same procedure for Au NP synthesis, except for the Au salt solution was replaced by 12 mL of a H₂PdCl₄ solution (2.49 mM) diluted in 68 mL of DI water and the boiling time was increased to 25 min [46]. A dark coffee-brown sol containing ~4 nm Pd NPs (with a calculated particle concentration of 1.27×10¹⁴ NP/mL) resulted.

**Detailed method for headspace gas analysis:** In a typical analysis, 200 μL of the headspace was collected and injected into an Agilent Technologies 6890N GC equipped with a flame induction detector (FID) and a Supelco 1-2382 40/60 Carboxen-1000 packed column. A GC method with a run time of 5.5 min, helium carrier gas at a flow rate of 35 mL/min, and an oven temperature of 210 ºC was used. Peak assignments were verified using a GC-MS (Varian Saturn 3800 GC with a Varian 2000 mass spectrometer detector) equipped with a GS-GasPro capillary column (helium carrier gas flowing at 1.5 ml/min, oven temperature from 175 ºC to 225 ºC at a ramp rate of 20 ºC/min).
Figure S2.1. The linear relationships between (a) observed reaction rate constant $k_{\text{meas}}$ and Pd reactor content, and (b) $1/k_{\text{meas}}$ and $1/C_{\text{Pd}}$. The red circles mark the default Pd content for the PCE HDC batch reaction studies. The line in panel (a) was fitted with Pd reactor content from 0 to $3.94 \times 10^{-5}$ g$_{\text{Pd}}$/L. Reaction conditions: 60 sc% Pd-on-Au NPs, 23 °C, atmospheric pressure, 800 rpm stir rate, H$_2$ headspace, pH = 7.0, citrate buffer, $C_{\text{PCE},0} = 16.6$ ppm = 0.1 mM.

Determination of mass transfer resistances for Pd/Al$_2$O$_3$: The gas-liquid mass transfer resistance for Pd/Al$_2$O$_3$ is assumed to be the same that for the NPs because it is independent of the catalyst. The liquid-solid mass transfer coefficient $k_{ls}$ is estimated using the Ranz-Marshall correlation, $Sh = 2 + 0.6 \times Re^{1/2} Sc^{1/3}$ [49, 89]. For Pd/Al$_2$O$_3$ in this study, the maximum Reynolds number, Re, is calculated to be 113, and the Schmidt number, Sc, is 1220, assuming the particles were spherical (diameter $d_p = 50$ μm) [43]. This gives a Sh value of 70.2, allowing $k_{ls}$ to be estimated as $1.15 \times 10^{-3}$ m/s from the definition of the Sherwood number, $Sh = k_{ls} d_p / D_{\text{PCE}}$, where $D_{\text{PCE}} (= 8.2 \times 10^{-10}$ m$^2$/s [74]) is the diffusivity of PCE in 25 °C in water. The catalyst exterior surface area in the batch reactor liquid volume, $a_s$, is calculated to be 26.8 m$^2$/m$^3$ based on the bulk density of Pd/Al$_2$O$_3$ (0.65 g/mL [90]) and volume of the reactor (173 mL). The liquid-solid mass transfer resistance, $1/k_{ls a_s}$, is 0.541 min, smaller than the surface reaction resistance determined to be 10.5 min ($1/\eta k_a = 1/(C_{\text{Pd}} k_{\text{cat}}) - 1/k_{gl a_g} - 1/k_{ls a_s}$).
D_{eff} of PCE in a porous catalyst particle is estimated from \( D_{eff} = D_{PCE} \phi \sigma_c / \tau \), where \( \phi \) is porosity, \( \sigma_c \) is construction factor, and \( \tau \) is tortuosity [91]. The porosity of Pd/Al₂O₃ is estimated to be 0.13 (= pore volume \times \) bulk density \( = 0.20 \text{ cm}^3/\text{g} \times 0.65 \text{ g/mL} \) [90]), and the typical values for \( \sigma_c \) and \( \tau \) are 0.8 and 3.0, respectively. \( D_{eff} \) is calculated as \( 2.84 \times 10^{-11} \text{ m}^2/\text{s} \). The first-order Thiele modulus \( \Phi \) can be calculated from the following equation: \( \Phi[1/\tanh(3\Phi)-1/(3\Phi)] = -R_{PCE} a^2/(D_{eff} C_{PCE_s}) \), where \( C_{PCE_s} \) is PCE surface concentration (which is assumed to be equal to the bulk fluid PCE concentration of \( 1 \times 10^{-4} \text{ mol/L} \)), \( R_{PCE} \) is the observed reaction rate \( (= C_{Pd} k_{cat} C_{PCE_s} = 1.45 \times 10^{-3} \text{ gPd/L } \times 60 \text{ L/gPd/min } \times 1 \times 10^{-4} \text{ mol/L } \div 60 \text{ s/min } = 1.45 \times 10^{-7} \text{ mol/L/s} \), and \( a \) is the characteristic length \( (= d/6 \text{ for a sphere, } d = 50 \mu \text{m}) \) [92]. \( \Phi \) is calculated to be 0.06, much less than 1. The effectiveness factor \( \eta (=1/\Phi[1/\tanh(3\Phi)-1/(3\Phi)]) \) is calculated to be \~1.00, indicating the PCE HDC reaction with Pd/Al₂O₃ is not diffusion-limited. This further indicates that the surface reaction resistance of 10.5 min was not affected by diffusion.

### Table S2.1. Detailed rate constants of different catalysts.

<table>
<thead>
<tr>
<th>Pd catalyst type</th>
<th>Pd content in reactor ( C_{Pd} ) (gPd/L)</th>
<th>Catalyst concentration in reactor ( C_{Pd} ) (NP/mL)</th>
<th>Rate constant ( k_{cat} ) (L/gPd/min)</th>
<th>Surface Pd content in reactor ( C_{Pd}' ) (g_{surfacePd}/L)</th>
<th>Rate constant ( k_{cat}' ) (L/g_{surfacePd}/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 sc%</td>
<td>0</td>
<td>6.20 \times 10^{11}</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10 sc%</td>
<td>3.94 \times 10^{-5}</td>
<td>3.47 \times 10^{12}</td>
<td>685 ± 45</td>
<td>3.94 \times 10^{-5}</td>
<td>685 ± 45</td>
</tr>
<tr>
<td>20 sc%</td>
<td>3.94 \times 10^{-5}</td>
<td>1.74 \times 10^{12}</td>
<td>1500 ± 388</td>
<td>3.94 \times 10^{-5}</td>
<td>1500 ± 388</td>
</tr>
<tr>
<td>40 sc%</td>
<td>3.94 \times 10^{-5}</td>
<td>8.68 \times 10^{11}</td>
<td>1842 ± 109</td>
<td>3.94 \times 10^{-5}</td>
<td>1842 ± 109</td>
</tr>
<tr>
<td>60 sc%</td>
<td>3.94 \times 10^{-5}</td>
<td>5.78 \times 10^{11}</td>
<td>2406 ± 78</td>
<td>3.94 \times 10^{-5}</td>
<td>2406 ± 78</td>
</tr>
<tr>
<td>67 sc%</td>
<td>3.94 \times 10^{-5}</td>
<td>5.18 \times 10^{11}</td>
<td>3380 ± 205</td>
<td>3.94 \times 10^{-5}</td>
<td>3380 ± 205</td>
</tr>
<tr>
<td>80 sc%</td>
<td>3.94 \times 10^{-5}</td>
<td>4.34 \times 10^{11}</td>
<td>4971 ± 701</td>
<td>3.94 \times 10^{-5}</td>
<td>4971 ± 701</td>
</tr>
<tr>
<td>90 sc%</td>
<td>3.94 \times 10^{-5}</td>
<td>3.86 \times 10^{11}</td>
<td>3064 ± 269</td>
<td>3.94 \times 10^{-5}</td>
<td>3064 ± 269</td>
</tr>
</tbody>
</table>
Error propagation analysis of Pd surface coverage calculations: Quantified as the standard deviation $\Delta \text{sc}\%$, the uncertainty or error in the calculated Pd surface coverage values comes primarily from the uncertainties in the amount of Pd salt added to the synthesis volume ($N_{\text{Pd}}$) and the amount of Au NPs used ($N_{\text{AuNP}}$). The surface coverage is related to $N_{\text{Pd}}$ and $N_{\text{AuNP}}$ in the following way:

$$\text{sc}\% = \frac{N_{\text{Pd}}}{N_{\text{AuNP}}[10(n+1)^2 + 2]}$$

where the number of closed shells of the Au NP, $n$, is 7.

The uncertainty in sc% is:

$$\Delta \text{sc}\% = \frac{1}{[10(n+1)^2 + 2]} \left\{ \frac{(\Delta N_{\text{Pd}})^2}{N_{\text{AuNP}}} + \left[ \frac{-N_{\text{Pd}} \Delta N_{\text{AuNP}}}{(N_{\text{AuNP}})^2} \right]^2 \right\}^{1/2} = \text{sc}\% \left\{ \frac{(\Delta N_{\text{Pd}})^2}{N_{\text{Pd}}} + \left( \frac{\Delta N_{\text{AuNP}}}{N_{\text{AuNP}}} \right)^2 \right\}^{1/2}$$

The uncertainty in $N_{\text{Pd}}$ comes from weighing the Pd salt and pipetting the salt solution. A maximum of ~1% relative standard deviation for this experimental variable is estimated, based on the precision of scale and pipette. The uncertainty in $N_{\text{AuNP}}$ comes from pipetting the Au NPs stock sol, yielding an estimated relative standard deviation of 0.1%.

The standard deviation for sc% is thus calculated to be:

$$\Delta \text{sc}\% = \text{sc}\% \sqrt{(1\%)^2 + (0.1\%)^2} = 0.01 \times \text{sc}\%$$
Thus the standard deviations for 60, 70, and 80 sc% are ± 0.6, ± 0.7, ± 0.8 sc%, respectively.

**Table S2.2.** Calculated metals cost of Pd-on-Au NPs and Pd NPs.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pd-on-Au NPs (80 sc%)</th>
<th>Pd NPs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction rate constant (L/g\text{Pd}/min)</td>
<td>4971</td>
<td>238</td>
</tr>
<tr>
<td>Total Pd amount (mg)</td>
<td>0.332</td>
<td>6.94</td>
</tr>
<tr>
<td>Total Au amount (mg)</td>
<td>1.69</td>
<td>0</td>
</tr>
<tr>
<td>Total cost of metals\textsuperscript{a}</td>
<td>$0.108</td>
<td>$0.174</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Based on the January 2013 spot prices of palladium (~710 US$/oz) and gold (~1670 US$/oz)
Scheme S2.1. Derivation of the differential equations describing PCE HDC

Gas-liquid mass transfer: \(PCE(g) \xleftarrow{H_{PCE}} PCE(aq)\) .......................................................(1)

\(TCE(g) \xleftarrow{H_{TCE}} TCE(aq)\) .......................................................................................(2)

\(DCE_i(g) \xleftarrow{H_{DCE_i}} DCE_i(aq)\) \((i=1,1\text{-DCE, trans-1,2-DCE, cis-1,2-DCE})\) .............................................(3)

\(VC(g) \xleftarrow{H_{VC}} VC(aq)\) ..............................................................................................(4)

\(\text{ethene}(g) \xleftarrow{H_{\text{ethene}}} \text{ethene}(aq)\) .................................................................................(5)

\(\text{ethane}(g) \xleftarrow{H_{\text{ethane}}} \text{ethane}(aq)\) .............................................................................(6)

\(\text{butene}(g) \xleftarrow{H_{\text{butene}}} \text{butene}(aq)\) .................................................................................(7)

\(\text{bu tan} e(g) \xleftarrow{H_{\text{bu tan} e}} \text{bu tan} e(aq)\) ..............................................................................(8)

Adsorption and desorption\(^a\):

\(H_2 + S \xleftarrow{K_{H_2}} 2H \cdot S\) ..............................................................................................(9)

\(PCE + S \xleftarrow{K_{PCE}} PCE \cdot S\) ............................................................................................(10)

\(TCE + S \xleftarrow{K_{TCE}} TCE \cdot S\) .............................................................................................(11)

\(DCE_i + S \xleftarrow{K_{DCE_i}} DCE_i \cdot S\) \((i=1,1\text{-DCE, trans-1,2-DCE, cis-1,2-DCE})\) ......................................(12)

\(VC + S \xleftarrow{K_{VC}} VC \cdot S\) ....................................................................................................(13)

\(\text{ethene} + S \xleftarrow{K_{\text{ethene}}} \text{ethene} \cdot S\) ...............................................................................(14)

\(\text{ethane} + S \xleftarrow{K_{\text{ethane}}} \text{ethane} \cdot S\) ...............................................................................(15)

\(\text{butene} + S \xleftarrow{K_{\text{butene}}} \text{butene} \cdot S\) ...............................................................................(16)

\(\text{bu tan} e + S \xleftarrow{K_{\text{bu tan} e}} \text{bu tan} e \cdot S\) ...............................................................................(17)

\(HCl + S \xleftarrow{K_{HCl}} HCl \cdot S\) ................................................................................................(18)

Surface reactions:
\[ PCE \cdot S + H \cdot S \xrightarrow{k_{PCE}} TCE \cdot S + Cl \cdot S \] \hspace{1cm} \text{(19)}

\[ TCE \cdot S + H \cdot S \xrightarrow{k_{TCE}} DCE_i \cdot S + Cl \cdot S \] \hspace{1cm} \text{(20)}

\[ DCE_i \cdot S + H \cdot S \xrightarrow{k_{DCE_i}} VC \cdot S + Cl \cdot S \] \hspace{1cm} \text{(21)}

\[ VC \cdot S + H \cdot S \xrightarrow{k_{VC}} Ethene \cdot S + Cl \cdot S \] \hspace{1cm} \text{(22)}

\[ ethene \cdot S + 2H \cdot S \xrightarrow{k_{ethene}} ethane \cdot S + S \] \hspace{1cm} \text{(23)}

\[ ethene \cdot S + ethene \cdot S \xrightarrow{k_{ethene}} butene \cdot S + S \] \hspace{1cm} \text{(24)}

\[ butene \cdot S + H \cdot S \xrightarrow{k_{butene}} butene \cdot S + S \] \hspace{1cm} \text{(25)}

\[ Cl \cdot S + H \cdot S \xrightarrow{k_{Cl}} HCl \cdot S + S \] \hspace{1cm} \text{(26)}

\(^a\) S represents catalytic active sites.

By solving the adsorption and desorption equations (1-26), we obtain the concentrations of surface activated species as in the following equations (27-37):

\[ [H \cdot S] = \sqrt{K_{H_2}[H_2] \times [S]_0} \] \hspace{1cm} \text{(27)}

\[ [PCE \cdot S] = K_{PCE}[PCE] \times [S]_0 \] \hspace{1cm} \text{(28)}

\[ [TCE \cdot S] = K_{TCE}[TCE] \times [S]_0 \] \hspace{1cm} \text{(29)}

\[ [DCE_i \cdot S] = K_{DCE_i}[DCE_i] \times [S]_0 \] \hspace{1cm} \text{(30)}

\[ [VC \cdot S] = K_{VC}[VC] \times [S]_0 \] \hspace{1cm} \text{(31)}

\[ [ethene \cdot S] = K_{ethene}[ethene] \times [S]_0 \] \hspace{1cm} \text{(32)}

\[ [ethane \cdot S] = K_{ethane}[ethane] \times [S]_0 \] \hspace{1cm} \text{(33)}

\[ [butene \cdot S] = K_{butene}[butene] \times [S]_0 \] \hspace{1cm} \text{(34)}

\[ [butene \cdot S] = K_{butene}[butene] \times [S]_0 \] \hspace{1cm} \text{(35)}

\[ [Cl \cdot S] = \frac{K_{HCl}[HCl]}{K_{Cl-HCl} \times \sqrt{K_{H_2}[H_2]}} \times [S]_0 \] \hspace{1cm} \text{(36)}
\[ [HCl \cdot S] = K_{HCl} [HCl] \times [S]_0 \] ....................................................................................................................(37)

The concentration of active sites is balanced by the following equation (38):

\[ [S]_{total} = [S]_0 + [H \cdot S] + [PCE \cdot S] + [TCE \cdot S] + [DCE_i \cdot S] + [VC \cdot S] + [ethene \cdot S] + [ethane \cdot S] + [butene \cdot S] + [butane \cdot S] + [Cl \cdot S] + [HCl \cdot S] \] ............(38)

Simplifications 1:

1. Mass balance calculation and experimental data both showed that the amount of \( H_2 \) did not drop during the reaction. Thus, it is reasonable to make the assumption \( [H_2] = [H_2]_0 \).

2. TCE, DCE isomers, VC, and ethene are intermediates. Their concentrations are too low to compete with surface adsorption with PCE.

3. Ethane, butene, butane and HCl are products generated. Under experimental condition, their adsorptions to active sites are too weak to compete with PCE.

Then,

\[ [S]_0 = \frac{\alpha [S]_{total}}{1 + \beta [PCE]} \] .................................................................................................................... (39)

where \( \alpha = \frac{1}{1 + K_{H_2} [H_2]_0} \), \( \beta = \sqrt{K_{H_2} [H_2]_0 \alpha [S]_{total}} \).

Simplifications 2:

1. Surface reactions are the rate limiting steps.

2. Forward reaction is much faster than backward reaction, thus neglecting backward reaction is acceptable.

Then,
\[
\frac{d[PCE \cdot S]}{dt} = -k_{PCE} [PCE \cdot S][H \cdot S] = -k_{PCE} K_{PCE} \sqrt{K_{H_2} [H_2]} \alpha^2 [S]^{\text{total}} \frac{[PCE]}{(1 + \beta [PCE])^2} \quad \text{(40)}
\]

If the concentration of PCE is very low, then \( \beta [PCE] \) is small enough to be negligible compared with 1. Then,

\[
\frac{d[PCE]}{dt} = \frac{d[PCE \cdot S]}{dt} \times K_{PCE} [S]_0 = -\beta k_{PCE} [PCE] \quad \text{(41)}
\]

In this regime, the degradation of PCE follows pseudo 1st order reaction kinetic which has been substantiated by the good linearity of \( \ln(C/C_0) \) vs. time data using 16.6 ppm PCE. Thus, it is reasonable to model the PCE surface reaction with 1st order kinetic in our study.

The differential equations describing the liquid phase concentrations of all the rest species are then developed as listed below:

\[
\frac{d[TCE]}{dt} = \frac{d[TCE \cdot S]}{dt} \times K_{TCE} [S]_0 = \beta \times (k_{TCE} K_{PCE} [PCE] - \sum_i k_{TCE_i} [TCE_i]) \quad \text{(42)}
\]

\[
\frac{d[DCE_i]}{dt} = \beta \times (k_{TCE_i} K_{TCE} [TCE] - k_{DCE_i} [DCE_i]) \quad (i=1,1-DCE, \text{trans}-1,2-DCE, \text{cis}-1,2-DCE) \quad \text{(43)}
\]

\[
\frac{d[VC]}{dt} = \beta \times (\sum_i k_{DCE_i} K_{DCE} [DCE_i] - k_{VC} [VC]) \quad \text{(44)}
\]

\[
\frac{d[ethene]}{dt} = \beta \times \frac{K_{VC}}{K_{ethene}} k_{ethene} [VC] - \beta^2 \times k_{ethene} [ethene] - 2\alpha [S]^{\text{total}} K_{ethene} k_{ethene}^2 [ethene]^2 \quad \text{(45)}
\]

\[
\frac{d[butene]}{dt} = \alpha [S]^{\text{total}} \times K_{ethene}^2 k_{ethene}^2 [ethene]^2 - \beta \times k_{butene} [butene] \quad \text{(46)}
\]

\[
\frac{d[butane]}{dt} = \beta \times \frac{K_{butene}}{K_{butane}} k_{butene} [butene] \quad \text{(47)}
\]

\[
\frac{d[ethane]}{dt} = \beta^2 \times \frac{K_{ethene}}{K_{ethene}} k_{ethene} [ethene] \quad \text{(48)}
\]
As the concentrations of ethene were detected to be zero or trace for all three catalysts, the mathematical fitting of Eqn. 48 based on [ethene] will become problematic. To minimize the fitting error, Pseudo Steady State Hypothesis (PSSH) can be applied for ethene so that Eqn. 48 could be solved with VC experimental data:

\[
\frac{d[\text{ethene}]}{dt} = \beta \times \frac{K_{\text{VC}}}{K_{\text{ethene}}} k_{\text{VC}}[\text{VC}] - \beta^2 \times k_{\text{ethene}_1}[\text{ethene}] - 2\alpha[S]_{\text{total}} K_{\text{ethene}} k_{\text{ethene}_2}[\text{ethene}]^2
\]

\[
\approx \beta \times \frac{K_{\text{VC}}}{K_{\text{ethene}}} k_{\text{VC}}[\text{VC}] - \beta^2 \times k_{\text{ethene}_1}[\text{ethene}] \approx 0
\]

\[
\frac{d[\text{ethane}]}{dt} = \beta \times \frac{K_{\text{VC}}}{K_{\text{ethane}}} k_{\text{VC}}[\text{VC}]
\]

Since [VC] profile was not fitted for Pd/Al2O3 as its concentration was too low, a constant number of [VC] averaged from the experimental values instead was used to fit Eqn. 50 for Pd/Al2O3.
Table S2.3. Fitted kinetic parameters using modified Langmuir-Hinshelwood kinetics model.

<table>
<thead>
<tr>
<th>Species</th>
<th>Fitted kinetic parameters</th>
<th>60 sc% Pd-on-Au NPs</th>
<th>Pd NPs</th>
<th>Pd/Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCE</td>
<td>$\beta k_{PCE}$</td>
<td>0.082 ± 0.006</td>
<td>0.015 ± 0.001</td>
<td>0.093 ± 0.007</td>
</tr>
<tr>
<td>TCE</td>
<td>$\frac{K_{PCE}}{K_{TCE}}$</td>
<td>0.29 ± 0.02</td>
<td>0.0034 ± 0.0003</td>
<td>0.019 ± 0.002</td>
</tr>
<tr>
<td></td>
<td>$\beta \sum_{i} k_{TCE_i}$</td>
<td>0.51 ± 0.03</td>
<td>0.075 ± 0.007</td>
<td>1.5 ± 0.12</td>
</tr>
<tr>
<td>DCE’s</td>
<td>$\beta k_{TCE_i}$ $\frac{K_{TCE}}{K_{DCE_i}}$</td>
<td>$i=$1,1-DCE 0.30 ± 0.03</td>
<td>0.015 ± 0.001</td>
<td>0.20 ± 0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$i=$cis-1,2-DCE 0.11 ± 0.01</td>
<td>0.0048 ± 0.0003</td>
<td>0.14 ± 0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$i=$trans-1,2-DCE 0.007 ± 0.0006</td>
<td>0.0011 ± 0.0001</td>
<td>0</td>
</tr>
<tr>
<td>DCE’s</td>
<td>$\beta k_{DCE_i}$</td>
<td>$i=$1,1-DCE 0.70 ± 0.06</td>
<td>0.040 ± 0.003</td>
<td>0.70 ± 0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$i=$cis-1,2-DCE 0.30 ± 0.03</td>
<td>0.020 ± 0.001</td>
<td>0.80 ± 0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$i=$trans-1,2-DCE 0.50 ± 0.05</td>
<td>0.080 ± 0.007</td>
<td>0</td>
</tr>
<tr>
<td>VC</td>
<td>$\beta \sum_{i} k_{DCE_i} \frac{K_{DCE_i}}{K_{VC}}$</td>
<td>0.90 ± 0.3</td>
<td>0.35 ± 0.12</td>
<td>Not fitted</td>
</tr>
<tr>
<td>VC</td>
<td>$\beta k_{VC}$</td>
<td>0.90 ± 0.3</td>
<td>0.11 ± 0.04</td>
<td>Not fitted</td>
</tr>
<tr>
<td>ethane</td>
<td>$\beta \times \frac{K_{VC}}{K_{ethane}} k_{VC}$</td>
<td>0.50 ± 0.04</td>
<td>0.064 ± 0.006</td>
<td>0.56 ± 0.04</td>
</tr>
</tbody>
</table>

Complete Matlab code:

```matlab
function dc=hdcsolver1(t,c,k1)
    dc=zeros(1,1);
    dc(1)=-k1*c(1); %PCE
end

function dc=hdcsolver2(t,c,k2)
    dc=zeros(2,1);
    dc(1)=-k1*c(1); %PCE
    dc(2)=k2(1)*c(1)-k2(2)*c(2); %TCE
```
function dc=hdcsolver3(t,c,k3)
dc=zeros(3,1);
dc(1)=-k1*c(1);  %PCE
dc(2)=k21*c(1)-k22*c(2);  %TCE
dc(3)=k3(1)*c(2)-k3(2)*c(3);  %1-1DCE
end

function dc=hdcsolver4(t,c,k4)
dc=zeros(3,1);
dc(1)=-k1*c(1);  %PCE
dc(2)=k21*c(1)-k22*c(2);  %TCE
dc(3)=k4(1)*c(2)-k4(2)*c(3);  %cis-dce
end

function dc=hdcsolver5(t,c,k5)
dc=zeros(3,1);
dc(1)=-k1*c(1);  %PCE
dc(2)=k21*c(1)-k22*c(2);  %TCE
dc(3)=k5(1)*c(2)-k5(2)*c(3);  %trans-dce
end

function dc=hdcsolver6(t,c,k6)
dc=zeros(6,1);
dc(1)=-k1*c(1);  %PCE
dc(2)=k21*c(1)-k22*c(2);  %TCE
dc(3)=k31*c(2)-k32*c(3);  %1-1-dce
dc(4)=k41*c(2)-k42*c(4);  %cis-dce
dc(5)=k51*c(2)-k52*c(5);  %trans-dce
dc(6)=k6(1)*(c(3)+c(4)+c(5))-k6(2)*c(6);  %VC
end
function dc=hdcsolver7(t,c,k7)
dc=zeros(7,1);
dc(1)=-k1*c(1); %PCE
dc(2)=k21*c(1)-k22*c(2); %TCE
dc(3)=k31*c(2)-k32*c(3); %1-1-dce
dc(4)=k41*c(2)-k42*c(4); %cis-dce
dc(5)=k51*c(2)-k52*c(5); %trans-dce
dc(6)=k61*(c(3)+c(4)+c(5))-k62*c(6); %VC
dc(7)=k7(1)*c(6); %Ethane
end

function y=trial(k,tspan)
global y0
tspan=[0:0.1:52.1];
[tt y] = ode45(@hdcsolver,tspan,y0,[],k);
end

clc;clear;
global y0
data=load('load.txt');
tdata=data(:,1)';cdata=data(:,2:8)';
k0= [1,1,1,1,1,1,1,1,1,1,1,1];
lb=[0,0,0,0,0,0,0,0,0,0,0,0];
ub=[10,10,10,10,10,10,10,10,10,10,10,10];
options=optimset('TolFun',1e-20,'TolX',1e-20,'MaxFunEvals',100,'Algorithm','trust-region-reflective','Display','iter');
beta=lsqcurvefit(@trial,k0,tdata,cdata,lb,ub,options);
optimtool;%change to L-M algorithm if default does not work
Jc=trial(k,tdata);
plot(tdata,cdata,'o',tdata,Jc);

load.txt
<table>
<thead>
<tr>
<th>Time</th>
<th>Value 1</th>
<th>Value 2</th>
<th>Value 3</th>
<th>Value 4</th>
<th>Value 5</th>
<th>Value 6</th>
<th>Value 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100.6397</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.4544</td>
<td>90.4052</td>
<td>2.2992</td>
<td>0.0800</td>
<td>0.2131</td>
<td>0.0099</td>
<td>0.2399</td>
<td></td>
</tr>
<tr>
<td>1.0905</td>
<td>78.4649</td>
<td>3.7284</td>
<td>0.1400</td>
<td>0.4261</td>
<td>0.0213</td>
<td>0.4799</td>
<td></td>
</tr>
<tr>
<td>3.1991</td>
<td>57.3135</td>
<td>3.7092</td>
<td>0.3399</td>
<td>0.5468</td>
<td>0.0270</td>
<td>0.8197</td>
<td></td>
</tr>
<tr>
<td>7.6963</td>
<td>35.1386</td>
<td>2.6241</td>
<td>0.3119</td>
<td>0.3977</td>
<td>0.0213</td>
<td>0.7598</td>
<td></td>
</tr>
<tr>
<td>10.8377</td>
<td>20.8103</td>
<td>1.4495</td>
<td>0.2599</td>
<td>0.2486</td>
<td>0.0170</td>
<td>0.6598</td>
<td></td>
</tr>
<tr>
<td>13.1763</td>
<td>11.5992</td>
<td>0.8247</td>
<td>0.1719</td>
<td>0.1562</td>
<td>0.0085</td>
<td>0.3999</td>
<td></td>
</tr>
<tr>
<td>14.2031</td>
<td>7.3334</td>
<td>0.4998</td>
<td>0.1360</td>
<td>0.0781</td>
<td>0</td>
<td>0.2399</td>
<td></td>
</tr>
<tr>
<td>14.8101</td>
<td>4.4376</td>
<td>0.2499</td>
<td>0.0600</td>
<td>0.0014</td>
<td>0</td>
<td>0.1600</td>
<td></td>
</tr>
<tr>
<td>15.2048</td>
<td>2.0469</td>
<td>0.1749</td>
<td>0.0200</td>
<td>0</td>
<td>0</td>
<td>0.0800</td>
<td></td>
</tr>
<tr>
<td>15.6121</td>
<td>1.3646</td>
<td>0.0625</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>
2.7. References


90. Palladium, 0.3-1% on Alumina Catalysts (Pd/Al2O3), Kaida Technology Limited. 2006 http://www.kaida.co.uk/palladium-3-2.html.

Chapter 3

Volcano-shape Glycerol Oxidation Activity of Palladium-decorated Gold Nanoparticles

3.1. Introduction

Glycerol, a polyalcoholic compound with uses ranging from cosmetics, soaps, and pharmaceuticals to a chemical precursor for polyethers, polyols, polyesters, and alkyd resins manufacturing [1-3], has recently become an abundant and inexpensive compound due to its generation as a byproduct in biodiesel, oleo-chemical and bioethanol production processes [4-6]. The tremendous growth of these industries has led to a significant decrease in crude glycerol prices during recent years (from $0.25/lb in 2004 to ~$0.08/lb in 2011), leading to interest in the development of new and improved methods to generate higher-value products from glycerol [7].

Over the last 10 years, the selective oxidation of glycerol using supported precious metal catalysts, such as Pt, Pd, and Au, has been extensively studied.[8-13] Investigated for the selective oxidation of mono alcohols and diols under mild conditions [14-17], Au catalysts were shown by Carrettin et al. to be very active for glycerol oxidation at high-pH conditions, with 100% selectivity to glyceric acid [11, 13]. Other researchers reported that Au catalysts were more active than Pd catalysts at high pH, but also less selective to glyceric acid [18-23]. The inconsistency in literature probably stems from differences in preparation method, nanoparticle
size, support composition, and reaction conditions (e.g., pH, temperature, initial concentration of glycerol, and O$_2$ pressure) [20-26]. Nevertheless, the presence of base (typically NaOH) is required for Au catalysis to deprotonate glycerol [19, 27, 28]. Davis and co-workers showed that oxygen atoms originate from hydroxyl groups instead of molecular oxygen during glycerol oxidation by Au and Pt [19].

In comparison, supported Pd catalysts are active for glycerol oxidation under a wide range of pH values, with maximum glycerol oxidation activities found at high-pH conditions [13, 19, 29]. At neutral or acidic conditions, they favor the formation of dihydroxyacetone (from the oxidation of secondary alcoholic group of glycerol) and C$_1$/C$_2$ molecules (from cleavage of a glycerol C-C bond) [19, 30]. However, Pd catalysts can become over-oxidized, reducing their glycerol oxidation activity [10, 14, 31, 32]. Pd is also susceptible to poisoning by in situ-generated carbon monoxide.

PdAu catalysts have been studied by several research groups for glycerol oxidation. Hutchings and co-workers prepared Pd-Au alloyed nanoparticles (NPs) immobilized on activated carbon, and showed they were significantly more active than supported monometallic Pd and Au NPs [21]. They concluded that higher surface fraction of Au contributed to higher activity and selectivity to glyceric acid. They further showed that alloyed Pd-Au NPs immobilized on MgO were active for glycerol oxidation under base-free conditions with glyceric acid as the main product [33].

Prati and co-workers have extensively examined the effects of reaction conditions (e.g., catalyst amount, temperature, pressure, and NaOH amount) and catalyst preparation methods (e.g., sequence of metal salt reduction, reducing and stabilizing agent, particle size, and support) [20, 22-26, 34, 35]. They reported that simultaneous reduction of Pd and Au salts led to more
active and selective catalysts, compared to catalysts resulting from sequential reductions [25]. They observed a decrease in activity and an increase in glyceric acid as particle size increased (for Pd, Au, and PdAu compositions) [22]. The bimetallic catalysts were more active than either monometallic Pd and Au catalysts; the most active composition was a Pd/Au atomic ratio of 10/90 with 1wt% total metal loading on activated carbon [23, 26].

Davis and co-workers synthesized Au-covered Pd NPs through Au salt reduction onto activated carbon-supported Pd NPs [12]. The resulting AuPd bimetallic catalysts were less active than monometallic Au but more selective to glyceric acid. They proposed that Pd kept the Au metal in a highly dispersed form which decreased the formation of H$_2$O$_2$ that was responsible for C-C bond cleavage [12].

Despite these efforts, there remains limited understanding about how the bimetallic structure affects glycerol oxidation. We propose Pd-coated Au nanoparticles (Pd-on-Au NPs) can be used to address this issue, by allowing for a systematic study of Pd surface coverage effects. The synthesis involves the reduction of palladium salt species onto colloidal Au NPs at ambient conditions using H$_2$ gas, and surface coverage is readily controlled through the amount of Pd precursor added. Previously, we investigated the structure-property relationship of Pd-on-Au NPs for the catalytic hydrodechlorination (HDC) of trichloroethene (TCE) and other organochlorides [36-42]. The catalytic NPs showed a volcano-shaped TCE HDC activity dependence on Pd surface coverage, and had significantly higher activity and greater deactivation resistance to chloride and sulfide ions than monometallic Pd catalysts. XAS (x-ray absorption spectroscopy) analysis confirmed the Au-core, Pd-shell structure of the NPs [39, 40]. Pd-on-Au NPs can carry out HDC reduction reactions, but have not been studied in oxidation reactions before.
This study reports the catalytic behavior of carbon-supported bimetallic Pd-on-Au NPs for the water-phase oxidation of glycerol as a function of Pd surface coverage. Au NPs with a diameter of 4 nm were decorated with Pd metal and immobilized onto carbon support. The catalytic activity of these materials was tested using a semi-batch reactor, and activity was reported in terms of metal-normalized first-order rate constant $k_{\text{cat}}$ and initial turnover frequency values (corrected for mass transfer effects and normalized to surface metal atoms). Catalytic activity, selectivity to glyceric acid, and deactivation resistance were quantified in relation to Pd surface coverage. Selectivity values were extrapolated to zero glycerol conversion to differentiate the primary and secondary reaction products as a function of catalyst composition also. *ex situ* XAS spectroscopy analysis of selected samples before and after reactions was carried out to assess the oxidative reaction conditions on the state of the two metals. This work has been published as: Z. Zhao, J. Arentz, L. A. Pretzer, P. Limpornpipat, J. M. Clomburg, R. Gonzalez, N. M. Schweitzer, T. Wu, J. T. Miller, M. S. Wong, "Volcano-shape glycerol oxidation activity of palladium-decorated gold nanoparticles" *Chemical Science*, online (2014) [43].

### 3.2. Experimental

#### 3.2.1. Catalyst Preparation

##### 3.2.1.1. Monometallic NPs

Aqueous monometallic gold and palladium nanoparticles (Au NPs, Pd NPs) were synthesized through a tannic acid-sodium citrate reduction method [37, 44]. The synthesis details are found in Supporting Information.

##### 3.2.1.2. Bimetallic Pd-on-Au NPs
Bimetallic Pd-on-Au NPs were prepared by adding, then subsequently reducing, the Pd salt precursor in the Au sol with hydrogen gas. Utilizing the magic cluster model, we calculated the specific volumes of 2.49 mM H$_2$PdCl$_4$ sol needed to add in the Au NPs sol for various surface coverages (sc%) on the Au NP [36, 37]. To prepare Pd-on-Au NPs with Pd surface coverages of 10, 30, 50, 60, 80, 100, 150 and 300 sc%, corresponding Pd solution volumes of 0.92, 2.77, 4.62, 5.55, 7.39, 9.24, 15.1, and 35.4 mL were added dropwise to 201 mL of the Au sol under vigorous stirring. The mixture was stirred at ~1000 rpm for an additional 15 min followed by H$_2$ gas (99.99%, Matheson) bubbling at a flow rate of ~200 mL/min through the liquid for 30 min. All resultant Pd-on-Au sols had the same total number of NPs ($1.07\times10^{14}$ NP/mL × 201 mL) and color (brownish red) as the parent Au sol.

3.2.1.3. Carbon supported NPs

Prior to catalysis, NPs were immobilized onto activated carbon. For a carbon-supported Au catalyst with a loading of 1 wt% Au (Au/C), 1.0 g of activated carbon (Darco G-60, Sigma-Aldrich) was added to 201 mL of Au NP sol (49.7 mg Au/L). The mixture was stirred for ~24 h at 700 rpm, cooled to 4 °C, and centrifuged for 40 min at 14,000 rpm. The carbon slurry was collected and dried in a vacuum oven at 70 °C overnight until no further mass loss from evaporated water was observed. The material was then ground into powder form and stored in the dark at ambient conditions. Activated carbon, in the untreated (“as-is” carbon) and treated forms (“as-processed” carbon), was used for control experiments.

For carbon-supported Pd-on-Au catalysts, the immobilization procedure was the same except that the as-synthesized Pd-on-Au sols were used in place of the Au sol. The Au loading for all Pd-on-Au/C catalysts was kept constant at 1 wt%, while the Pd loading varied according to the Pd surface coverage. Specifically, 10, 30, 50, 60, 80, 100, 150 and 300 sc% Pd-on-Au/C
catalysts have calculated Pd loadings of 0.025, 0.074, 0.123, 0.147, 0.196, 0.245, 0.400, and 0.938 wt%, respectively. Carbon-supported with 1 wt% Pd (Pd/C) was prepared in the same manner by mixing 314 mL of Pd sol (31.8 mg Pd/L) with 1.0 g of activated carbon.

3.2.2. Catalyst Characterization

Synthesized catalyst samples were characterized with transmission electron microscopy, nitrogen physisorption, inductively coupled plasma-atomic emission spectroscopy and X-ray absorption spectroscopy [37, 39].

3.2.2.1. Transmission Electron Microscopy (TEM)

The colloidal NPs and NP/C solid samples were imaged using a JEOL 2010 transmission electron microscope (TEM). TEM samples were prepared by depositing droplets of sol or methanol-suspended NP/C (0.2 mg/mL) onto 200-mesh carbon/Formvar TEM grids, and then dried at room temperature. The ImageJ program was used for the size distribution measurements [45]; at least 250 particles were measured from each sample.

3.2.2.2. Nitrogen Physisorption Studies

Specific surface area measurements were performed on a Micromeritics ASAP 2010 gas adsorption analyzer using ultrahigh purity nitrogen (Matheson). Samples were vacuum-dried overnight (>8 h) at 250 °C until the rate of degassing was less than 4×10^{-3} mmHg/min. The specific surface area was calculated using the BET (Brunauer–Emmett–Teller) equation in the P/P_0 range of 0.06-0.20 with 5 points.

3.2.2.3. X-ray Absorption Spectroscopy (XAS)

Au L_3 (11.919 keV) or Pd K (24.350 keV) edge XAS measurements were carried out on the insertion and bending magnet devices (beamline 10-ID-B and 10-BM-B) of the Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon Source at Argonne.
National Laboratory. The X-ray beam was $0.5 \times 0.5 \text{ mm}^2$ at the ID beamline and $0.5 \times 2.0 \text{ mm}^2$ at the BM beamline, and measurements were made in transmission mode with the ionization chambers optimized for maximum current with linear response, and were obtained simultaneously with Au or Pd foil spectra for energy calibration. The collected XAFS (x-ray absorption fine structure) spectra span the extended x-ray absorption fine structure (EXAFS) and x-ray absorption near edge structure (XANES) energy ranges. XANES is typically used to evaluate the metal oxidation state and the fraction of reduced and oxidized metal species. To determine the extent of oxidized Pd and Au, the Pd K edge and Au L$_3$ edge XANES spectra were firstly normalized and energy calibrated. The spectra were then least-square fitted with a linear combination of the catalyst in 100% reduced form (treated at 200 °C under 4% H$_2$/He for ~30 min, purged with He and cooled to room temperature) and a corresponding 100% oxidized form (metal salts of PdO and AuCl$_3$).[46] Additional instrumentation and spectral analysis details are found in our previous studies [39, 40].

Catalysts were treated in a continuous-flow reactor, which consisted of a quartz tube (1 inch OD, 10 inch length) sealed with Kapton windows by two Ultra-Torr fittings. Ball valves were welded to each Ultra-Torr fitting and served as the gas inlet and outlet. An internal K type thermocouple (Omega) was placed against the catalyst sample holder to monitor temperature. Catalyst samples were pressed into a cylindrical sample holder consisting of six wells, forming a self-supporting wafer. The catalyst amount used was calculated to give an absorbance ($\mu x$) of approximately 1.0. XAS spectra were collected on the reduced samples and in air at room temperature. A minimum metal loading of 1 wt% for both Pd and Au was needed for a satisfactory signal-to-noise ratio in the collected XAS spectra. Two compositions representative of <100 sc% and >100 sc% NPs were chosen: 60 sc% Pd-on-Au and 150 sc% Pd-on-Au. For the
60 sc% Pd-on-Au/C sample, 1407 mL of sol were mixed with 1 g of C, followed by the rest of the immobilization procedure described in Section 2.1.3. The resulting solid was calculated to have 1 wt% Pd and 6.8 wt% Au. For the 150 sc% Pd-on-Au/C sample, 542 mL of sol were mixed with 1 g of C; the calculated metal contents were 1 wt% Pd and 2.5 wt% Au. Pd/C and Au/C used for the glycerol oxidation reaction (with the appropriate 1 wt% metal loading) were also used for XAS analysis.

Each of the 4 catalyst materials (Au/C, Pd/C, 60 sc% Pd-on-Au/C, and 150 sc% Pd-on-Au/C) were treated in two different ways, generating 8 treated samples and 4 untreated samples (as references) for XAS analysis. The "0 hr Rxn" treatment refers to catalysts charged to the reaction medium and recovered, without performing the glycerol reaction. The "3 hr Rxn" treatment refers to the catalysts charged to the reaction medium and recovered after 3 hr. of glycerol reaction time. The reaction conditions were the same as those used for catalytic testing (Section 2.3). Catalysts were recovered after immersing the bottle reactor in an ice bath to quench the reaction and bubbling the reaction medium with flowing He (>99.99%, Matheson) for 15 min. The reaction medium was cooled to 4 °C and centrifuged at 14,000 rpm for 40 min. After decanting, the carbon slurry was re-suspended in DI water and centrifuged. This wash step was repeated, and the collected samples were dried in a vacuum oven at 70 °C until no further mass loss from evaporated water was observed. XAS spectra of each sample were collected under air at room temperature.

To assess the level of any oxidation of Pd and Au, all 12 samples were then reduced in flowing 3.5% H₂ in He (50 cm³(STP) min⁻¹) at 200°C, purged with flowing He for 10 min and then cooled to room temperature. Traces of oxygen and moisture in the gases were removed by means of a purifier (Matheson PUR-Gas Triple Purifier Cartridge). Based on our previous work,
this treatment method fully reduces oxidized Pd without altering the bimetallic nanostructure [39]. These reduced samples were analyzed under He at room temperature.

3.2.3. Catalytic Testing

All NP compositions were studied for catalysis in the supported form. Glycerol oxidation was performed in a screw-cap bottle (250 mL, Alltech) sealed with a Teflon-silicone septum as a semi-batch reactor. A magnetic stirrer, 101.65 mL of DI water, 4.28 mL of NaOH solution (10 M; prepared by dissolving 40 g NaOH (≥99.5%, Sigma-Aldrich) in DI water for a final volume of 100 mL), and 1.07 mL of glycerol solution (10 M; prepared by dissolving 92.1 g of glycerol (≥99.5%, Sigma-Aldrich) in DI water for a final volume of 100 mL) were placed in the reactor such that the final liquid volume was 107 mL and the concentrations of NaOH and glycerol in the reactor were 0.4 M and 0.1 M, respectively. The reactor content was heated to 60 °C (± 0.5 °C) in a water bath, bubbled with O₂ gas (99.99%, Matheson) for 15 min, and continuously stirred at 1000 rpm. After this, O₂ was bubbled into the reaction medium at 120 mL/min and 0.2 g of catalyst was charged, marking the start of the reaction.

Aliquots of the reaction fluid (500 µL) were periodically withdrawn via a stainless steel needle, and passed through a 0.2 µm microfiber syringe filter (25 mm, VWR) and analyzed through ion-exclusion high-performance liquid chromatography (HPLC). A Shimadzu Prominence SIL 20 system (Shimadzu Scientific Instruments, Inc., Columbia, MD, USA) equipped with an HPX-87H organic acid column (Bio-Rad, Hercules, CA, USA) and a refractive index detector (RID) was used. The column was operated at 315 K, with 30 mM H₂SO₄ mobile phase flowing at 0.3 cm³/min. The retention times and concentration calibration curves were determined for the eight compounds of glycerol, glyceric acid, oxalic acid, glycolic acid, tartronic acid, formic acid, acetic acid, and lactic acid. A slight loss in liquid volume due to water
Evaporation was observed during the reaction (~3 mL volume loss after 3 hr), for which the measured concentrations were corrected.

Selectivity to a reaction product ($S_i$) was calculated as the percentage of glycerol that converted into that product, i.e., product concentration $C_i$ divided by the sum of the concentrations of the seven product compounds detected (glyceric acid, oxalic acid, glycolic acid, tartronic acid, formic acid, acetic acid, and lactic acid). The products of CO and CO$_2$ were not monitored but they were inferred to form in small amounts (Section 3.4), allowing $S_i \approx C_i/(C_{gly,0} - C_{gly})$, where $C_{gly,0}$ is the initial concentration of glycerol and $C_{gly}$ is glycerol concentration. Selectivity values were also extrapolated to zero glycerol conversion by fitting the experimentally determined selectivity values to a monotonic, third-order polynomial function.

Glycerol oxidation kinetics was modeled as a first-order reaction (Eqn. 1) with respect to glycerol (Fig. S3.1) and zero-order with respect to O$_2$ (Fig. S3.2). The apparent initial first-order reaction rate constant $k_{meas}$ (with units of h$^{-1}$) was calculated from fitting Eqn. 2 to the first 2 hr of the concentration-time profiles, where $t$ is the reaction time. For catalysts observed with deactivation, $k_{meas}$ was also calculated by fitting Eqn. 2 to the first 1 hr of the concentration-time profiles as a comparison.

$$\frac{-dC_{gly}}{dt} = k_{meas} \times C_{gly} \quad \text{(Eqn. 1)}$$

$$C_{gly} = C_{gly,0} \times e^{-k_{meas} \times t} \quad \text{(Eqn. 2)}$$

Glycerol conversion $X$ was calculated as $(C_{gly,0} - C_{gly})/C_{gly,0}$, such that product yield is $Y_i = S_i \times X$.

The metal-normalized rate constant $k_{cat}$ (with units of L/g$_{metal}$/h) was defined as $k_{meas}$ divided by the total metal content charged to the reactor ($C_{total}$):

$$k_{cat} = \frac{k_{meas}}{C_{total}} \quad \text{(Eqn. 3)}$$
To represent catalytic activity at the particle surface, initial turnover frequency (TOF) was defined as

\[ \text{TOF} = k_{\text{corr}} \times \frac{C_{\text{gly,0}}}{C_{\text{surf}}} \]  
(Eqn. 4)

(with units of mol-glycerol/mol-surface-atom/h), where \( k_{\text{corr}} \) (with units of h\(^{-1}\)) is the rate constant corrected for mass transfer effects, \( C_{\text{surf}} \) is the surface metal content of the reactor. The corrected rate constants \( k_{\text{corr}} \) were calculated from \( k_{\text{meas}} \), using a method we previously developed (see Sec. 3.2).[47] For the carbon-supported monometallic Au and Pd NPs, metal dispersions (i.e., percentage of Au or Pd atoms as surface atoms) were calculated to be 34.8% assuming 4-nm NPs were a magic cluster of 7 shells of Au or Pd atoms [37, 48-50]. For carbon-supported Pd-on-Au NPs with Pd surface coverages lesser than 100 sc\%, all Pd atoms were assumed to be surface Pd atoms in the 8\(^{th}\) shell (i.e., Pd dispersion = 100\%) and uncovered Au atoms in the 7\(^{th}\) shell were considered as exposed surface Au atoms. For Pd surface coverages greater than 100 sc\%, the surface Pd content was calculated assuming a magic cluster model of the Pd-on-Au NPs. For example, the surface atoms of 150 sc\% Pd-on-Au NPs were counted as those Pd atoms in the 9\(^{th}\) shell and those Pd atoms in 8\(^{th}\) shell that were not covered; the calculated Pd dispersion was 73.4\%.

Apparent activation energy values were determined for Au/C, 30 sc\%, 60 sc\%, 150 sc\% and 300 sc\% Pd-on-Au/C, and Pd/C catalysts by running glycerol oxidation reaction at different temperatures. Reaction was conducted at 40, 50, 60, 70, and 80 °C for each catalyst with the following reaction conditions: 0.2 g catalyst, 1000 rpm stirring rate, 107 mL, 0.1 M glycerol, 0.4 M NaOH, and 120 mL/min \( \text{O}_2 \) flow. Apparent activation energy \( E_a \) was calculated from the Arrhenius equation:

\[ k_{\text{meas}} = A \times \exp(-E_a/RT) \]  
(Eqn. 5)
by plotting the natural log of \( k_{\text{meas}} \) vs. \( 1/T \), where A is the pre-exponential factor, R is the universal gas constant, and T is the temperature in Kelvin. Each \( E_a \) value came from an average of 3 runs.

Deviation of concentration profiles from first-order reaction kinetics was observed for several catalyst compositions, which was attributed to catalyst deactivation. When deactivation is caused by poisoning, it is often modeled as a power-law decay process [51-54]. To quantify the extent of deactivation, we modeled the process as first-order in glycerol concentration:

\[
\frac{-dC_{\text{gly}}}{dt} = a \times k^{0}_{\text{meas}} \times C_{\text{gly}} \\
\]

**Equation 6**

\[
a = \exp(-k_{\text{d}} \times t) \\
\]

**Equation 7**

where \( a \) is the activity function \((a = 1 \text{ at } t = 0)\), \( k^{0}_{\text{meas}} \) is the initial reaction rate constant determined in the first 0.5 hr of reaction run, and \( k_{\text{d}} \) is the first-order deactivation rate constant. Solving Eqn. 6 and 7 leads to the equation for glycerol concentration profile accounting for deactivation:

\[
C_{\text{gly}} = C_{\text{gly},0} \times \exp(k^{0}_{\text{meas}}/k_{\text{d}} \times (\exp(-k_{\text{d}} \times t)-1)) \\
\]

**Equation 8**

For a catalyst sample then, \( k_{\text{d}} \) was determined from a \( \ln(a) \)-time profile, with the activity function determined from the natural log of the fractional glycerol concentration \((\ln(C_{\text{gly}}/C_{\text{gly},0}))\) versus time using a second-order polynomial fitting. Each \( k_{\text{d}} \) value was based on 3 experimental runs for each sample.
3.3. Results and Discussion

3.3.1. Catalyst Structure

Typical TEM images for Au NPs, 60 sc% Pd-on-Au NPs, 150 sc% Pd-on-Au NPs, Pd NPs and their immobilized forms are shown in Figure 3.1. The mean diameters (and relative standard deviations) for NPs were measured to be 4.1 nm (21%), 4.2 nm (22%), 4.2 nm (24%), and 4.2 nm (32%) for Au NPs, 60 sc% Pd-on-Au NPs, 150 sc% Pd-on-Au NPs and Pd NPs, respectively, consistent with our previous studies [37, 39, 55, 56]. The mean diameters (and relative standard deviations) for the carbon-supported NPs were measured to be 4.1 nm (23%), 4.2 nm (24%), 4.3 nm (26%) and 4.2 nm (35%) for Au/C, 60 sc% Pd-on-Au/C, 150 sc% Pd-on-Au/C, and Pd/C, respectively. Thus, this nanoparticle immobilization method has a negligible effect on the mean size and size distribution of our NPs. The immobilization procedure did not modify the NP atomic structure, as shown in our previous studies [39, 40]. The BET surface areas for Au/C, 60 sc% Pd-on-Au/C, 150 sc% Pd-on-Au/C, and Pd/C were determined to be 859, 800, 900, and 744 m$^2$/g, respectively. These values were somewhat close to the BET surface area of as-processed carbon (872 m$^2$/g) and lower than that of as-is carbon (1013 m$^2$/g), indicating some surface area loss after the immobilization method was carried out.
3.3.2. Mass Transfer Resistances Analysis

Mass transfer analysis during our glycerol oxidation reaction was performed to ensure kinetics controlled regime and to quantify mass transfer resistances for more accurate TOF calculations. The solubility of O$_2$ in 60 °C DI water is 28 mg/L (= 0.875 mM) [57] much lower than the 100 mM initial glycerol concentration in the reactor, requiring a continuous feed of O$_2$ gas through the reaction medium. Without the O$_2$ flow, the reaction was much slower and glycerol conversion was low (Fig. S3.2). Our reactor consisted of three phases: the headspace gas, liquid water, and solid catalyst. To ensure that the reaction rates were quantified properly, i.e., to account for any mass transfer resistances, we carried out the 3-phase reactor mass transfer test [47]. Specifically, we determined the observed reaction rate constant $k_{\text{meas}}$ of one of the most active catalysts (60 sc% Pd-on-Au/C catalyst) at different charges and at three different stirring rates (Figure 3.2).
Figure 3.2. The relationships between (a) observed reaction rate constant $k_{\text{meas}}$ and catalyst mass concentration, (b) $1/k_{\text{meas}}$ and $1/(\text{mass of catalyst})$ at 350, 700, and 1000 rpm stirring rates. The red circles mark the default catalyst charge and stirring rate for the glycerol oxidation reaction. The line in panel (a) was fitted with catalyst mass concentration from 0 to 1.87 g/L; the red and black lines in panel (b) were fitted with data points only within linearity (solid points). Reaction conditions: 60 sc% Pd-on-Au/C, 60 °C, 107 mL, 0.1 M glycerol, 0.4 M NaOH, and 120 mL/min O$_2$.

At a stirring rate of 1000 rpm, $k_{\text{meas}}$ values varied linearly with catalyst mass concentration from 0 to 1.87 g/L (catalyst mass from 0 to 0.2 g) (Fig. 3.2a), with the slope corresponding to $k_{\text{cat}} = 57.4$ L/g$_{\text{metal}}$/h. This value was within 10% error of $k_{\text{cat}}$ calculated using the typical catalyst charge of 0.2 g (= 21.4 mg-metal/L) for 60 sc% Pd-on-Au/C (61.0 L/g$_{\text{metal}}$/h, Table 3.1). A higher catalyst charge resulted in a sub-linear rate constant, indicating that the typical glycerol oxidation semi-batch reaction conditions (red circle, Fig. 3.2) were appropriately chosen to avoid external mass transfer limitation. Lower stirring rates reduced the $k_{\text{meas}}$ values, as a result of poor external mass transfer (Figure 3.2a). In fact, a stirring rate of 350 rpm was too low to keep the catalyst particles suspended in solution.

The values of mass transfer resistances were determined utilizing a method previously developed for TCE HDC reaction catalyzed by Pd-on-Au NPs [47]. The gas-liquid mass transfer resistance ($1/k_{\text{gl\&ag}}$) was determined to have a significant effect on the observed rate constants,
with corrected rate constants \( k_{\text{corr}} \) calculated using \( 1/k_{\text{corr}} = 1/k_{\text{meas}} - 1/k_{\text{gl}} \) (Supporting Information).

3.3.3. Glycerol Oxidation Activity of Carbon-supported Au NPs and Pd NPs

Monometallic Au/C and Pd/C catalysts were firstly tested for glycerol oxidation. The Au/C catalyst was active for glycerol oxidation (Figure 3.3a,b). Glycerol reached a conversion of \(~36\%\) after 3 hr. Glyceric acid was the major product, resulting from the oxidation of one of the two terminal OH groups. Other \( \text{C}_3 \) compounds detected were lactic acid, and tartronic acid. The \( \text{C}_2 \) compounds of oxalic acid, glycolic acid, and acetic acid and the \( \text{C}_1 \) compound of formic acid were found in smaller amounts, consistent to previous reports \([20, 21, 58]\). The carbon balance, determined by summing the carbons of the detected \( \text{C}_1, \text{C}_2 \) and \( \text{C}_3 \) compounds and dividing by initial carbon content of glycerol was \(~92\%\) at the end of the 3-hr reaction. The \(~8\%\) difference was attributed to the generation of mostly CO and \( \text{CO}_2 \) formation, which was not monitored in this study but was observed in previous studies \([13, 58]\). The pH at the end of the reaction (13.4) did not change significantly from the initial pH of 13.5. The reaction rate constants \( k_{\text{cat}} \) and initial TOF of Au/C were calculated to be 7.67 L/g_{\text{metal}}/h, and 445 h\(^{-1}\), respectively. This TOF was somewhat similar to what previous studies have reported: 321 h\(^{-1}\) for Au/graphite by Prati and coworkers \([25]\), and 500 h\(^{-1}\) for Au/C by Hutchings and coworkers \([21]\). Prati and coworkers reported TOFs of 845 and 1090 h\(^{-1}\) for Au/C catalysts in their later studies \([20, 23, 24]\), and Davis and coworkers reported a TOF value of 17 s\(^{-1}\) (= 61200 h\(^{-1}\)) for their Au/C catalyst \([12, 27, 58]\).

These variations are attributable to differences in catalyst preparation methods, Au particle size, and reaction conditions. Table S3.1 compares reaction rate constants from various published reports. Au/C prepared through sol-gel immobilization method was more active than from wet
impregnation; and smaller Au NPs, higher NaOH/glycerol mol ratio, and higher reaction temperature favored higher TOF values.

**Figure 3.3.** Glycerol oxidation using (a,b) Au/C and (c,d) Pd/C catalysts: (a,c) glycerol concentration and carbon balance, and (b,d) reaction products. Reaction conditions: 0.2 g Au/C or Pd/C, 60 °C, 1000 rpm stirring rate, 107 mL reaction volume, 0.1 M glycerol, 0.4 M NaOH, and 120 mL/min O₂ flow.

The Pd/C catalyst was more active for glycerol oxidation, reaching a conversion of ~41% at the end of 3 hr (Fig. 3c,d). The rapid drop in glycerol concentration followed by a slower decrease with time suggested an initially high reaction rate constant, followed by deactivation, as observed by others [12, 23, 24]. Pd/C was estimated to have an initial TOF of 424 h⁻¹, close to that of Au/C, if deactivation was not taken into account (Table 3.1). Considering only the rapid
drop in glycerol concentration within the first 0.5 hr gave a higher initial TOF of 1601 h$^{-1}$. This value is somewhat close to that of commercial Pd/C catalyst and of Pd/C (2-3 nm) synthesized from sol-gel immobilization, but greater than that of sol-gel immobilized Pd/C with bigger Pd NPs size (5 nm) (Table S3.1).

The deactivation of platinum group metal catalysts in the liquid phase oxidation of alcohols has been known for decades, and is one of the major obstacles in scale-up. Besson et al. and Mallat et al. concluded that deactivation of Pt-group metal catalysts in selective oxidation of alcohols mainly came from the degradation of catalyst structure (metal particle growth or metal leaching), poisoning of the metal sites by irreversibly adsorbed species (products, by-products, or impurities), and/or over-oxidation of the surface [31, 32, 59]. Prati and coworkers proposed that Pd catalyst deactivation in ethylene glycol and glycerol oxidation was due to competitive adsorption with O$_2$ which led to more oxidized, less active Pd metal sites [10, 14]. They also observed a significant loss of Pd metal after recycle tests in the ethylene glycol oxidation reaction [14]. Zope and Davis recently showed that strong adsorption of ketone intermediates and their condensation products contributed mostly to the inhibition of Pt catalysts for glycerol oxidation [60]. The carbon balance using the Pd/C catalyst was only 79% at the end of the reaction, correlating to catalyst deactivation by undetected reaction products.
Table 3.1. Initial glycerol/metal mole ratios and catalytic activity results for carbon-immobilized Au, Pd, and Pd-on-Au NPs. Reaction condition: 0.2 g catalyst, 60 ºC, 1000 rpm stirring rate, 107 mL, 0.1 M glycerol, 0.4 M NaOH, and 120 mL/min O₂ flow. Each reaction rate constant was the average of three runs.

<table>
<thead>
<tr>
<th>Catalyst type</th>
<th>Glycerol/metal mol ratio</th>
<th>Glycerol conversion after 3 hr reaction (%)</th>
<th>Carbon balance after 3 hr reaction (%)</th>
<th>Reaction rate constants&lt;sup&gt;a&lt;/sup&gt;</th>
<th>k&lt;sub&gt;meas&lt;/sub&gt; (h&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>k&lt;sub&gt;cat&lt;/sub&gt; (L/g&lt;sub&gt;metal&lt;/sub&gt;/h)</th>
<th>k&lt;sub&gt;corr&lt;/sub&gt; (h&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>TOF (h&lt;sup&gt;-1&lt;/sup&gt;)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>C&lt;sub&gt;received&lt;/sub&gt;</td>
<td>-</td>
<td>0</td>
<td>-</td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C&lt;sub&gt;processed&lt;/sub&gt;</td>
<td>-</td>
<td>0</td>
<td>-</td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Au/C</td>
<td>1054:1</td>
<td>36.1</td>
<td>91.8</td>
<td></td>
<td>0.15</td>
<td>7.7</td>
<td>0.13</td>
<td>445</td>
</tr>
<tr>
<td>10 sc%</td>
<td>1054:1</td>
<td>23230:1</td>
<td>58.7</td>
<td>92.7</td>
<td>0.30</td>
<td>15.5</td>
<td>0.32</td>
<td>809</td>
</tr>
<tr>
<td>30 sc%</td>
<td>1054:1</td>
<td>7743:1</td>
<td>82.3</td>
<td>79.7</td>
<td>0.58</td>
<td>28.3</td>
<td>0.63</td>
<td>1582</td>
</tr>
<tr>
<td>50 sc%</td>
<td>1054:1</td>
<td>4646:1</td>
<td>96.7</td>
<td>76.7</td>
<td>1.04</td>
<td>49.0</td>
<td>1.25</td>
<td>3036</td>
</tr>
<tr>
<td>60 sc%</td>
<td>1054:1</td>
<td>3872:1</td>
<td>98.0</td>
<td>75.7</td>
<td>1.32</td>
<td>61.0</td>
<td>1.68</td>
<td>4038</td>
</tr>
<tr>
<td>80 sc%</td>
<td>1054:1</td>
<td>2904:1</td>
<td>99.4</td>
<td>76.3</td>
<td>1.83</td>
<td>81.0</td>
<td>2.59</td>
<td>6076</td>
</tr>
<tr>
<td>100 sc%</td>
<td>1054:1</td>
<td>2323:1</td>
<td>98.4</td>
<td>75.9</td>
<td>1.60</td>
<td>67.8</td>
<td>2.14</td>
<td>4915</td>
</tr>
<tr>
<td>150 sc%</td>
<td>1054:1</td>
<td>1423:1</td>
<td>95.2</td>
<td>79.3</td>
<td>1.59</td>
<td>60.1</td>
<td>2.13</td>
<td>4084</td>
</tr>
<tr>
<td>300 sc%</td>
<td>1054:1</td>
<td>607:1</td>
<td>94.7</td>
<td>78.1</td>
<td>1.43</td>
<td>39.1</td>
<td>1.86</td>
<td>2728</td>
</tr>
<tr>
<td>Pd/C</td>
<td>-</td>
<td>569:1</td>
<td>41.2</td>
<td>79.1</td>
<td>0.22</td>
<td>12.0</td>
<td>0.23</td>
<td>424</td>
</tr>
</tbody>
</table>

<sup>a</sup>First-order reaction rate constants were calculated using data points in the first 2 hr. Reaction rate constants in parentheses were calculated from the first 0.5 hr of the concentration-time profile for Pd/C, and for the first 1 hr of the concentration-time profile for 100, 150, and 300 sc% Pd-on-Au/C catalysts.

<sup>b</sup>Units of initial TOF are mol-glycerol/mol-surface-atom/h.

3.3.4. Glycerol Oxidation Activity of Carbon-supported Pd-on-Au NPs

In comparison, the bimetallics showed very different catalysis behavior. After 3 hr, glycerol conversion reached ~98% with 60 sc% Pd-on-Au/C, indicating a much more active catalyst compared to Au/C and Pd/C (Figs. 3.4 and S3.5a). This sample had the same Au loading as Au/C (1.0 wt% Au loading) and the reactions were carried out under the same conditions (glycerol:Au
= 1054:1). The presence of surface Pd atoms (0.025 wt% Pd loading) greatly increased the TOF (4038 h\(^{-1}\)) by 9.1 times over that of Au/C (445 h\(^{-1}\)) and Pd/C (424 h\(^{-1}\)). The pH decreased from 13.5 to 13.3 over the course of the reaction, indicating negligible pH change (Fig. S3.3).

**Figure 3.4.** Reaction profile of glycerol oxidation reaction using 60 sc% Pd-on-Au/C catalyst (a) glycerol and carbon balance, and (b) reaction products. Reaction conditions: 0.2 g 60 sc% Pd-on-Au/C, 60 °C, 1000 rpm stirring rate, 107 mL, 0.1 M glycerol, 0.4 M NaOH, and 120 mL/min O\(_2\) flow.

The reaction rates of Pd-on-Au NPs with varying surface coverages were quantified in the same fashion (Table 3.1). The conversion-time profiles for all catalyst compositions followed first-order kinetics well (Fig. S3.4). The effect of Pd surface coverage on catalytic activity was strong, as seen by the volcano plots of k\(_{\text{cat}}\) and initial TOF (Fig. 3.5a,b). Since the k\(_{\text{cat}}\) values are based on total Au and Pd metal content, the initial TOF values (normalized to total surface Au and Pd atoms) more realistically reflects the catalytic activity of the materials. Observed previously for reduction reactions, *i.e.*, hydrodechlorination (HDC) of chlorinated ethenes [37, 40, 56, 61], the volcano dependence on Pd surface coverage is seen clearly for an oxidation reaction for the first time. The most active catalyst was 80 sc% Pd-on-Au/C, which was 13.7×
and 14.3× more active than Au/C and Pd/C catalysts, respectively, based on initial TOF's. In fact, all Pd-on-Au compositions were more active than the monometallic forms.

**Figure 3.5.** Plots of (a) $k_{\text{cat}}$, (b) initial TOF, (c) apparent activation energy, and (d) deactivation constant values with Pd surface coverage. Reaction conditions for (a), (b), and (d): 0.2 g catalyst, 60 °C, 1000 rpm stirring rate, 107 mL, 0.1 M glycerol, 0.4 M NaOH, and 120 mL/min O$_2$ flow. Reaction temperature range for (c): 40-80 °C.

3.3.5. Glycerol Oxidation Selectivity

Selectivity profiles to various products were extensively analyzed for all catalysts to understand reaction mechanism better and to infer its dependence on Pd surface coverage. For all compositions, the main reaction product was glyceric acid, determined at 30% glycerol
conversion. The next largest quantity was lactic acid, followed by tartronic acid (Table S3.2, Fig. S3.5b). Au/C produced less glyceric acid and more tartronic acid compared to the rest of the catalysts. Pd/C was more selective towards glyceric acid than Au/C (consistent with published values) and Pd-on-Au/C catalysts.[18-23] Glyceric acid selectivity for Pd-on-Au catalysts was higher than Au/C, and it varied as a function of Pd surface coverage, with the highest selectivity detected at ~60 sc% (Fig. 3.6b). Glyceric acid selectivity for all catalysts decreased with glycerol conversion, as glyceric acid oxidized further to form tartronic acid (Fig. S3.6a). Lactic acid selectivity did not change with conversion (Fig. S3.6b). As glycerol conversion approached 100%, the glyceric acid selectivity decreased precipitously as glyceric acid out-competed glycerol for the active sites.

Product yields \( Y_i = S_i \times X \) can be calculated from selectivity-conversion plots readily (Fig. 3.6b). With Pd/C, glyceric acid yield was maximum (~22%) at a glycerol conversion of ~41%. With Au/C, glyceric acid yield was maximum (~16%) at a glycerol conversion of ~36%. Maximum yields for Pd-on-Au/C were 17%, 36%, 41%, 43%, 42%, 42%, 40%, and 38%, at 10, 30, 50, 60, 80, 100, 150, and 300 sc%, respectively.
Figure 3.6. (a) Scheme of glycerol oxidation reaction and its products; Plots of (b) glyceric acid selectivity vs. glycerol conversion and (c,d) selectivity values extrapolated to zero conversion (“initial selectivity”) for Au/C, Pd/C, and Pd-on-Au/C catalysts. Reaction conditions: 0.2 g catalyst, 60 °C, 1000 rpm stirring rate, 107 mL, 0.1 M glycerol, 0.4 M NaOH, and 120 mL/min O2 flow.

Clearer trends were gained after estimating the product selectivity values at zero glycerol conversion. The zero-conversion selectivities to glyceric acid, lactic acid and tartronic acid (C3 products) were non-zero for Au, Pd, and Pd-on-Au of all Pd surface coverages, indicating these products were primary reaction products of glycerol oxidation (Fig. 3.6c). Glyceric acid selectivity increased with Pd surface coverage from 45% (for Au/C) to 60% (for Pd/C), whereas selectivities to all other products (if formed) generally decreased. The multiple primary products
are concluded to be the result of multiple active site types activating different glycerol reaction pathways, with a majority of the active site population being glycerol-forming. The gradual change in zero-conversion selectivities must reflect the subtle structural changes as the catalyst transitions from monometallic Au to monometallic Pd, via the Pd-on-Au nanostructure.

Some products were not formed at zero glycerol conversion, indicating they resulted from a secondary reaction. The detected C₁ (formic acid) and C₂ (glycolic acid, acetic acid, and oxalic acid) species were primary or secondary products, depending on the catalyst (Fig. 3.6d). Au/C and Pd/C generated formic and glycolic acids as primary products; and oxalic and acetic acids are primary products for Au/C and secondary ones for Pd/C. For Pd-on-Au/C with Pd surface coverages ≤ 80 sc%, formic, glycolic and oxalic acids were primary. Above 80 sc%, all detected C₁ and C₂ species were generally secondary products.

The C₁ and C₂ products come from undesirable carbon-carbon bond cleavage. The oxidative glycol cleavage of glyceric acid can yield glyoxylic acid and formaldehyde, which then oxidize into the detected oxalic acid and formic acid, respectively. Carbon-carbon bond cleavage in C₂ and C₃ compounds can occur to generate other products like glycolic acid, acetic acid, and CO₂. Davis and co-workers found that H₂O₂ formed during glycerol oxidation with monometallic Pd and Au, and PdAu bimetallic catalysts. They showed that H₂O₂ contributed to C-C cleavage reactions and that Pd metal helped decompose H₂O₂ such that C-C cleavage products were lessened [12, 27, 58]. They concluded that Au had a higher H₂O₂ formation rate than Pd, and that Pd had much higher H₂O₂ decomposition rate than Au.

The presence of H₂O₂ introduces into the selective glycerol oxidation reaction system a set of secondary, non-selective oxidation reactions. For the Pd-on-Au NP catalysts, the H₂O₂ formation and decomposition rates are unknown with relation to Pd surface coverage. It is
difficult to relate the surface coverage effect on product distribution, though some trends with carbon balance can be seen. The carbon balance for all compositions decreased with increasing conversion, when comparing values at 30% conversion (Table S3.2) to values at >30% conversion (i.e., end of 3-hr reaction, Table 3.1). This loss in carbon can be attributed to increased formation of undetected CO, CO$_2$ and possibly adsorbed ketone-like products [60]. With increasing Pd surface coverage, the carbon balance decreased, likely for the same reasons. This carbon loss may be responsible for the increasing deactivation observed at >80 sc% via CO poisoning of the Pd metal or surface fouling by adsorbed products (Fig. 3.5d).

These zero-conversion and high-conversion selectivity data can be summarized into a reaction scheme (Scheme S3.1). Glycerol reversibly deprotonates at high pH at one of its primary alcohol groups, forming glycerolate that presumably binds to, and oxidizes on, the catalyst surface into glyceraldehyde (via oxidative dehydrogenation). It would then form a hydrated surface species that oxidizes into glyceric acid, via a mechanism analogous to solution-phase aldehyde oxidation. Glyceraldehyde and its isomer dihydroxyacetone were not detected in our reaction system, but others have reported detecting both species using Pd and Pt catalysts at low pH [8, 29, 30]. The significant amounts of lactic acid detected in this study and in other studies using Au/C [58] infer the presence of glyceraldehyde, because lactic acid can form via the hydration of acrolein-methylglyoxal tautomers (which result from glyceraldehyde dehydration). Glyceric acid is converted into tartronic acid via oxidation of its primary alcohol group. All catalyst types contain active sites that lead to glyceric, lactic, and tartronic acids formation; lactic acid does not undergo further oxidation whereas glyceric acid does. Most catalyst types contain active sites that lead to minor amounts of C$_1$, C$_2$, and CO/CO$_2$ products.
with concentrations increasing at the expense of glyceric acid. They also contain active sites that lead to \( \text{H}_2\text{O}_2 \) which, in turn, generate these products.

### 3.3.6. Activation Energy and Deactivation Analysis

The apparent activation energy \( E_a \) was determined in the temperature range of 40-80 °C for several compositions: 45±5, 40±2, 39±2, 40±3, 41±3, and 51±3 kJ/mol, for Au/C, 30 sc%, 60 sc%, 150 sc%, and 300 sc% Pd-on-Au/C, and Pd/C catalysts, respectively. The measured value for Au/C was somewhat close to published values of \( E_a \) (50±5 kJ/mol from experiment [62] and 49.6±2.9 kJ/mol from kinetic modeling [63]). The \( E_a \) values of Pd and PdAu bimetallic catalysts have not been reported for glycerol oxidation before. All these values exceeded 25 kJ/mol, a value below which mass transfer processes (i.e., gas-liquid or liquid-solid mass transfer, or intraparticle diffusion) have their apparent activation energies [64]. This corroborates our mass transfer analysis that the reaction runs were carried out in the kinetically controlled regime.

In the classical oxidative dehydrogenation mechanism model of alcohol oxidation over transition metals (e.g., Pt, Pd, Ru, and Au), it is commonly accepted that \( \beta \)-C-H bond cleavage is the rate-limiting step (rls) during catalysis (Scheme S3.1) [59, 65, 66]. The implication is that the activation energy values measured for the different catalytic structures correspond to the metal-mediated scission of the first \( \beta \)-C-H bond of glycerol molecule. The PdAu compositional effect on activation energy has been studied for reactions like acetylene hydrogenation [67], \( \text{CCl}_2\text{F}_2 \) hydrodechlorination [68], thiophene hydrodesulfurization [69], methane oxidation [70], and formic acid decomposition [71]. In these reported cases, the presence of Pd lowered activation energies relative to monometallic Au. The various Pd-on-Au compositions had \( E_a \)’s lower than that of Au/C by ~5 kJ/mol, correlating to their higher catalytic activities (Fig. 3.5c).
A compensation effect was observed in comparing the monometallic compositions with the bimetallic ones, in which $\ln(A)$ values varied linearly with $E_a$ values (Table S3.3, Fig. S3.7). The Pd-on-Au NP/C catalysts had $E_a$ values close to an average of ~40 kJ/mol and an average $\ln(A)$ value of 13.6. Within experimental uncertainty, there was no difference among these bimetallics. The Au/C catalyst had higher values of $E_a$ and $\ln(A)$, and Pd/C had the highest. This compensation effect implies that the $E_a$ and $\ln(A)$ values are related due to a linear relationship between the rls activation energy and the adsorption energy of the surface reaction intermediate, i.e., the Brønsted-Evans-Polanyi relationship [72, 73]. At conditions where Langmuir-like adsorbate surface coverage is close to 100%, the observed activation energy equals the rls activation energy plus the heat of adsorption. Here, assuming the active sites are mostly occupied by the presumptive glycerolate surface intermediate, the Pd-on-Au NP/C samples are more active than Pd/C and Au/C due to lower rls activation energies and due to weaker adsorption strength of the glycerolate. Both are indicative of differences in active site population.

The deactivation could be seen to worsen with increasing Pd surface coverage, by comparing the rate constants determined after the first 2 hr of reaction and those determined after the first 0.5-1 hr (Table 3.1). The deactivation rate constant $k_d$ was determined for each of the catalysts, assuming a power-law model for poisoning (Fig. 3.5d). The Pd-on-Au NPs with Pd surface coverage from 0 sc% to 80 sc% had $k_d$ values very close to zero, indicating no or negligible deactivation was observed. Above 80 sc%, $k_d$ increased to 0.2±0.1 h$^{-1}$ (at 100 sc%) and further to 0.7±0.2 and 0.7±0.2 h$^{-1}$ for 150 and 300 sc% Pd-on-Au/C respectively, approaching the $k_d$ for Pd/C (1.1±0.2 h$^{-1}$). Pd-on-Au catalysts with calculated sub-monolayer Pd coverages did not deactivate during glycerol oxidation, while Pd-on-Au with higher Pd coverages had increasingly poor deactivation resistance. Accounting for deactivation, rate
constants and TOF values did not fall off from their peak values at 80 sc% as significantly, indicating there were other factors responsible for decreased activity above 80 sc%. Overall, the Pd-on-Au structure was both more active and more deactivation resistant than monometallic Pd/C. The Pd-on-Au catalysts with surface coverages below 80 sc% had the deactivation resistance of Au but had higher activity than Au.

3.3.7. Assessment of Reaction Environment on Metal Oxidation State through XANES Characterization

In a previous study, we analyzed using EXAFS the bimetal structure of ~3-nm (as well as ~7-nm and ~10-nm) Pd-on-Au NPs [40]. Showing a Au-rich core and a Pd-rich surface, these NPs had the well-established volcano-shape dependence of TCE HDC activity on Pd surface coverage. At the volcano peak location of 50 sc%, the Pd atoms were metallic and in the form of two-dimensional (2-D) ensembles on the Au surface, based on coordination numbers derived from EXAFS fitting. At lower Pd surface coverages, Pd atoms were metallic and less coordinated to one another, on average, due to smaller ensembles and/or more isolated Pd atoms. At higher Pd surface coverages, the atoms tended towards higher Pd-Pd coordination numbers, on average, due to larger 2-D ensembles and 3-D Pd ensemble formation. A fraction of the Pd atoms was bound to oxygen, which we attributed to the topmost Pd atoms of the ensembles being oxidized.

The ~4-nm Pd-on-Au NPs of this work have similar metal structural features as described above, and so the detailed EXAFS data and coordination number (CN) analysis are not presented here [74]. Briefly, Pd-on-Au/C (60 sc%) had a Pd-Pd CN of 2.0 and a Pd-Au CN of 7.2, indicating very small Pd ensembles (one Pd atom contacts ~2 other Pd atoms, on average) bound directly to the Au surface (one Pd atom contacts ~7.2 Au atoms, on average). Pd-on-Au/C with a
higher Pd content (150 sc%) had Pd-Pd CN = 2.4 and Pd-Au CN = 5.4, indicating Pd ensembles were larger and were bound to the Au surface with less contact per Pd atom. These two samples were chosen for XAS analysis, because they had similar catalytic activity on either side of the volcano peak (Fig. 3.5a,b).

It was not known how the oxidation states of Pd-on-Au would be affected by the harsher conditions of glycerol oxidation (60 °C, O₂ atmosphere, and pH ~ 13.5) compared to those of TCE HDC (room temperature, H₂ atmosphere, near-neutral pH) [36-42]. We thus performed ex situ XANES characterization on 4 samples (Au NPs, Pd NPs, and the two Pd-on-Au NP compositions) under 3 conditions: as-prepared, before the oxidation reaction, and after the oxidation reaction.

The 3 sets of XANES spectra for Au/C were essentially the same (Fig. 3.7a), indicating that the as-synthesized catalyst structure did not change after being charged to the reactor or after the reaction run. The entire spectrum was essentially the same as that for reduced Au/C, and the lack of change indicated the Au was in the metallic state in all cases. The oxidation state of the Au in the 60 sc% and 150 sc% Pd-on-Au NPs was also invariant, and Au stayed metallic for all samples (Fig. 3.7b,c).
Figure 3.7. XANES spectra at the Au L\textsubscript{III} edge for (a) Au/C and Pd-on-Au/C with (b) 60 sc\% and (c) 150 sc\%; and at the Pd K edge for (d) Pd/C and Pd-on-Au/C with (e) 60 sc\% and (f) 150 sc\%.

In comparison, the Pd/C catalyst behaved differently. From the linear combination fitting of PdO and reduced Pd/C (treated at 200 °C under 4\% H\textsubscript{2}/He for ~30 min, purged with He and cooled to room temperature) spectra, the percentage of Pd atoms that was oxidized increased from 10\% (for the as-synthesized case) to ~20\% (for the "0 hr Rxn" case), and remained at ~20\% after the reaction (Fig. 3.7d). Accounting for a calculated Pd dispersion of 34.8\%, the corresponding percentages of oxidized surface Pd were estimated as ~29\%, ~58\%, and ~58\%, respectively.

The XANES spectra for 60 sc\% Pd-on-Au/C were negligibly different under the three different conditions (Fig. 3.7e). The percentage of oxidized Pd stayed at ~20\% in the as-synthesized, pre-reaction and post-reaction samples; most of the Pd (~80\%) was metallic. In terms of surface Pd, a minimum of ~20\% would be oxidized if 100\% Pd dispersion is assumed.
In comparing the 60 sc% case with the monometallic Pd case, Au appears to suppress Pd oxidation greatly.

The XANES spectra for 150 sc% Pd-on-Au/C also did not vary much under the different conditions either (Fig. 3.7f). However, the 150 sc% Pd-on-Au/C contained a generally higher percentage of oxidized Pd: ~35%, ~40% and ~30% for as-synthesized, pre-reaction and post-reaction samples. Assuming a calculated Pd dispersion of 73.4%, the corresponding percentages of oxidized surface Pd were ~48%, ~55% and ~41%. Thus, the 150 sc% sample was more oxidized than the 60 sc% one in all three cases. The 150 sc% sample was more oxidized than Pd/C in the as-synthesized case, had comparable oxidation percentage before the reaction, and was less oxidized after the reaction.

While in situ XAS analysis would provide stronger evidence, there appears to be a correlation between the extent of Pd oxidation (assessed under ex situ conditions) and smaller glycerol oxidation rate constants, i.e., the more oxidized the Pd, the less active it is, consistent with literature. Baiker and co-workers examined the effect of Pd oxidation state on benzyl alcohol oxidation using O₂ with Pd/Al₂O₃ under non-aqueous condition [75]. Through XANES analysis, they showed that as-synthesized Pd/Al₂O₃ had its surface Pd fully oxidized and exhibited little activity for alcohol oxidation at 50 °C. After treatment under H₂ at 50 °C, the surface Pd was fully reduced, resulting in much higher catalytic activity. The Pd over-oxidized during the reaction (leading to deactivation), if the O₂ content was too high. They also examined the oxidation state of supported Au catalysts in the aerobic organic-phase oxidation of 1-phenylethanol at 80 °C. They concluded that metallic Au was the most active phase and oxidized Au was less active, through in situ XAS [76]. Maclellan and coworkers studied the structural
change of Pd-Au core-shell nanoparticles during crotyl alcohol oxidation using in situ XAS and observed that Au prevented the re-oxidation of surface Pd atoms [77].

Additional insights into Pd metal oxidation can be understood in terms of metal corrosion. The Pourbaix diagram for Pd metal shows that Pd can be metallic or can form an oxidized passivating layer based on the reduction potential of the water environment, at a given pH [78]. Under our reaction conditions (1 atm O₂, 60 °C, and pH = 13.5), the reduction potential of the reaction fluid (quantified as pE) is calculated to be 5.14, corresponding to a voltage potential (Eₘₚ) of +0.30 V (Supporting Information). This is higher than the minimum voltage potential (~0.01 V calculated at 60 °C and pH 13.5) at which metallic Pd oxidizes to form a PdO layer, indicating that the glycerol oxidation reaction conditions thermodynamically favor the oxidation of Pd metal. This point is consistent with surface Pd atoms of Pd/C becoming more oxidized (up to ~60%) once in contact with the reaction fluid. That the surface Pd atoms of 60 sc% Pd-on-Au/C sample showed less oxidation (~20%) indicated the supporting Au metal directly modified the oxidation potential of the Pd ensembles (i.e., electronic effect), such as to increase Pd resistance to oxidation under reaction conditions. If the Pd content was high enough, such as in the 150 sc% case, then the Au had less ability to increase oxidation resistance of the larger Pd ensembles.

3.4. Conclusions

Pd-on-Au nanoparticles comprising 4-nm Au particles decorated with Pd metal of varying amounts were synthesized and immobilized onto carbon. First-order glycerol oxidation kinetics and reaction product analyses showed that catalytic activity, selectivity, and deactivation resistance strongly varied with Pd surface coverage. All bimetallic compositions were more active than the monometallic counterparts, with maximum catalytic activity at 80 sc% such that
near complete glycerol conversion can be achieved. The apparent activation energies for the bimetallics were similar in value, and at least 5 kJ/mol less than those for the monometallics. The observed compensation effect suggested the Pd-on-Au catalysts had lower adsorption energy and lower 'true' activation energies, reflecting the different reactivities of the surface active sites across the compositional spectrum. At surface coverages above 80 sc%, the active sites became susceptible to deactivation, perhaps by CO poisoning or by adsorbate fouling. The seven detected reaction products accounted for most of the carbon balance for all catalyst compositions, with glyceric, tartronic, and lactic acids as the three-carbon products. Pd-on-Au had glyceric acid selectivities between those of the monometallics at a given conversion, but gave the highest glyceric acid yields. The other products resulted from C-C cleavage, either catalyzed directly at the Pd-on-Au particle surface or promoted by reaction with in situ formed H₂O₂. The glycerol oxidation reaction conditions favor the oxidation of Pd metal, and ex situ XANES results suggest the possibility of Au usefully suppressing Pd oxidation during reaction. The metal-on-metal materials design allows Au to improve the stability of the supported metal, leading to a more robust and active bimetallic catalyst.

3.5. Supplementary Information

Detailed Au and Pd NP synthesis method:

For Au NPs, 5 wt% HAuCl₄ solution (0.126 M) was prepared by dissolving 5 g of HAuCl₄·3H₂O (>99%, Sigma-Aldrich) in 100 mL of deionized (DI) water (>18 MΩ.cm, Barnstead NANOpure Diamond). Separate solutions of 1 wt% sodium citrate, 1 wt% tannic acid (TA), and 25 mM potassium carbonate (K₂CO₃) were prepared by dissolving 0.2 g of sodium citrate dihydrate (>99.5%, Fisher), 0.2 g of tannic acid (>99.5%, Sigma–Aldrich) and 0.049 g of potassium
carbonate (>99.5%, Sigma-Aldrich) into 20 mL of H$_2$O, respectively. A gold salt precursor solution was prepared by adding 200 µL of 5 wt% HAuCl$_4$ solution into 79.8 mL of H$_2$O and heating to 60 °C in a water bath with moderate stirring. The reducing agent was prepared by adding 5 mL of TA solution, 5 mL of K$_2$CO$_3$ solution, and 4 mL of citrate solution into 6 mL of DI water and also heating to 60 °C. The two solutions were kept at 60 °C for at least 2 min before combining and mixing. Au NP formation occurred instantaneously after adding the reducing agent to the diluted gold solution, evidenced by a color change from clear to ruby-red. The resulting solution was heated to a boil, left boiling for 2 min, and removed from the heat source. The sol was then diluted with H$_2$O to 100 mL, and left to cool overnight to ambient temperature before being refrigerated. The Au NP concentration was calculated to be 1.07×10$^{14}$ NP/mL (= 49.7 mg Au/L), assuming complete reduction of the Au salt and a 7-shell magic cluster model of a 4-nm Au particle [37, 47-50].

The Pd NPs were prepared in the same manner, except that the Au salt precursor solution was replaced with a palladium salt solution (12 mL of H$_2$PdCl$_4$ solution (2.49 mM) diluted in 68 mL of H$_2$O) and the boiling time was increased to 25 min. The H$_2$PdCl$_4$ solution was prepared by dissolving 42.2 mg PdCl$_2$ (99.99%, Sigma-Aldrich) in 95 mL DI water containing 500 µL HCl solution (1 M, Fisher Scientific). The resulting sol was dark coffee-brown in color, with a calculated particle concentration of 1.27×10$^{14}$ NP/mL (= 31.8 mg Pd/L) assuming complete reduction of the Pd salt and a 7-shell magic cluster model of a 4-nm Pd particle [37, 47-50].

**Determination of mass transfer effects:**

The gas-liquid, liquid-solid, intraparticle diffusion resistances (1/k$_{gl}$, 1/k$_{ls}$ and 1/k$_{i}$) and surface reaction resistance (1/k$_{aNP}$) can be correlated in the relation:
\[ \frac{1}{k_{\text{meas}}} = C_1 + C_2 \times 1/C_{\text{metal}} \………………………………………(1) \]

where \( C_1 \) relates to \( 1/k_{gl}a_{gl} \) and the slope \( C_2 \) relates to \( 1/k_{ls}a_s \), \( 1/k_a_{\text{NP}} \), \( k_{gl} \) is the gas-liquid mass transfer coefficient, \( a_{gl} \) is the gas-liquid interface specific areas, \( k_{ls} \) is the liquid-solid mass transfer coefficient, \( a_s \) is the exterior specific surface areas of carbon, \( k_i \) is the intraparticle diffusion coefficient, \( a_i \) is the interior specific surface areas of carbon, \( k \) is the rate constant for surface reaction, and \( a_{NP} \) is the specific surface areas of NPs.

The liquid-solid mass transfer coefficient \( k_{ls} \) toward a spherical particle could be estimated by the Ranz-Marshall correlation, \( Sh = 2 + 0.6 \times Re^{1/2} Sc^{1/3} \). For our catalytic heterogeneous system, the maximum Reynolds number, \( Re \), is calculated to be 1514, and the Schmidt number, \( Sc \), is 243 at 60 °C assuming the carbon particles were well suspended with ideal spherical shapes \( (d_p = 125 \mu m) \). This gives a Sh value of 147.7. \( k_{ls} \) can be estimated to be \( 2.27 \times 10^{-3} \) m/s from \( Sh = k_{ls}d_p/D_{\text{gly}} \), where \( D_{\text{gly}} = 1.925 \times 10^{-9} \) m²/s) is the diffusivity of glycerol in 60 °C water [63, 79]. Catalyst exterior surface area in overall batch reactor liquid volume, \( a_s \) was calculated to be \( 2.24 \times 10^{2} \) m²/m³ based on the density of carbon (0.40 g/mL) and volume of the reactor (107 mL). \( 1/k_{ls}a_s \) can be then calculated to be \( 5.46 \times 10^{-3} \) h.

Intraparticle diffusion resistance can be analyzed by the first-order Thiele modulus \( \Phi \) from the following equation: \( \Phi[1/\tanh(3\Phi)-1/(3\Phi)] = -R_{gly}a^2/(D_{\text{eff}}C_{GLYS}) \), where \( C_{GLYS} \) is glycerol surface concentration (which is assumed to be equal to the bulk fluid glycerol concentration of 0.1 mol/L), \( R_{gly} \) is the observed reaction rate \( (= k_{meas} \times C_{GLYS} = -1.32 h^{-1} \times 0.1 \text{ mol/L } \div 3600 \text{ s/h} = -3.67 \times 10^{-5} \text{ mol/L/s}) \), and \( a \) is the characteristic length \( (=d_p/6 \text{ for a sphere, } d_p = 20.8 \mu m) \). \( D_{\text{eff}} \) of glycerol in typical carbon material is \( 6.83 \times 10^{-10} \) m²/s (Demirel et al., Top. Catal., 2007, 44, 299). This gives a \( \Phi \) value of 0.015, much smaller than 1. The effectiveness factor \( \eta (=1/\Phi \times [1/\tanh(3\Phi)-1/(3\Phi)]) \) is then calculated to be ~1.00, indicating the intra-particle diffusion
for 60 sc% Pd-on-Au/C catalyst can be neglected for glycerol oxidation. C1 and C2 can be calculated from Fig. 3.2b, where the reciprocal of non-zero k_{meas} was plotted against the reciprocal of the concentration of catalyst charged. At a stirring rate of 1000 rpm, the mass transfer resistances terms were determined to be 0.1577, 5.46×10^{-3}, and 0.5999 (1/\eta_k = 1/(C_{Pd} \times k_{cat}) - 1/k_{gl}a_{lg} - 1/k_{ls}a_i) h for 1/k_{gl}a_{lg}, 1/k_{ls}a_i, 1/k_{i}a_i and 1/k_{NP}, respectively. The relative order 1/k_{NP} > 1/k_{gl}a_{lg} >> 1/k_{ls}a_i indicates that resistance from liquid-solid is negligible, while resistance from surface reaction is dominating and gas-liquid mass transfer resistance should be corrected. To exclude the gas-liquid mass transfer effect, observed rate constant should be corrected from:

\[
1/k_{corr} = 1/k_{meas} - 1/k_{gl}a_{lg} ................................................(2)
\]

For 60 sc% Pd-on-Au/C catalyst, k_{corr} was calculated to be 1.67 h^{-1}, which is 26% higher than the k_{meas} (1.32 h^{-1}, Table. 3.2). Since mass transfer resistances are independent of the active species on catalyst surface, we performed similar calculations for all the rest catalysts to provide k_{corr} values for more accurate calculation of TOF values.

At 700 rpm stirring rate, the gas-liquid mass transfer resistance (y-intercept) was found much greater than at 1000 rpm while liquid-solid and intraparticle diffusion resistances (slope) were the same as at 1000 rpm (Fig. 3.2b). At 350 rpm stirring rate, the catalyst powder was found to be agglomerating and precipitating at the bottom of the reactor, in which case the mass transfer equation is no longer applicable.
Figure S3.1. Plot of ln(1-x) vs. time for 60 sc% Pd-on-Au/C catalyst. Reaction conditions: 0.2 g 60 sc% Pd-on-Au/C, 60 ºC, 1000 rpm, 107 mL, 0.1 M glycerol, 0.4 M NaOH, and 120 mL/min O₂ flow.

Figure S3.2. Glycerol conversion-time profiles for glycerol oxidation reaction with O₂ flowing at 120 mL/min, 300 mL/min, and without O₂ flow (1 atm 150 mL headspace O₂ only). Reaction
conditions: 0.2 g 60 sc% Pd-on-Au/C, 60 °C, 1000 rpm, 107 mL, 0.1 M glycerol, and 0.4 M NaOH.

Table S3.1. Comparison of preparation method, metal loading, NP size, TOF, and selectivity to glyceric acid for various catalysts in literature.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Preparation method</th>
<th>Metal loading (wt%)</th>
<th>NP size (nm)</th>
<th>TOF (mol/mol total-atom/h)</th>
<th>TOF (mol/mol surface-atom/h)</th>
<th>Selectivity to glyceric acid</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/graphite</td>
<td>sol immobilization</td>
<td>1.0</td>
<td>N/A</td>
<td>321.3&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-</td>
<td>78.5% (S&lt;sub&gt;50&lt;/sub&gt;)</td>
<td>[25]</td>
</tr>
<tr>
<td>Au/C</td>
<td>sol immobilization</td>
<td>1.0</td>
<td>4.0</td>
<td>500&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1438</td>
<td>35.8% (S&lt;sub&gt;100&lt;/sub&gt;)</td>
<td>[21]</td>
</tr>
<tr>
<td>Pd/C</td>
<td>sol immobilization</td>
<td>1.0</td>
<td>5.0</td>
<td>106&lt;sup&gt;b&lt;/sup&gt;</td>
<td>337</td>
<td>74.5% (S&lt;sub&gt;21.1&lt;/sub&gt;)</td>
<td>[21]</td>
</tr>
<tr>
<td>AuPd/C</td>
<td>sol immobilization</td>
<td>total: 1.0</td>
<td>5.1</td>
<td>3999&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-</td>
<td>44.1% (S&lt;sub&gt;100&lt;/sub&gt;)</td>
<td>[21]</td>
</tr>
<tr>
<td>Au/C</td>
<td>wet impregnation</td>
<td>1.0</td>
<td>2-10</td>
<td>43&lt;sup&gt;c&lt;/sup&gt;</td>
<td>-</td>
<td>42.5% (S&lt;sub&gt;34.5&lt;/sub&gt;)</td>
<td>[21]</td>
</tr>
<tr>
<td>Pd/C</td>
<td>wet impregnation</td>
<td>1.0</td>
<td>2-10</td>
<td>50&lt;sup&gt;c&lt;/sup&gt;</td>
<td>-</td>
<td>61.6% (S&lt;sub&gt;39.8&lt;/sub&gt;)</td>
<td>[21]</td>
</tr>
<tr>
<td>AuPd/C</td>
<td>wet impregnation</td>
<td>Au: 2.5, Pd: 2.5</td>
<td>3-8</td>
<td>110&lt;sup&gt;c&lt;/sup&gt;</td>
<td>-</td>
<td>72.5% (S&lt;sub&gt;87.6&lt;/sub&gt;)</td>
<td>[21]</td>
</tr>
<tr>
<td>Au/C</td>
<td>sol immobilization</td>
<td>1.0</td>
<td>2-3</td>
<td>1090&lt;sup&gt;d&lt;/sup&gt;</td>
<td>-</td>
<td>64.5% (S&lt;sub&gt;50&lt;/sub&gt;)</td>
<td>[20]</td>
</tr>
<tr>
<td>Pd/C</td>
<td>sol immobilization</td>
<td>1.0</td>
<td>2-3</td>
<td>1151&lt;sup&gt;d&lt;/sup&gt;</td>
<td>-</td>
<td>80.6% (S&lt;sub&gt;50&lt;/sub&gt;)</td>
<td>[20]</td>
</tr>
<tr>
<td>AuPd/C</td>
<td>sol immobilization</td>
<td>total: 1.0 (atomic ratio Au:Pd=1:1)</td>
<td>2-3</td>
<td>1774.5&lt;sup&gt;d&lt;/sup&gt;</td>
<td>-</td>
<td>77.2% (S&lt;sub&gt;50&lt;/sub&gt;)</td>
<td>[20]</td>
</tr>
<tr>
<td>AuPd/C</td>
<td>sol immobilization</td>
<td>total: 1.0 (atomic ratio Au:Pd=1:1)</td>
<td>2-3</td>
<td>1765.2&lt;sup&gt;d&lt;/sup&gt;</td>
<td>-</td>
<td>76.5% (S&lt;sub&gt;50&lt;/sub&gt;)</td>
<td>[20]</td>
</tr>
<tr>
<td>AuPd/C</td>
<td>sol immobilization</td>
<td>total: 1.0 (atomic ratio Au:Pd=1:1)</td>
<td>2-3</td>
<td>1510.0&lt;sup&gt;d&lt;/sup&gt;</td>
<td>-</td>
<td>76.7% (S&lt;sub&gt;50&lt;/sub&gt;)</td>
<td>[20]</td>
</tr>
<tr>
<td>Au/C</td>
<td>sol immobilization</td>
<td>1.0</td>
<td>N/A</td>
<td>1000&lt;sup&gt;e&lt;/sup&gt;</td>
<td>-</td>
<td>68% (S&lt;sub&gt;50&lt;/sub&gt;)</td>
<td>[23]</td>
</tr>
<tr>
<td>Pd/C</td>
<td>sol immobilization</td>
<td>1.0</td>
<td>N/A</td>
<td>1000&lt;sup&gt;e&lt;/sup&gt;</td>
<td>-</td>
<td>80% (S&lt;sub&gt;50&lt;/sub&gt;)</td>
<td>[23]</td>
</tr>
<tr>
<td>AuPd/C</td>
<td>sol immobilization</td>
<td>total: 1.0 (atomic ratio Au:Pd=9:1)</td>
<td>N/A</td>
<td>4400&lt;sup&gt;e&lt;/sup&gt;</td>
<td>-</td>
<td>75% (S&lt;sub&gt;50&lt;/sub&gt;)</td>
<td>[23]</td>
</tr>
<tr>
<td>Au/C</td>
<td>sol immobilization</td>
<td>0.5</td>
<td>5.0</td>
<td>61200&lt;sup&gt;f&lt;/sup&gt;</td>
<td>30527</td>
<td>65% (S&lt;sub&gt;50&lt;/sub&gt;)</td>
<td>[12]</td>
</tr>
<tr>
<td>Pd/C</td>
<td>commercial reduction of Au onto Pd/C</td>
<td>2.9</td>
<td>2.9</td>
<td>3600&lt;sup&gt;f&lt;/sup&gt;</td>
<td>2404</td>
<td>82% (S&lt;sub&gt;50&lt;/sub&gt;)</td>
<td>[12]</td>
</tr>
<tr>
<td>AuPd/C</td>
<td>sol immobilization</td>
<td>Pd: 2.9, Au: 0.8</td>
<td>3.2</td>
<td>16560&lt;sup&gt;f&lt;/sup&gt;</td>
<td>-</td>
<td>84% (S&lt;sub&gt;50&lt;/sub&gt;)</td>
<td>[12]</td>
</tr>
</tbody>
</table>

<sup>a</sup> Calculated after 1 h of reaction. Reaction conditions: 50 °C, 10 mL, 0.3 M glycerol, NaOH: glycerol= 4, glycerol: M= 500, 3 bar O<sub>2</sub>.

<sup>b</sup> Calculated at 0.5 h reaction, based on the total loading of metals. Reaction conditions: 60 °C, 20 mL, 0.6 M glycerol, NaOH: glycerol= 2, glycerol: M= 2000, 10 bar O<sub>2</sub>.

<sup>c</sup> Calculated at 0.5 h reaction, based on the total loading of metals. Reaction conditions: 60 °C, 20 mL, 0.6 M glycerol, NaOH: glycerol= 2, glycerol: M= 500, 10 bar O<sub>2</sub>.

<sup>d</sup> Calculated after 0.25 h of reaction, based on the total loading of metals. Reaction conditions: 50 °C, 10 mL, 0.3 M glycerol, NaOH: glycerol= 4, glycerol: M= 500, 3 bar O<sub>2</sub>.

<sup>e</sup> Calculated after 0.25 h of reaction, based on the total loading of metals. Reaction conditions: 50 °C, 10 mL, 0.3 M glycerol, NaOH: glycerol= 4, glycerol: M= 1000, 3 bar O<sub>2</sub>. 

<sup>f</sup> Calculated at 0.5 h reaction, based on the total loading of metals. Reaction conditions: 60 °C, 20 mL, 0.6 M glycerol, NaOH: glycerol= 2, glycerol: M= 500, 10 bar O<sub>2</sub>.
f Normalized for the surface atoms using the inverse of the surface average diameter. Reaction conditions: 60 °C, 10 mL, 0.3 M glycerol, NaOH: glycerol= 2, glycerol: Au= 50000 for Au/C and AuPd/C, glycerol: Pd= 3000 for Pd/C, 10 bar O₂.

₉ TOF was calculated only when an exact NP size and clear surface composition were reported.

ₙ S₅₀ in parentheses represents the selectivity to glyceric acid at 50% glycerol conversion.

**Figure S3.3.** pH of reaction medium-time profile for glycerol oxidation reaction. Reaction conditions: 0.2 g 60 sc% Pd-on-Au/C, 60 °C, 1000 rpm, 107 mL, 0.1 M glycerol, 0.4 M NaOH, and 120 mL/min O₂ flow.
Figure S3.4. Plot of ln(1-x) vs. time for (a) Au/C, Pd/C, and 10 sc% to 80 sc% Pd-on-Au/C catalysts, (b) 80 sc% to 300 sc% Pd-on-Au/C catalysts. Solid lines are the fitted values to the first 2 hr of reaction profiles using 1st order kinetics for each catalyst.

Figure S3.5. (a) Conversion-time profiles and (b) selectivity distributions at 30% glycerol conversion for Au/C, Pd/C and 60 sc% Pd-on-Au/C catalysts. Reaction conditions: 0.2 g catalyst, 60 °C, 1000 rpm, 107 mL, 0.1 M glycerol, 0.4 M NaOH, and 120 mL/min O₂ flow.

Figure S3.6. Plot of selectivity to (a) tartronic acid or (b) lactic acid vs. conversion of glycerol for Au/C, Pd/C, and Pd-on-Au/C catalysts. Reaction conditions: 0.2 g catalyst, 60 °C, 1000 rpm stirring rate, 107 mL, 0.1 M glycerol, 0.4 M NaOH, and 120 mL/min O₂ flow.
Table S3.2. Selectivity (normalized to all detected products) and carbon balance (sum of all carbons of detected $\text{C}_1$, $\text{C}_2$ and $\text{C}_3$ compounds divided by initial carbon content of glycerol) for Au/C, Pd/C and Pd-on-Au/C catalysts at 30% glycerol conversion.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Selectivity at 30% glycerol conversion (%)</th>
<th>Carbon balance at 30% glycerol conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Glyceric acid</td>
<td>Tartronic acid</td>
</tr>
<tr>
<td>Au/C 10 sc%</td>
<td>45.3</td>
<td>11.4</td>
</tr>
<tr>
<td>Au/C 30 sc%</td>
<td>47.5</td>
<td>7.5</td>
</tr>
<tr>
<td>Au/C 50 sc%</td>
<td>46.5</td>
<td>7.2</td>
</tr>
<tr>
<td>Au/C 60 sc%</td>
<td>51.3</td>
<td>7.8</td>
</tr>
<tr>
<td>Au/C 80 sc%</td>
<td>48.9</td>
<td>6.9</td>
</tr>
<tr>
<td>Au/C 100 sc%</td>
<td>51.6</td>
<td>7.0</td>
</tr>
<tr>
<td>Au/C 150 sc%</td>
<td>52.9</td>
<td>6.0</td>
</tr>
<tr>
<td>Au/C 300 sc%</td>
<td>50.2</td>
<td>6.7</td>
</tr>
<tr>
<td>Au/C</td>
<td>56.3</td>
<td>9.5</td>
</tr>
</tbody>
</table>
Scheme S3.1. Proposed surface reaction of scission of glycerolate and scission of tartronate, and relation to detected species (major products in bold) using Au, Pd, and Pd-on-Au catalysts. Species in dashed boxes and surface intermediates (labeled "ad") were not detected and were inferred to be formed. The blue-colored subscript represents the surface activated species, and the red arrow shows the rate-limiting step of C-H bond cleavage at the beta carbon position to the secondary alcohol group. Reaction products are shown in their acid forms.
Table S3.3. List of apparent activation energies (E<sub>a</sub>), and natural log of pre-exponential factors (ln(A)) for Au/C, Pd/C, and 30 sc%, 60 sc%, 150 sc%, and 300 sc% Pd-on-Au/C catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>E&lt;sub&gt;a&lt;/sub&gt; (kJ/mol)</th>
<th>ln(A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/C</td>
<td>45.4 ± 5.0</td>
<td>15.6 ± 3.1</td>
</tr>
<tr>
<td>Pd/C</td>
<td>50.6 ± 2.8</td>
<td>16.5 ± 0.8</td>
</tr>
<tr>
<td>30 sc%</td>
<td>40.0 ± 2.1</td>
<td>13.1 ± 0.9</td>
</tr>
<tr>
<td>60 sc%</td>
<td>38.7 ± 2.0</td>
<td>13.4 ± 1.0</td>
</tr>
<tr>
<td>150 sc%</td>
<td>39.5 ± 3.0</td>
<td>14.0 ± 0.5</td>
</tr>
<tr>
<td>300 sc%</td>
<td>40.9 ± 2.5</td>
<td>13.8 ± 0.8</td>
</tr>
</tbody>
</table>

Figure S3.7. Plot of natural logarithm of pre-exponential factor ln(A) against apparent activation energy E<sub>a</sub>.
Calculation of voltage potential $E_h$ at reaction conditions:

The potential of water $pE$ is associated with the redox couple: $O_2 (g) + 4H^+ + 4e^- \rightarrow 2H_2O$. It can be calculated from: $pE = pE^0 + \log(P_{O2}^{1/4}[H^+])$, where $pE^0$ is the standard potential at 333 K, $P_{O2}$ is the pressure of $O_2$ in atm and $[H^+]$ is the concentration of $H^+$ [80].

Since $pE^0 \sim 1/T$, where $T$ is temperature, $pE^0(333K) = pE^0(298K)\times298/333 = 20.8\times298/333 = 18.6$. Then $pE = 18.6 + \log(10^{-13.5}) = 5.1$. The voltage potential of water is: $E_h = 0.0591\times pE = 0.30$ V.

For the redox reaction: $Pd + H_2O \rightarrow PdO + 2H^+ + 2e^-$, the voltage potential of this reaction is expressed as: $E_h = E^0 - 2.303 \times RT/F \times pH$, where $E^0$ is the standard voltage potential at 298 K, $R$ is the universal gas constant, $T$ is temperature, and $F$ is the Faraday constant [78]. $E^0$ is dependent on temperature, and at elevated temperatures, $E^0$ is: $E^0(T) = E^0(298K) + (T - 298) \times (dE_0/dT)$.[81] From literature, $E^0(298K) = 0.917$ V,[82, 83] and $dE_0/dT = -0.45 \times 10^{-3}$ V/K [81]. Thus, $E^0(333K) = 0.917 + (333-298) \times (-0.45 \times 10^{-3}) = 0.901$ V.

At 298K and pH = 13.5, $E_h = 0.901 - 2.303 \times RT/F \times pH = 0.10$ V. At 333K (glycerol oxidation reaction temperature) and pH = 13.5 (reaction pH), $E_h = 0.901 - 2.303 \times RT/F \times pH = +0.01$ V.
3.6. References


Chapter 4

EXAFS Characterization of Palladium-on-Gold Catalysts Before and After Glycerol Oxidation

4.1. Introduction

The partial oxidation of glycerol can lead to the formation of a number of valuable compounds such as glyceric acid, glycolic acid, oxalic acid, and tartronic acid [1, 2]. Precious metals (e.g., Pt, Pd and Au) and their bimetallic combinations have been extensively investigated as supported catalysts, through different preparation methods, support compositions and metal percentages [3-5]. Less is known about how the state of the metal, e.g. the extent of oxidation and particle size, is affected by the reaction conditions of glycerol oxidation, which typically is carried out in water at high pH, moderate temperatures, and under an oxidative environment.

Davis and co-workers examined the effect of glycerol oxidation reaction on Pd/C and AuPd/C catalysts through \textit{ex situ} x-ray absorption spectroscopy (XAS) [6]. Fourier transforms of \(k^3\)-weighted extended x-ray absorption fine structure (EXAFS) showed that the Pd metal of a commercial Pd/C catalyst became more reduced after aqueous treatment under anaerobic conditions (60 °C, 0.3 M glycerol, 0.6 M NaOH, 1 atm N\(_2\), 3 h) and under aerobic conditions (60 °C, 0.3 M glycerol, 0.6 M NaOH, 10 atm O\(_2\), 6 h). They concluded that glycerol is an adequate
reducing agent for maintaining Pd in the metallic state, even under high oxygen pressure. They showed that AuPd catalysts, prepared by reducing Au salt from solution at 80 °C onto the commercial Pd/C (3 wt%) with different Au loadings (0.8, 1.5, 2.2, and 2.9 wt%) and by immobilization of polyvinyl alcohol-synthesized AuPd NPs onto carbon (0.8 wt% Au, 1.1 wt% Pd), had Pd and Au in the metallic state and Au preferentially located on top of the Pd. After exposure to the aqueous reaction environment (60 °C, 0.3 M glycerol, 0.6 M NaOH, 10 atm O₂, 6 h), both metals of the AuPd catalysts remained in metallic form, and there was no change in size or metal structure. These results motivated our interest in assessing the glycerol oxidation reaction conditions on AuPd catalysts with a systematically more controlled structure, namely, Au nanoparticles decorated with Pd metal ("Pd-on-Au NPs").

We have studied Pd-on-Au NPs as a metal-on-metal model catalyst, synthesized by coating aqueous Au NPs with controlled amounts of Pd metal [7-18]. This method allows for control of both the Au particle size and Pd surface coverage at the synthesis stage [10, 11, 16]. We recently demonstrated that catalytic activity follows a volcano-shape dependence on Pd surface coverage for water phase glycerol oxidation reaction[8]. Based on x-ray absorption near edge structure (XANES) analysis of 60 sc% and 150 sc% versions of 4-nm Pd-on-Au NPs (before and after glycerol oxidation), we ascertained that the Pd atoms in the Pd-on-Au NPs was, on average, less oxidized than the surface Pd atoms of monometallic Pd. In this study, we provide extended X-ray absorption fine structure (EXAFS) data and analysis for the same samples and compare with those of 4-nm Pd-only and Au-only catalysts. The resulting coordination number and oxidation state results give additional atomic-level information about how the 60 and 150 sc% Pd-on-Au and monometallic materials differ. This work has been submitted to Topics in Catalysis for review.
4.2. Experimental

4.2.1. Materials and Chemicals

Tetrachloroauric(III) acid (HAuCl\textsubscript{4}·3H\textsubscript{2}O, >99%, Sigma-Aldrich), tannic acid (C\textsubscript{76}H\textsubscript{52}O\textsubscript{46}, >99.5%, Sigma–Aldrich), sodium citrate dihydrate (Na\textsubscript{3}C\textsubscript{6}H\textsubscript{5}O\textsubscript{7}·2H\textsubscript{2}O, >99.5%, Fisher), potassium carbonate (K\textsubscript{2}CO\textsubscript{3}, >99.5%, Sigma–Aldrich), palladium(II) chloride(PdCl\textsubscript{2}, 99.99%, Sigma-Aldrich), glycerol (≥99.5%, Sigma-Aldrich), NaOH (≥99.5%, Sigma-Aldrich). Helium (99.99%) gas, oxygen (99.99%) and hydrogen gas (99.99%) were purchased from Matheson. All experiments were conducted in Nanopure water (>18 M\textOmega·cm, Barnstead NANOpure Diamond). All chemicals were used as received unless otherwise noted.

4.2.2. Catalyst Preparation

The detailed synthesis of ~ 4-nm Au and Pd-on-Au NPs was reported in our earlier studies [10, 11, 16]. Briefly, for the synthesis of Au NPs, 80 mL HAuCl\textsubscript{4} solution (0.315 mM) and a 20 mL reducing mixture (4.43 mM K\textsubscript{2}CO\textsubscript{3}, 6.80 mM sodium citrate, 1.47 mM tannic acid) were preheated to 60 °C. The reaction occurred instantaneously after adding the reducing mixture into the gold solution. To ensure the competition of reaction, the solution was further heated to boiling for 2 min with moderate stirring. The Au metal concentration for Au NP sol with all sizes was 49.7 mg Au/L, while the Au NP concentration was calculated to be 1.07×10\textsuperscript{14} NP/mL, assuming complete reduction of the Au salt and a magic cluster model of Au particle [12, 16, 19-21].

4-nm Pd NPs were synthesized as a control sample by replacing Au salt solution with an 80 mL H\textsubscript{2}PdCl\textsubscript{4} solution (0.374 mM) and increasing the boiling time to 25 min. The resulting Pd NPs sol had a calculated particle concentration of 1.27×10\textsuperscript{14} NP/mL (= 31.8 mg Pd/L) [12, 16, 19-21].
Bimetallic Pd-on-Au NPs were prepared by adding the Pd salt precursor solution to the Au sol, then reducing the Pd with hydrogen gas under room temperature [10, 11]. Table S4.1 shows the specific volumes of 2.49 mM H₂PdCl₄ sol needed to add in the Au NPs sol for various surface coverages (sc%, calculated using the magic cluster model) on the Au NP assuming complete reduction of Pd onto the surface of the Au NPs.

Prior to characterization and kinetic testing, all NPs were immobilized onto activated carbon (Darco G-60, Sigma Aldrich) by mixing NPs sol with activated carbon for 24 h, followed by centrifuging (14,000 rpm, 40 min) and subsequent drying of slurry in vacuum oven (70 °C, until no mass loss). 201 mL Pd-on-Au NP sol were used to synthesize 1 g of Pd-on-Au/C catalysts for all Pd surface coverages. The Au loading for all Pd-on-Au/C catalysts was targeted to be at 1 wt%, while the calculated Pd loading varied according to the Pd surface coverage (Table S2). Carbon-supported with 1 wt% Pd (Pd/C) was prepared in the same manner by mixing 314 mL of Pd sol (31.8 mg Pd/L) with 1.0 g of activated carbon.

4.2.3. Transmission Electron Microscopy (TEM)

The NP/C solid samples were imaged using a JEOL 2010 transmission electron microscope (TEM). TEM samples were prepared by depositing droplets of methanol-suspended NP/C (0.2 mg/mL) onto 200-mesh carbon/Formvar TEM grids, and then dried at room temperature. ImageJ was used for the size distribution measurements [22]; at least 250 particles were measured from each sample.

4.2.4. Reaction data analysis

All the carbon supported NPs were tested for glycerol oxidation without pretreatment and under reaction conditions previously described [8]. Briefly, a screw-cap bottle (250 mL, Alltech) sealed with a Teflon-silicone septum was used as a semi-batch reactor with the following reaction
conditions: 0.2 g catalyst, 60 °C, 1000 rpm stirring rate, 107 mL volume, 0.1 M glycerol, 0.4 M NaOH, and 120 mL/min O₂ flow. Liquid samples at different time intervals were collected, filtered and analyzed through ion-exclusion high-performance liquid chromatography (HPLC) [8].

4.2.5. X-ray Absorption Spectroscopy (XAS)

XAS measurements were carried out on the insertion and bending magnet devices (beamline 10-ID-B and 10-BM-B) of the Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon Source at Argonne National Laboratory. A more detailed description of the instrumentation can be found in our earlier studies [7, 8, 11].

A minimum metal loading of 1 wt% for both Pd and Au was needed for a satisfactory signal-to-noise ratio in the collected XAS spectra. XAS samples were synthesized based on our previous study [8]. Table S4.3 lists the volumes of Au and Pd-on-Au NP sol used to synthesize Au/C and Pd-on-Au/C suitable for XAS analysis and their calculated respective metal contents. Our earlier study using inductively coupled plasma-optical emission spectroscopy indicated that >90% of the NPs had been immobilized onto carbon support [7]. The immobilization procedure did not modify the NP atomic structure, as shown in our previous studies [7, 11].

Each of the 4 catalyst materials (Au/C, Pd/C, 60 sc% Pd-on-Au/C, and 150 sc% Pd-on-Au/C) were charged to the reaction medium and immediately recovered, generating four "0 hr Rxn" samples. Another set of the 4 catalysts were charged to the reaction medium and recovered after 3 hours, generating four "3 hr Rxn" samples. And 4 untreated reference samples ("as-synthesized") were also used for XAS analysis. The reaction conditions were the same as those used for catalytic testing (Section 2.4). Catalysts were recovered as follows: immerse the bottle reactor in an ice bath and purge with He (>99.99%, Matheson) to quench the reaction, cool the
reaction medium to 4 °C and centrifuge at 14,000 rpm for 40 min, re-suspend the carbon slurry in DI water and centrifuge after decanting. The final wash step was repeated, and the collected samples were dried in a vacuum oven at 70 °C until constant mass.

XAS spectra of each sample were collected first under air at room temperature. The catalysts were then subjected to flowing 4% H\textsubscript{2}/He gas for ~30 min at 200 °C and cooled to room temperature under a He purge, and XAS spectra collected again. Based on our previous studies, this treatment method completely reduces oxidized Pd while maintaining the bimetallic nanostructure [7]. These reduced samples were then analyzed under He at room temperature, to ascertain the metal-on-metal structure via our Punnett square analysis, and to help determine the extent of Pd oxidation in the Pd/C and Pd-on-Au/C samples. In Punnett square analysis, the experimentally determined coordination numbers of Pd-on-Au NPs are compared against the coordination numbers of Pd-Pd, Pd-Au, Au-Pd and Au-Au scatters calculated for a theoretical alloyed NP of the same bulk composition (Electronic Supplementary Material). The differences and similarities in values for the 4 different scattering pairs can be conveniently seen in a 2×2 matrix. In our earlier study, we performed this analysis to confirm the core-shell structures of 3 and 7 nm Pd-on-Au NPs [11].

4.3. Results and Discussion

4.3.1. 4-nm Au/C catalysts

The fitting of the XAS spectra of the as synthesized Au/C catalyst gives a Au-Au coordination number (CN) of ~9.3, bond distance (R) of 2.86 Å (Table 1), in good agreement with our previous results[7]. A Au-Au CN value of 9.3 corresponds to an average NP size of ~4.3 nm based on TEM-EXAFS size correlation developed for supported Au materials [23]. This number
matches closely with our TEM size for Au NPs \( (4.1 \pm 0.9 \text{ nm}, \text{Fig. 1a}) \). Oxidized Au was not detected, and \( \text{H}_2 \) treatment at 200 °C did not change the material (Table 1, Fig. S1a).

**Table 4.1.** EXAFS fit parameters for 4 nm Au/C samples on Au edge.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Treatment</th>
<th>Scattering path</th>
<th>( \text{CN}^a (\pm 10%) )</th>
<th>( R^b, \text{Å} (\pm 0.02 \text{ Å}) )</th>
<th>( \text{DWF}^c (\times 10^3 \text{ Å}^2) )</th>
<th>( E_0^d ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As synthesized</td>
<td>Air RT</td>
<td>Au-Au</td>
<td>9.3</td>
<td>2.86</td>
<td>1.0</td>
<td>-1.0</td>
</tr>
<tr>
<td>H(_2) 200 °C</td>
<td>H(_2)-treated</td>
<td>Au-Au</td>
<td>9.3</td>
<td>2.86</td>
<td>1.0</td>
<td>-0.3</td>
</tr>
<tr>
<td>0 hr Rxn</td>
<td>Air RT</td>
<td>Au-Au</td>
<td>9.8</td>
<td>2.86</td>
<td>1.0</td>
<td>-0.0</td>
</tr>
<tr>
<td>H(_2) 200 °C</td>
<td>H(_2)-treated</td>
<td>Au-Au</td>
<td>10.1</td>
<td>2.86</td>
<td>1.0</td>
<td>-0.4</td>
</tr>
<tr>
<td>3 hr Rxn</td>
<td>Air RT</td>
<td>Au-Au</td>
<td>10.0</td>
<td>2.87</td>
<td>1.0</td>
<td>0.3</td>
</tr>
<tr>
<td>H(_2) 200 °C</td>
<td>H(_2)-treated</td>
<td>Au-Au</td>
<td>10.0</td>
<td>2.86</td>
<td>1.0</td>
<td>-0.8</td>
</tr>
</tbody>
</table>

a. CN: coordination number  
b. R: bond distance  
c. DWF: Debye-waller factor  
d. \( E_0 \): energy difference in edge correction

**Figure 4.1.** TEM images of Au/C sample (a) as synthesized, (b) 0 hr Rxn, (c) 3 hr Rxn.

4.3.2. 4-nm Pd-on-Au/C (60 sc% and 150 sc%) catalysts

The addition of the Pd did not change the overall size of the NPs (Fig. 4.2a). The 4-nm Pd-on-Au NPs were verified to have a metal-on-metal nanostructure via our Punnett square analysis of the CN values of the as-synthesized, \( \text{H}_2 \)-treated samples (Fig. 4.3, Tables 4.2 and 4.3). The CN
values for alloyed PdAu NPs were calculated using equations described in our previous study (Electronic Supplementary Material) [11]. The measured Au-Au CN of 60 sc% Pd-on-Au NPs (9.5) was larger than the calculated Au-Au CN of alloyed NPs with equivalent composition (9.0), and the measured Au-Pd CN (1.9) was smaller than the corresponding calculated CN (2.4), consistent with the two metals being not randomly mixed as in an alloy and with the NPs having a Au-rich core. The measured Pd-Pd CN pair (2.4) was slightly larger than the corresponding calculated CN (2.2), and the measured Pd-Au CN (8.2) was slightly smaller than the corresponding CN (8.4), indicating that Pd atoms were more aggregated as small Pd ensembles than compared to the alloyed NP case.

Figure 4.2. TEM images of 60 sc% Pd-on-Au/C sample (a) as synthesized, (b) 0 hr Rxn, (c) 3 hr Rxn.
Figure 4.3. (a) XAS-measured CNs for Pd-on-Au NPs with 60 sc% and calculated CNs for alloyed 4 nm PdAu NPs (in parenthesis) with the same metal content (21.4 mol% Pd), total Au CN (11.4), and total Pd CN (10.6); (b) XAS-measured CNs for Pd-on-Au NPs with 150 sc% and calculated CNs for alloyed 4 nm PdAu NPs (in parenthesis) with the same metal content (42.5 mol% Pd), total Au CN (10.9), and total Pd CN (9.7). Experimental CNs were those of NPs after hydrogen reduction at 200 °C.

Similar numerical analysis can be applied to 150 sc% Pd-on-Au NPs (Fig. 4.3b), leading to the conclusion that 150 sc% Pd-on-Au NPs had a Au-rich core. However, the measured Pd-Pd CN value (3.3) was smaller than the calculated Pd-Pd CN of alloyed NPs with equivalent composition (4.2), and the measured Pd-Au CN value (6.4) was larger than the corresponding calculated CN (5.5). These values suggest that Pd atoms were aggregated into smaller Pd ensembles than compared to the alloyed NP case.

Table 4.2. EXAFS fit parameters for 60 sc% 4 nm Pd-on-Au/C samples on Au and Pd edges.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Treatment</th>
<th>Scattering path</th>
<th>CN (± 10%)</th>
<th>R, Å (± 0.02 Å)</th>
<th>DWF (× 10³ Å²)</th>
<th>E₀ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Au-Au</td>
<td>9.6</td>
<td>2.86</td>
<td>0.0</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Au-Pd</td>
<td>2.0</td>
<td>2.80</td>
<td>0.0</td>
<td>4.2</td>
</tr>
<tr>
<td>As synthesized</td>
<td>H₂ 200 °C</td>
<td>Au-Au</td>
<td>9.5</td>
<td>2.86</td>
<td>0.0</td>
<td>-0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Au-Pd</td>
<td>1.9</td>
<td>2.80</td>
<td>0.0</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>Air RT</td>
<td>Au-Pd</td>
<td>9.4</td>
<td>2.86</td>
<td>0.0</td>
<td>-0.2</td>
</tr>
<tr>
<td>0 hr Rxn</td>
<td>Air RT</td>
<td>Au-Au</td>
<td>1.8</td>
<td>2.80</td>
<td>0.0</td>
<td>3.1</td>
</tr>
<tr>
<td>Sample</td>
<td>Treatment</td>
<td>Scattering path</td>
<td>CN (±10%)</td>
<td>R, Å (± 0.02 Å)</td>
<td>DWF $(\times 10^3 \text{Å}^2)$</td>
<td>$E_o$ (eV)</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
<td>-----------------</td>
<td>-----------</td>
<td>-----------------</td>
<td>-------------------------------</td>
<td>------------</td>
</tr>
<tr>
<td></td>
<td>Au-Au</td>
<td>9.7</td>
<td>2.86</td>
<td>0.0</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>H$_2$ 200 °C</td>
<td>Au-Pd</td>
<td>2.2</td>
<td>2.80</td>
<td>0.0</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>3 hr Rxn</td>
<td>Au-Au</td>
<td>9.5</td>
<td>2.86</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>Air RT</td>
<td>Au-Pd</td>
<td>1.7</td>
<td>2.80</td>
<td>0.0</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>H$_2$ 200 °C</td>
<td>Au-Au</td>
<td>9.4</td>
<td>2.86</td>
<td>0.0</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Au-Pd</td>
<td>2.2</td>
<td>2.80</td>
<td>0.0</td>
<td>2.3</td>
<td></td>
</tr>
</tbody>
</table>

**Table 4.3.** EXAFS fit parameters for 150 sc% 4 nm Pd-on-Au/C samples on Au and Pd edges.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Treatment</th>
<th>Scattering path</th>
<th>CN (±10%)</th>
<th>R, Å (± 0.02 Å)</th>
<th>DWF $(\times 10^3 \text{Å}^2)$</th>
<th>$E_o$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pd-O</td>
<td>1.0</td>
<td>2.04</td>
<td>2.0</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>As synthesized</td>
<td>Air RT</td>
<td>Pd-Pd</td>
<td>2.0</td>
<td>2.74</td>
<td>0.0</td>
<td>-4.8</td>
</tr>
<tr>
<td></td>
<td>Pd-Au</td>
<td>7.2</td>
<td>2.80</td>
<td>0.0</td>
<td>-2.9</td>
<td></td>
</tr>
<tr>
<td>H$_2$ 200 °C</td>
<td>Pd-Pd</td>
<td>2.4</td>
<td>2.74</td>
<td>0.0</td>
<td>-3.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pd-Au</td>
<td>8.2</td>
<td>2.80</td>
<td>0.0</td>
<td>-2.5</td>
<td></td>
</tr>
<tr>
<td>0 hr Rxn</td>
<td>Pd-O</td>
<td>0.9</td>
<td>2.04</td>
<td>2.0</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>Air RT</td>
<td>Pd-Pd</td>
<td>1.6</td>
<td>2.74</td>
<td>0.0</td>
<td>-5.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pd-Au</td>
<td>6.8</td>
<td>2.80</td>
<td>0.0</td>
<td>-4.0</td>
<td></td>
</tr>
<tr>
<td>H$_2$ 200 °C</td>
<td>Pd-Pd</td>
<td>1.8</td>
<td>2.74</td>
<td>0.0</td>
<td>-6.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pd-Au</td>
<td>8.6</td>
<td>2.80</td>
<td>0.0</td>
<td>-3.5</td>
<td></td>
</tr>
<tr>
<td>3 hr Rxn</td>
<td>Pd-O</td>
<td>0.9</td>
<td>2.02</td>
<td>2.0</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>Air RT</td>
<td>Pd-Pd</td>
<td>1.8</td>
<td>2.74</td>
<td>0.0</td>
<td>-6.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pd-Au</td>
<td>7.3</td>
<td>2.80</td>
<td>0.0</td>
<td>-4.9</td>
<td></td>
</tr>
<tr>
<td>H$_2$ 200 °C</td>
<td>Pd-Pd</td>
<td>2.0</td>
<td>2.74</td>
<td>0.0</td>
<td>-6.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pd-Au</td>
<td>8.9</td>
<td>2.80</td>
<td>0.0</td>
<td>-3.4</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Treatment</th>
<th>Scattering path</th>
<th>CN (±10%)</th>
<th>R, Å (± 0.02 Å)</th>
<th>DWF $(\times 10^3 \text{Å}^2)$</th>
<th>$E_o$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pd-O</td>
<td>1.6</td>
<td>2.04</td>
<td>2.0</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td>As synthesized</td>
<td>Air RT</td>
<td>Pd-Pd</td>
<td>2.4</td>
<td>2.74</td>
<td>0.0</td>
<td>-4.0</td>
</tr>
<tr>
<td></td>
<td>Pd-Au</td>
<td>5.4</td>
<td>2.79</td>
<td>0.0</td>
<td>-4.1</td>
<td></td>
</tr>
</tbody>
</table>

**Pd Edge**
The as-synthesized 60 sc% Pd-on-Au NPs had the Pd in a partially oxidized state, with a Pd-O CN of 1.0 (Table 4.2). Dividing the fitted CN of Pd-O by 4 (since PdO has a Pd-O CN value of 4) [7, 11] gives 25% for the percentage of Pd atoms that is oxidized, consistent with the 20% value derived from XANES analysis of our earlier study.[8] If 100% Pd dispersion is assumed, then a minimum of ~20% of surface Pd atoms can be considered oxidized. With a Pd-Pd CN of 2.0 and Pd-O CN of 1.0, the 60 sc% Pd-on-Au NPs are inferred to have Pd atoms mostly in the form of metallic clusters (i.e., 2-D ensembles with all Pd atoms in contact with the Au) and partially oxidized clusters (i.e., 3-D ensembles with some Pd atoms not in contact with the Au) [7, 11].

The as-synthesized 150 sc% Pd-on-Au NPs had a higher fraction of oxidized Pd, with a Pd-O CN of 1.6 (Table 4.2). The percentage of oxidized Pd was 40%, consistent with the ~35% value derived from XANES [8]. Assuming a calculated Pd dispersion of 73.4%, the corresponding percentage of oxidized surface Pd was ~48%. Their higher values of Pd-Pd CN and Pd-O CN indicated that the 150 sc% Pd-on-Au NPs had more 3-D Pd ensembles and less 2-D ensembles than the 60 sc% ones [11].
4.3.3. 4-nm Pd/C catalysts

The Pd/C catalyst had Pd NP sizes of 4.2±1.3 nm, according to TEM analysis (Fig. 4.4a). The material had a Pd-Pd CN of 5.8 (Table 4.4), which corresponded to a smaller size of ~1.5 nm following the TEM-EXAFS size correlation developed for supported Pd materials [7, 23]. After H₂ reduction, the Pd-Pd CN increased to 8.2, corresponding to a particle size of ~3.4 nm. These values are smaller than the TEM particle size, which is attributed to EXAFS being more sensitive to smaller particles present in the material [7]. The as-synthesized Pd NPs had a Pd-O CN of 0.5 (Table 4.4), corresponding to 12.5% of Pd being oxidized (close to the 10% value from XANES analysis). Assuming a calculated Pd dispersion of 34.8%, ~29% of surface Pd atoms are oxidized.

![TEM images of Pd/C sample (a) as synthesized, (b) 0 h rxn, (c) 3 h rxn.](image)

**Figure 4.4.** TEM images of Pd/C sample (a) as synthesized, (b) 0 h rxn, (c) 3 h rxn.

**Table 4.4.** EXAFS fit parameters for 4 nm Pd/C samples on Pd edge.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Treatment</th>
<th>Scattering path</th>
<th>CN (±10%)</th>
<th>R, Å (± 0.02 Å)</th>
<th>DWF (× 10³ Å²)</th>
<th>E₀ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As synthesized</td>
<td>Air RT</td>
<td>Pd-O</td>
<td>0.5</td>
<td>2.03</td>
<td>-4.5</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pd-Pd</td>
<td>5.8</td>
<td>2.76</td>
<td>3.0</td>
<td>1.6</td>
</tr>
</tbody>
</table>
4.3.4. Effect of exposure to the reaction solution ("0-hr Rxn" samples)

The catalytic materials were exposed to the reaction medium, and then immediately filtered and recovered prior to TEM and EXAFS characterization. For Au/C, the CN value for Au-Au scatter increased slightly from 9.3 (as-synthesized) to 9.8 while Au remained metallic, within the uncertainty range of XAS measurements (10%). TEM images of Au/C indicated no change in particle size (Fig. 4.1b). Contacting with the glycerol reaction medium did not affect the Au NPs.

For 60 sc% Pd-on-Au/C, the CN values for the Au-Au, Au-Pd, Pd-Au, Pd-Pd and Pd-O scattering paths were 9.4, 1.8, 6.8, 1.6 and 0.9, respectively. The increase/decrease of 2%, 10%, 6%, 20%, and 10% relative to the CN values of the as-synthesized material was negligible and within the uncertainty range of XAS measurements (Fig. 4.5). The Au remained metallic and the oxidized Pd percentage was at 23% (= 0.9/4), not much different from as-synthesized sample (25%). TEM images indicated no change in particle size (Fig. 4.2b). For 150 sc% Pd-on-Au/C, the CN values for the Au-Au, Au-Pd, Pd-Au, Pd-Pd and Pd-O scattering paths were 8.9, 2.0, 4.5, 2.4 and 1.8, respectively, corresponding to a negligible increase/decrease of 1%, 0%, 17%, 0%, and 13%. Au also remained metallic while the fraction of oxidized Pd increased slightly from 40% (as-synthesized) to 45%, corresponding to a ~61% of surface Pd being oxidized.

Exposure to the reaction medium caused significant changes in the Pd/C catalyst. The CNs for Pd-Pd scatter increased from 5.8 to 8.1 (Table 4.4, Fig. 4.5c) for unreduced sample of Pd/C after exposure, an increase of 40% from the as-synthesized samples. Increases in CN general
indicate a size increase. Based on a previously published TEM-EXAFS size correlation,[23] unreduced Pd/C sample had an increased Pd NP size from ~1.5 nm to ~3.0 nm. After H₂ reduction at 200 °C, the CNs for Pd-Pd scatter increased by 12% from 8.2 to 9.2, corresponding to a Pd NP size increase from ~3.4 to ~4.1 nm. This result was confirmed by TEM measurements, where the average Pd NP size increased from 4.2 ± 1.3 nm to 4.6 ± 1.6 nm (Fig. 4.4b). An increase in CN values for the Pd-O scatter (from 0.5 to 1.0) indicated an increase in the fraction of oxidized Pd from 12.5% to 25%, matching what we observed in XANES (Fig. 4.5f).
Figure 4.5. Coordination numbers of (a) Au-Au, (b) Au-Pd, (c) Pd-Pd, (d) Pd-Au and (e) Pd-O scatters (Pd-C(O) scatter for Pd/C) from EXAFS and (f) percentage of Pd-O from XANE for untreated samples of Au/C, 60 sc% and 150 sc% Pd-on-Au/C, and Pd/C catalysts as-synthesized,
before (0 hr Rxn) and after glycerol oxidation reaction (3 hr Rxn). "N/A" = no detection of scattering signal or no available number.

4.3.5. Effect of glycerol reaction on NPs ("3-hr reaction")

In these experiments, the catalysts were immediately filtered and recovered after carrying out the glycerol reaction for 3 hr. No significant changes were found in the CN values for Au-Au, Au-Pd, Pd-Pd, Pd-Au, and Pd-O scattering paths of Au/C, 60 sc% and 150 sc% Pd-on-Au/C (within 10%, Figs. 4.5a-4.5e). As for oxidation states, Au stayed metallic in all cases for all catalysts; the percentage of Pd-O was little changed for 60 sc% Pd-on-Au/C after reaction (25% for as synthesized, 23% for 0 hr Rxn, and 23% for 3 hr Rxn). A fluctuation in percentage of Pd-O (40% for as synthesized, 45% for 0 hr Rxn, and 37.5% for 3 hr Rxn) was noted for 150 sc% Pd-on-Au/C, but it was considered as small due to the detection limits. We conclude that all Au-based catalysts (Au/C, 60 sc% and 150 sc% Pd-on-Au/C) did not change in their NP sizes, metal distribution, and oxidation states after exposure to the oxidizing and basic conditions of the glycerol reaction, consistent with our earlier ex situ XANES analysis [8].

In contrast, more changes were observed for the Pd/C catalyst after reaction. As can be seen from Figure 4.5c and Figure S4.1c, the CNs of Pd-Pd scatter for both unreduced and reduced Pd/C samples changed before and after the reaction as compared to the as-synthesized sample. The Pd NPs of Pd/C increased from 3.4 nm to 4.1 nm before reaction, and later to 5.4 nm after 3 hours of reaction, using TEM-EXAFS size correlation information.[23] Our own TEM analysis showed that the Pd NP size increased from 4.2±1.5 nm (as-synthesized), to 4.6±1.6 nm (0-hr reaction), and further to 6.5±1.5 nm (after 3 hours of reaction) (Figure 4b-c). Although the CNs of Pd-Pd scatter and sizes overlap to some extent by considering error bars, there is a clear trend toward growth. Moderate size growth of catalytic NPs has previously been
reported by Schuurman et al., who showed a Pt particle size increase from 1.9 to 2.5 nm in liquid phase methyl-α-glucoside oxidation under similar conditions (323 K, pH = 9, 1 atm O₂).[24] This size growth was attributed to Ostwald ripening (dissolution and subsequent redeposition of Pt onto larger particles), which can be accelerated by high pH, high metal potential (from excess oxygen) and chelating molecules such as carboxylic acids [24, 25]. The observed increased in Pd NP size contributes to Pd/C catalyst deactivation due to a decrease in the number of available surface sites.[8]

4.3.6. Correlation to catalytic activity

Our previous kinetic results show that catalytic reaction rate increased dramatically for glycerol oxidation by depositing Pd onto Au surface (Table 5), that a volcano-shape activity dependence on Pd surface coverage was ascertained, and that samples of a compositional range retained gold's high resistance to deactivation and palladium's high selectivity to glyceric acid [8]. Table 5 lists the TOF values of Au/C, Pd/C, and 60 sc% and 150 sc% Pd-on-Au/C catalysts tested for glycerol oxidation reaction from our earlier study. Au/C and Pd/C showed comparable activity; the latter had higher initial activity but also showed significant deactivation (associated with the observed Pd particle growth).

Adding Pd atoms onto Au NPs significantly increased the glycerol oxidation, by almost an order of magnitude. The 60 sc% and 150 sc% had similar TOF values (which was normalized to number of surface Pd and Au atoms) even though the total Pd content and oxidized Pd content differed. If we account for deactivation, the 150 sc% catalyst is initially more active than the 60 sc% catalyst (cf. ~5900 h⁻¹ v. ~4000 h⁻¹, Table 5). Further accounting for the ex situ observations of the as-synthesized 150 sc% material being more oxidized than the 60 sc% and of it being
more susceptible to oxidation state changes, we reason that the easier Pd can oxidize (e.g., in samples with a larger amount of 3-D ensembles), the less resistant the Pd-on-Au catalyst is to deactivation. While one may attempt to conclude that the 150 sc% material is initially more active than 60 sc% due to its higher content of oxidized Pd, we caution that our XAS data were collected under *ex situ* conditions. *In situ* or *operando* XAS data collection and analysis would provide Pd oxidation state information for the catalysts during reaction.

**Table 4.5.** Glycerol oxidation reaction TOF values for Au/C, Pd/C, and 60 sc% and 150 sc% Pd-on-Au/C. Reaction condition: 0.2 g catalyst, 60 °C, 1000 rpm stirring rate, 107 mL, 0.1 M glycerol, 0.4 M NaOH, and 120 mL/min O\(_2\) flow.[8]

<table>
<thead>
<tr>
<th>Catalyst type</th>
<th>Au/C</th>
<th>Pd/C</th>
<th>60 sc% Pd-on-Au/C</th>
<th>150 sc% Pd-on-Au/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOF(^a) (h(^{-1}))</td>
<td>445</td>
<td>424</td>
<td>4038</td>
<td>4084</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1601)(^b)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Initial turnover frequency (TOF) was defined as TOF = k\(_{corr}\) × C\(_{gly}\) / C\(_{surf}\) (with units of mol-glycerol per mol-surface-atom per h), where k\(_{corr}\) (with units of h\(^{-1}\)) is the rate constant corrected for mass transfer effects, C\(_{surf}\) is the surface metal content of the reactor.

\(^b\) TOF values were calculated using data points in the first 2 h. TOF values in parentheses were calculated from the first 0.5 h of the concentration–time profile for Pd/C, and for the first 1 h of the concentration–time profile for 150 sc% Pd-on-Au/C catalysts.

In reviewing relevant literature, we found that the structure of PdAu catalysts and the state of Pd species during glycerol and other alcohol oxidation reactions were reported with varying conclusions. For glycerol oxidation, Davis and co-workers showed that Pd metal was the active phase, and glycerol was an adequate reducing agent in keeping Pd in the metallic state even under high oxygen pressure.[6] Grunwaldt and co-workers found that Pd/Al\(_2\)O\(_3\) with oxidized surface Pd was hardly active for liquid-phase benzyl alcohol oxidation (50 °C in cyclohexane[26]) and Pd/Al\(_2\)O\(_3\) with metallic surface Pd was much more active.[26-28] Through XAS, they showed that gaseous oxygen content was an important determinant of the surface Pd oxidation state: Pd surface is over-oxidized if there is too much O\(_2\), and hydrogen surface species
and other formed compounds are not effectively removed if there is not enough O$_2$. Baiker and co-workers reported evidence of over-oxidized surface Pd as being less active site for benzyl alcohol oxidation ($50 \, ^\circ\mathrm{C}$ in cyclohexane [29]) using $\textit{in situ}$ attenuated total reflectance infrared spectroscopy.[29, 30] Iglesia and co-workers examined the gas-phase oxidation of methanol ($40 \, ^\circ\mathrm{C}$) using both metallic and oxidized Pd/Al$_2$O$_3$, and reported that metallic Pd clusters were much more active than PdO clusters and reaction rates were inhibited by O$_2$ [31].

In contrast, Kaneda and co-workers showed that cinnamyl alcohol oxidation to cinnamaldehyde ($60 \, ^\circ\mathrm{C}$, 1 bar O$_2$ in acetic acid) occurred over ~4-nm Pd particles with surface oxidized Pd [32]. Lee and co-workers reported that the oxidized Pd was the active phase, using $\textit{operando}$ and $\textit{ex situ}$ XAS to show that crotyl and cinnamyl alcohol oxidation rates were directly proportional to the concentration of surface oxidized Pd [33-36]. These differences in conclusions can be traced to differences in alcohol type, preparation method of catalysts, nanoparticle size, support composition, and reaction conditions (e.g., pH, temperature, initial concentration of alcohol, and O$_2$ pressure). One way to probe the role of oxidized Pd of Pd-on-Au catalysts for alcohol oxidation reactions is to synthesize "Au-on-Pd" NPs, in which Au metal is deposited onto Pd NPs.

One way to probe the role of oxidized Pd of Pd-on-Au catalysts for alcohol oxidation reactions is to synthesize "Au-on-Pd" NPs, in which Au metal is deposited onto Pd NPs. In a recent study by Monnier and coworkers, a series of Au-Pd/C catalysts was prepared by reduction of Au salt onto commercial Pd/C $\textit{via}$ electroless deposition and studied for glycerol oxidation ($60 \, ^\circ\mathrm{C}$, 80 mL, 0.1 M glycerol, 1.0 M NaOH, 1200 rpm, and 11 bar O$_2$).[37] They too observed volcano-shape activity dependence on Au surface coverage, though they did not carry out XAS characterization of their materials. The authors ruled out the electronic effect via XPS analysis,
and further ruled out the ensemble effect by showing no enhanced activity of similarly prepared Ag-Pd/C catalysts. They proposed the bifunctional effect to explain the increased activity of their catalysts, in which Au-Pd surface sites are the active sites (i.e., Au can stabilize absorbed glycerolate species and Pd can help with dehydrogenation of β-C-H bond to form glyceraldehyde).

In our earlier studies on Pd-on-Au NPs catalyzed hydrodechlorination reactions, geometric effect was proposed to explain the volcano shape activity dependence on Pd surface coverage that 2-D Pd ensembles are the most active sites for C-Cl bond cleavage. Electronic effect was proposed to play an important role since 150 and 300 sc% Pd-on-Au NPs were still much more active than Pd NPs, which can be considered to have a "Pd-on-Pd" metal structure.[10, 11, 16] For alcohol oxidation reactions over transition metals (e.g., Pt, Pd, Ru, and Au), β-C–H bond cleavage is widely accepted to be the rate-limiting step according to the classical oxidative dehydrogenation mechanism.[38-40] For our Pd-on-Au catalyzed glycerol oxidation reaction, similar volcano shaped activity dependence was observed, indicating a similar geometric effect that 2-D Pd ensembles are still the most active sites for β-C-H bond cleavage. Pd-on-Au/C being much more active than Pd/C can be ascribed to the electronic effect where Au helps Pd atoms stay in metallic form which is more active than the oxidized surface Pd atoms of Pd NPs.

Finally, we suggest that the exposed Au surface is an additional factor in enhanced catalysis, since pure Au is active for glycerol oxidation. In a recent surface-enhanced Raman spectroscopy study of surface species during glycerol oxidation using Au nanoshells [41], we proposed that O2 and/or O2-activated hydroxyl anions adsorb on Au surface and directly react with free glycerolate species (via Eley-Rideal kinetics). For Pd-on-Au NPs then, we speculate
that the Au metal activates the oxidant and the Pd surface ensembles provide the binding sites for both glycerolate species and activated oxygen species (bifunctional effect).

4.4. Conclusions

In this study, we used ex situ extended x-ray absorption fine structure spectroscopy (EXAFS) to analysis the structural change (oxidation state and coordination numbers) of ~4-nm Au, Pd and Pd-on-Au catalysts with two Pd surface coverages (sc%) before and after glycerol oxidation reaction. As-synthesized Au NPs had Au atoms all in metallic state, and Pd NPs had ~29% of its surface Pd oxidized. The core-shell structure of as-synthesized 60 sc% and 150 sc% Pd-on-Au NPs catalysts was confirmed by Punnett square analysis. 60 and 150 sc% Pd-on-Au NPs had ~20% and ~48% of surface Pd atoms in the oxidized state, respectively. Contact with the glycerol reaction medium and a glycerol reaction time of 3 h did not significantly change the oxidation states and coordination numbers of Au/C and 60 sc% Pd-on-Au/C. Under the same conditions, the oxidized Pd content and coordination numbers of as-synthesized 150 sc% Pd-on-Au/C varied slightly. The 60 and 150 sc% materials had similar first-order rate constants for glycerol oxidation, but the latter showed catalyst deactivation whereas the former did not. Pd/C had an increased Pd NP size and it became more oxidized post-reaction, correlating to the observed catalyst deactivation. These results indicate that supporting Pd onto a Au surface eliminates undesired growth of Pd NPs in an oxidative reaction environment and that Au-supported Pd metal is less susceptible to oxidation if the Pd content is not too high, i.e., more of the Pd atoms are in contact with the Au.
4.5. Supplementary Information

Table S4.1. Composition of reducing mixture to synthesize 4 nm sized Au NPs.

<table>
<thead>
<tr>
<th>Au NPs size (nm)</th>
<th>Sodium citrate&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Tannic acid&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Potassium carbonate&lt;sup&gt;c&lt;/sup&gt;</th>
<th>H&lt;sub&gt;2&lt;/sub&gt;O (mL)</th>
<th>Total (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>4</td>
<td>5</td>
<td>5</td>
<td>6</td>
<td>20</td>
</tr>
</tbody>
</table>

a. 1 wt% sodium citrate in H<sub>2</sub>O.
b. 1 wt% tannic acid in H<sub>2</sub>O.
c. 25 mM potassium carbonate in H<sub>2</sub>O.

Table S4.2. Volumes of PdCl<sub>4</sub><sup>2-</sup> used to synthesize Pd-on-Au NPs with various Pd surface coverages.

<table>
<thead>
<tr>
<th>Pd surface coverage (sc%)</th>
<th>Volume of PdCl&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;2-&lt;/sup&gt; precursor (mL)&lt;sup&gt;ab&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.00</td>
</tr>
<tr>
<td>10</td>
<td>0.46</td>
</tr>
<tr>
<td>30</td>
<td>1.36</td>
</tr>
<tr>
<td>50</td>
<td>2.27</td>
</tr>
<tr>
<td>60</td>
<td>2.73</td>
</tr>
<tr>
<td>80</td>
<td>3.64</td>
</tr>
<tr>
<td>100</td>
<td>4.55</td>
</tr>
<tr>
<td>150</td>
<td>7.42</td>
</tr>
</tbody>
</table>

a. Volumes shown are for a 2.49 mM PdCl<sub>4</sub><sup>2-</sup> solution added to 100 mL of Au NP sol.
b. All calculations are based on the magic cluster model.

Table S4.3. Calculated Au and Pd metal contents of Pd-on-Au/C catalysts<sup>a</sup>.

<table>
<thead>
<tr>
<th>Pd surface coverage (sc%)</th>
<th>Calculated Au metal content on C (wt%)</th>
<th>Calculated Pd metal content on C (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>0.000</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>0.025</td>
</tr>
<tr>
<td>30</td>
<td>1</td>
<td>0.074</td>
</tr>
<tr>
<td>50</td>
<td>1</td>
<td>0.123</td>
</tr>
<tr>
<td>60</td>
<td>1</td>
<td>0.147</td>
</tr>
<tr>
<td>80</td>
<td>1</td>
<td>0.196</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td>0.245</td>
</tr>
<tr>
<td>150</td>
<td>1</td>
<td>0.400</td>
</tr>
</tbody>
</table>

a. 201 mL Pd-on-Au NP sol were used to synthesize 1 g Pd-on-Au/C catalysts for all Pd surface coverages and all Au core sizes.

Table S4.4. Volumes of Au and Pd-on-Au NP sol used to synthesize 1 g of Pd-on-Au/C samples for XAS analysis and their calculated Au and Pd metal contents.
<table>
<thead>
<tr>
<th>Pd surface coverage (sc%)</th>
<th>Volume of Pd-on-Au NPs sol used (mL)</th>
<th>Calculated Au metal content on C (wt%)</th>
<th>Calculated Pd metal content on C (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>201</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>60</td>
<td>1407</td>
<td>6.80</td>
<td>1</td>
</tr>
<tr>
<td>150</td>
<td>542</td>
<td>2.50</td>
<td>1</td>
</tr>
</tbody>
</table>

**Coordination number calculation for alloyed PdAu NPs:**

CN values for alloyed PdAu NPs can be calculated using metal molar composition and the total Pd and total Au CNs with the following equations:

- Pd-Pd\textsubscript{alloy} CN = total Pd CN × mol% Pd
- Pd-Au\textsubscript{alloy} CN = total Pd CN × mol% Au
- Au-Au\textsubscript{alloy} CN = total Au CN × mol% Au
- Au-Pd\textsubscript{alloy} CN = total Au CN × mol% Pd
Figure S4.1. Coordination numbers for (a) Au-Au, (b) Au-Pd, (c) Pd-Pd, and (d) Pd-Au absorbing-scattering pairs for the reduced samples of 4 nm Au/C, 60 sc% and 150 sc% Pd-on-Au/C catalysts before and after reaction. "N/A" = no detection of scattering signal or no available number.

4.6. References


Chapter 5

Room Temperature Formic Acid Decomposition for Hydrogen Generation Using Carbon Supported Palladium-on-Gold Nanoparticles

5.1. Introduction

Due to its feasibility in transportation and safety in handling in aqueous form, (FA, a non-toxic liquid with a hydrogen content of 4.4 wt%) has been long deemed as a potential source for in situ H₂ generation for fuel cells and hydrogenation reactions [1]. The decomposition of FA can occur in the following two pathways:

Dehydrogenation: \( \text{HCOOH} \leftrightarrow \text{H}_2 + \text{CO} \quad \Delta G = -48.4 \text{ kJ/mol} \) ...........................................(1)

Dehydration: \( \text{HCOOH} \leftrightarrow \text{H}_2\text{O} + \text{CO} \quad \Delta G = -28.5 \text{ kJ/mol} \) ...........................................(2)

For continuous and stable H₂ production at near-ambient conditions reaction (1) is desired, whereas reaction (2) should be minimized since CO is a known fuel cell catalyst poison (<10 ppm CO). Noble metals have been long been known to selectively catalyze FA dehydrogenation via the first reaction pathway. These catalysts can be divided into two main categories: homogeneous metal-ligand complexes and supported metal catalysts. Homogeneous catalysts, based mainly on Ru, Ir, and Rh metals, have recently been shown to have excellent catalytic
activities in FA decomposition at ambient temperature [2]. However, catalyst recovery issues, use of expensive ligands and solvents, and excessive additives likely will limit their usefulness.

Monometallic Pd and Au catalysts have been both shown to exhibit some activity for FA decomposition [3-5], with some reports finding that PdAu bimetallic catalysts are much more active than monometallic ones [3-6]. However, nearly all catalysts reported were tested under gas or liquid phase with very high FA concentrations, and at elevated temperatures (>50 °C). Additionally, many of the catalysts were shown to form high amounts of CO (10 to 1000 ppm), which was believed to contribute to the deactivation of the catalyst.

Catalytic Pd-on-Au NPs are composed of a 4 nm Au NP core with atomically thin Pd layers corresponding to various Pd surface coverages (sc%). We have extensively studied these catalysts for the aqueous phase hydrodechlorination (HDC) of chlorinated compounds [7-14] and reduction of nitrite for groundwater remediation [15], as well as in aqueous glycerol oxidation [16]. The colloidal catalysts have extremely high reaction rate constants and much higher deactivation resistances to chloride and sulfur for trichloroethylene (TCE) HDC than monometallic Pd catalysts [8, 9]. The reactivity of Pd-on-Au NPs is dependent on the Pd surface coverage; such that a “volcano-shaped” dependence of activity on Pd surface coverage was observed for the HDC of TCE [8, 10]. One of our recent studies further showed that the reactivity of the NPs in HDC reactions was also a function of Au core size, with 7 nm Pd-on-Au NPs being the most active catalyst among those with 3, 7, and 10 nm Au core sizes [14].

Using X-ray absorption fine structure (XAFS), we confirmed that Pd-on-Au NPs have a core-shell structure where nearly all Pd atoms are located on the surface of the Au-rich core and only up to ~20% of them were oxidized (depending on surface coverage), whereas monometallic Pd NPs had 25–35% of its Pd atoms as surface atoms and nearly all of them were oxidized [8,
Au NPs appear to have a unique ability to stabilize surface Pd atoms in metallic form, leading to a set of highly active sites that are not present in monometallic Pd NPs under ambient-temperature reaction conditions [12]. The formation of different Pd ensembles at different Pd coverages on the Au surface was further proposed to explain the dependence of reactivity of HDC of TCE on Pd surface coverage and Au core size [12, 14]. The successful application of Pd-on-Au NPs and their tunable nature of activity through Pd surface coverage and Au core size have led to their further applications in some of our current works, such as HDC of PCE and chloroform, and the selective oxidation of glycerol. This work is currently in preparation for publication.

5.2. Experimental

5.2.1. Materials and Chemicals

Tetrachloroauric(III) acid (HAuCl₄·3H₂O, >99%, Sigma-Aldrich), tannic acid (C₇₆H₅₂O₄₆, >99.5%, Sigma–Aldrich), sodium citrate dihydrate (Na₃C₆H₅O₇·2H₂O, >99.5%, Fisher), potassium carbonate (K₂CO₃, >99.5%, Sigma–Aldrich), palladium(II) chloride(PdCl₂, 99.99%, Sigma-Aldrich), formic acid (≥99.5%, Sigma-Aldrich), sodium formate (≥99.5%, Sigma-Aldrich). Helium (99.99%) gas, oxygen (99.99%) and hydrogen gas (99.99%) were purchased from Matheson. All experiments were conducted in Nanopure water (>18 MΩ-cm, Barnstead NANOpure Diamond). All chemicals were used as received unless otherwise noted.

5.2.2. Catalyst Preparation

5.2.2.1. Au, Pd, and Pd-on-Au NPs sol Preparation

The detailed synthesis of ~ 4 nm Au and Pd-on-Au NPs was reported in our earlier studies [14, 17, 18]. Briefly, for the synthesis of Au NPs, 80 mL HAuCl₄ solution (0.315 mM) and a 20 mL
reducing mixture were preheated to 60 °C. The reducing mixture consisted of tannic acid, sodium citrate and potassium carbonate with various concentrations (4.43 mM K₂CO₃, 6.80 mM sodium citrate, 1.47 mM tannic acid). The reaction occurred instantaneously after adding the reducing mixture into the gold solution. To ensure the competition of reaction, the solution was further heated to boiling for 2 min with moderate stirring. The Au metal concentration for Au NP sol was 49.7 mg Au/L, while the Au NP concentration was calculated to be 1.07×10¹⁴ NP/mL for 4 nm respectively, assuming complete reduction of the Au salt and magic cluster model of Au particle [8, 11, 19-21].

4 nm Pd NPs were synthesized as a control sample by replacing Au salt solution with an 80 mL H₂PdCl₄ solution (0.374 mM) and increasing the boiling time to 25 min. The resulting Pd NPs sol had a calculated particle concentration of 1.27×10¹⁴ NP/mL (= 31.8 mg Pd/L) [8, 11, 19-21]. Bimetallic Pd-on-Au NPs were prepared by adding, then subsequently reducing, the Pd salt precursor in the Au sol with hydrogen gas under room temperature [14, 18]. Different volumes of 2.49 mM H₂PdCl₄ sol were added in the Au NPs sol for various calculated surface coverages (sc%) on the Au NP with different sizes.

5.2.2.2. C supported Au, Pd and Pd-on-Au NPs Preparation

Four compositions representative of less than a calculated 100 sc% and greater than100 sc% NPs were chosen: 30 sc%, 60 sc%, 150 sc% and 300 sc% Pd-on-Au. The Pd loading for all Pd-on-Au/C catalysts was kept constant at 1 wt%, while the Au loading varied according to the Pd surface coverage. For the 30 sc% Pd-on-Au/C sample, 2.814 L of sol from ~28 batches were mixed with 1 g of activated carbon (Darco G-60, Sigma-Aldrich). The mixture was stirred for ~24 h at 700 rpm, cooled to 4 °C, and centrifuged for 40 min at 14,000 rpm. The carbon slurry was collected and dried in a vacuum oven at 70 °C overnight until no further mass loss from
evaporated water was observed. The material was then ground into powder form and stored in the dark at ambient conditions. Activated carbon, in the untreated ("as-is" carbon) and treated forms ("as-processed" carbon), was used for control experiments.

For the 60, 150, 300 sc% Pd-on-Au/C sample, 1407, 542, and 290 mL of sol were mixed with 1 g of C, followed by the rest of the immobilization procedure. The resulting solids of 30, 60, 150, 300 sc% Pd-on-Au/C were calculated to have 13.5, 6.8, 2.5 and 1.4 wt% Au, respectively. Carbon-supported with 1 wt% Au (Au/C) was prepared in the same manner by mixing 204 mL of Au sol (49.7 mg Au/L) with 1.0 g of activated carbon; carbon-supported with 1 wt% Pd (Pd/C) was prepared in the same manner by mixing 314 mL of Pd sol (31.8 mg Pd/L) with 1.0 g of activated carbon.

5.2.3. Catalyst Characterization

Au, Pd and Pd-on-Au NPs and their supported forms have been comprehensively characterized in our earlier studies using transmission electron microscopy (TEM), nitrogen physisorption, inductively coupled plasma-atomic emission spectroscopy (ICP-AES), X-ray photoelectron spectrum (XPS), X-ray absorption fine structure (XAFS).

5.2.3.1. Ex situ X-ray Absorption Spectroscopy (XAS)

Catalyst samples were detected both in *ex situ* and *in situ* XAS modes. XAS measurements were carried out on Au L₃ (11.919 keV) or Pd K (24.350 keV) edges on the insertion device (beamline 10-ID-B) of the Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon Source at Argonne National Laboratory. Detailed instrumentation can be found in our earlier studies [12, 14].

*Ex situ* XAS spectra of each sample were collected first under air at room temperature, and then collected again after flowing 4% H₂/He gas for ~30 min at 200 °C and cooling to room
temperature under a He purge. Based on our previous studies, this treatment method fully reduces oxidized Pd without altering the bimetallic nanostructure.[12] These reduced samples were then analyzed under He at room temperature to determine the extent of Pd oxidation in the Pd/C and Pd-on-Au/C samples.

5.2.3.2. In situ X-ray Absorption Spectroscopy (XAS)

In situ XAS measurements were taken using a liquid cell fabricated out of polyether ether ketone (PEEK) with Kapton windows on the side of the cell. The cell had full gas inlet-outlet and injection ports, and was capped by a Swagelok VCR fitting with a hand-tightened O-ring seal. Deionized water was used as the liquid medium throughout. Prior to measurement, the cell was first loaded with 200 mg solid catalyst sample, then purged with He gas at 50 mL/min for 15 min to remove air. The gas inlet port was then turned off, and the outlet port was connected to a plastic pipe sealed with water at the end to avoid pressure build-up. Injecting 0.5 mL of 1 M formic acid solution through the liquid injection port marked the start of the reaction, after which in situ XAS measurements were taken in transmission mode every 5 min for 30 min.

5.2.4 Catalytic Testing

Catalytic experiments were conducted in a homemade batch reactor (Scheme 5.1). 500 mg of catalyst was loaded into a glass vial (40 mL, VWR), which was then sealed with Teflon tape and a Teflon-coated rubber septum. Catalytic activity was quantified by measuring the gas release rate from the reactor. The reactor was connected to a CO electro-chemical detector (0-300 ppm with 1 ppm precision, Environmental Sensors Co.), which was then connected to a plastic bottle (2 L, VWR) laid horizontally and loaded with 1.8 L water acidified to pH = 4 to minimize CO$_2$ solubility. Composition of the effluent gas was analyzed by injecting 250 μL of headspace sample into an Agilent Technologies 6890N gas chromatography (GC) equipped with a thermal
conductivity detector (TCD) and a ResTek PC 3533 Hayesep Q. 60180 packed column. A GC method with a run time of 4.5 min, helium carrier gas at a flow rate of 10 mL/min, and an oven temperature of 35 °C was used. The standard curves for H₂, CO, and CO₂ were prepared by injecting various volumes of the standard gas (100 ppm CO, 49.995% H₂, 49.995% CO₂, Matheson). CO content in ppm was directly read from the digital display of the CO electro-chemical detector which had been calibrated with known CO concentrations.

Scheme 5.1. Set-up for homemade batch reactor by measuring the gas releasing rate from formic acid

5.2.5 Reaction rate constants

5.2.5.1. Reaction rate constants

Formic acid conversion $X$ was calculated as $(C_{FA,0} - C_{FA}) / C_{FA,0}$. At 23 °C, the mole volume for CO₂ and H₂ are both 24.3 L/mol, and since the reaction generates equal amounts of CO₂ and H₂
and only parts per million (ppm) level of CO, the converted amount of FA (C_{FA,0}-C_{FA}) can be calculated as \( V/(2\times24.3) \), where \( V \) (with units of L) is the volume of the gas evolved. Thus \( C_{FA} \) can be further expressed as:

\[
C_{FA} = C_{FA,0} - \frac{V}{(2\times24.3)} \quad \text{(Eqn. 1)}
\]

Formic acid decomposition reaction kinetics was modeled as a first-order reaction (Eqn. 2) with respect to formic acid. The apparent initial first-order reaction rate constant \( k_{\text{meas}} \) (with units of \( h^{-1} \)) was calculated from fitting Eqn. 3 to the first 2 hr of the concentration-time profiles, where \( t \) is the reaction time. For catalysts in which deactivation was observed, \( k_{\text{meas}} \) was also calculated by fitting Eqn. 2 to the first 1 hr of the concentration-time profiles as a comparison.

\[
-dC_{FA}/dt = k_{\text{meas}}\times C_{FA} \quad \text{(Eqn. 2)}
\]

\[
C_{FA} = C_{FA,0}\times e^{-k_{\text{meas}}\times t} \quad \text{(Eqn. 3)}
\]

The metal-normalized rate constant \( k_{\text{cat}} \) (with units of L/g metal/h) was defined as \( k_{\text{meas}} \) divided by the Pd metal content charged to the reactor (\( C_{\text{Pd}} \)):

\[
k_{\text{cat}} = \frac{k_{\text{meas}}}{C_{\text{Pd}}} \quad \text{(Eqn. 4)}
\]

To represent catalytic activity at the particle surface, initial turnover frequency (TOF) was defined as:

\[
\text{TOF} = \frac{k_{\text{meas}}\times C_{FA,0}}{C_{sPd}} \quad \text{(Eqn. 5)}
\]

(with units of mol-FA/mol-surface-atom/h), where \( C_{sPd} \) is the surface metal content of the reactor.

5.2.5.2. Metal Dispersion

For the carbon-supported monometallic Au and Pd NPs, metal dispersions (\( i.e. \), percentage of Au or Pd atoms as surface atoms) were calculated to be 34.8% assuming 4-nm NPs were a magic cluster of 7 shells of Au or Pd atoms [8, 19-21]. For carbon-supported Pd-on-Au NPs with Pd
surface coverages lesser than 100 sc%, all Pd atoms were assumed to be surface Pd atoms in the 8\textsuperscript{th} shell (\textit{i.e.}, Pd dispersion = 100\%). For Pd surface coverages greater than 100 sc%, the surface Pd content was calculated assuming a magic cluster model of the Pd-on-Au NPs. For example, the surface atoms of 150 sc\% Pd-on-Au NPs were counted as those Pd atoms in the 9\textsuperscript{th} shell and those Pd atoms in 8\textsuperscript{th} shell that not covered by the 9\textsuperscript{th} shell which gives a calculated Pd dispersion of 73.4\%). For 300 sc\% Pd-on-Au NPs, the calculated Pd dispersion was 40.8\%.

5.3. Results and Discussion

5.3.1. Mass Transfer Analysis

Our reactor consists of three phases: the headspace gas, liquid water, and solid catalyst. Since formic acid is completely miscible with water and the decomposition reaction only takes place in the liquid phase, proper mass transfer tests need to be carried out to account for liquid-solid mass transfer, intraparticle diffusion resistances ($1/k_{ls}$ and $1/k_{ls}$), surface reaction resistance ($1/k_{NP}$), and to ensure that the reaction rates were calculated properly [11]. Following the analysis given in reference [11], we measured the observed reaction rate constant $k_{\text{meas}}$ of the most active catalyst (300 sc\% Pd-on-Au/C) at different charges to determine any effect of mass transfer on the observed rates (Fig. 5.1).
Figure 5.1. The relationships between (a) observed reaction rate constant $k_{\text{meas}}$ and Pd metal concentration, (b) $1/k_{\text{meas}}$ and $1/(\text{Pd metal concentration})$ at 1200 rpm stirring rate. The red circles mark the default catalyst charge for the formic acid decomposition reaction. Reaction conditions: 0.5 g catalyst, 23 °C, 1200 rpm stirring rate, 10 mL, 1 M formic acid.

At a stirring rate of 1200 rpm, $k_{\text{meas}}$ values varied linearly with catalyst mass from 0 to 0.75 g (Fig. 2a), with the slope corresponding to $k_{\text{cat}} = 6.57 \times 10^{-3}$ L/gPd/h. This value was within 10% error of $k_{\text{cat}}$ calculated using the typical catalyst charge of 0.5 g (= 5 mg-Pd/L) for 300 sc% Pd-on-Au/C ($6.67 \times 10^{-3}$ L/gmetal/h). A standard catalyst charge in this linear regime indicates the $k_{\text{cat}}$ values determined for all other catalytic materials were independent of catalyst amount. The values of mass transfer resistances were determined utilizing a method previously developed for TCE HDC reaction catalyzed by Pd-on-Au NPs [11]. The y-intercept of Fig. 2b gives the value of gas-liquid mass transfer resistance. Since this value is very small (3.82 h) compared with surface reaction resistance ($1/k_{\text{aNP}} = 30441$ h), indicating negligible gas-liquid mass transfer resistance. This is in agreement with the fact that formic acid decomposition only happens in the liquid phase. The liquid-solid mass transfer resistance ($1/k_{\text{ga}}$) was also determined to have an insignificant effect on the observed rate constants. Thus the rate constants were not corrected for mass transfer resistances.
5.3.2. Activity Analysis

The catalytic activity of formic acid decomposition at room temperature was evaluated for monometallic Au, Pd catalysts and bimetallic Pd-on-Au/C with various Pd surface coverages. Commercially available Pd/C (1 wt%, Sigma-Aldrich), and Au/Al₂O₃ (1.2 wt%, Mintek) were also tested as controls. Fig. 5.2 shows the volume of gas released versus time and Table 5.1 lists the calculated reaction rate constants.

Au/Al₂O₃ and 4 nm Au/C catalysts had no activity as no gas formation was observed after 3 hours of reaction time. Sabatier et al analyzed the surface affinity of different metals to formic acid in the vapor phase and found that the binding formic acid on Au was very weak such that the temperature required for Au to decompose formic acid at a given conversion was very high. Other metals, for examples Ru, Pt, Pd, Ni, Fe, etc., had different enthalpies of surface formation with formic acid at various temperatures, leading to the well-known Sabatier principle that a moderate affinity between catalyst surface and reagent is required for best catalyst performance [22]. Bi et al. recently reported the ultra-high activity of TEM-invisible Au supported on ZrO₂ catalyst, which had a TOF of 1590 h⁻¹ at 50 °C for formic acid decomposition in triethylamine [23]. They concluded that reaction proceeds uni-molecularly via an amine-assisted formate decomposition mechanism at the Au–ZrO₂ interface. Otherwise, Au is reported to have weak activity by most other researchers [3-5].

Pd-on-Au/C catalyst with 0 sc% Pd surface coverage generated a negligible amount (< 0.2 mL, Fig. 5.2, Table 5.1) of gas after 3 h of reaction time. 60 sc% Pd-on-Au/C was slightly more active with ~ 1.0 mL gas released within 3 h and a calculated TOF value of 2.6 h⁻¹. 150 sc% Pd-on-Au/C initially had a faster gas release during the first 10 min after which the release rate
slowed down, with a total of 22.5 mL gas generated at 3 h. The TOF value of 150 sc% Pd-on-Au/C was calculated to be 35.2 h\(^{-1}\), higher than the 60 sc% one by 13.5\(\times\).

300 sc% Pd-on-Au/C was the most active catalyst, generating 58.2 mL of gas in 3 h and exhibiting no apparent deactivation. Compared with published results using PdAu/C and homogeneous Ru catalysts (Table S5.1), our Pd-on-Au catalyst was much more active than PdAu/C measured at 92 \(\degree\)C, and was in the range of homogeneous Ru catalysts with a TOF value of 123 h\(^{-1}\), higher than 60 and 150 sc% ones by 47.3\(\times\) and 3.5\(\times\), respectively.
Table 5.1. Catalytic activity results for carbon-immobilized Au, Pd, and Pd-on-Au NPs. Reaction conditions: 0.5 g catalyst, 23 °C, 1200 rpm stirring rate, 10 mL, 1 M formic acid. Each reaction rate constant was the average of three runs.

<table>
<thead>
<tr>
<th>Catalyst type</th>
<th>Volume of gas released after 3 hr (mL)</th>
<th>Initial H₂ generation rate (mL/min/g Pd)</th>
<th>Reaction rate constants[^a]</th>
<th>H₂: CO₂ ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>C received</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>C processed</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>Au/Al₂O₃</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>Au/C</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>30 sc%</td>
<td>&lt; 0.2</td>
<td>0</td>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>60 sc%</td>
<td>1.0</td>
<td>~1</td>
<td>2.6</td>
<td>1.0</td>
</tr>
<tr>
<td>150 sc%</td>
<td>22.5</td>
<td>133</td>
<td>35.2</td>
<td>1.0</td>
</tr>
<tr>
<td>300 sc%</td>
<td>58.2</td>
<td>137</td>
<td>123</td>
<td>1.0</td>
</tr>
<tr>
<td>Pd/C</td>
<td>9.8</td>
<td>5</td>
<td>38</td>
<td>1.0</td>
</tr>
</tbody>
</table>

[^a]: First-order reaction rate constants were calculated using data points in the first 2 hr. Reaction rate constants in parentheses were calculated from the first 0.5 hr of the concentration-time profile for Pd/C, and for the first 1 hr of the concentration-time profile for 100, 150, and 300 sc% Pd-on-Au/C catalysts.

[^b]: Units of initial TOF are mol-FA/mol-surface-atom/h.

5.3.3. CO concentration

The CO₂ to H₂ ratio was 1.00 ± 0.05 at all reaction times for all catalysts (Table 5.1). CO concentration was monitored by injecting headspace gas into GC-TCD. Fig. 5.3 shows the CO concentration profiles in ppm for Au/C, Pd/C, and 30, 60, 150 and 300 sc% Pd-on-Au/C catalysts. Au/C was not active and did not generate any CO. Pd/C had an increasing amount of CO during reaction, reaching ~1 ppm after 3 h of reaction. 30 sc% Pd-on-Au/C catalyst had the highest amount of CO (~8 ppm) throughout reaction, while the 60 sc% and 150 sc% Pd-on-Au/C had less at ~5 ppm and ~1 ppm respectively. Furthermore, the most active catalyst 300 sc% Pd-on-Au/C had no detectable amount of CO. The trend in CO concentration is somewhat consistent with the observed activity order of those catalysts, indicating the possible correlation between...
deactivation and dehydration pathway. This also indicates that formic acid decomposes majorly via dehydrogenation pathway, generating equal amount of $\text{CO}_2$ and $\text{H}_2$. This result matches with what Tedsree and co-workers observed for Ag-Pd bimetallic NPs catalyzed room temperature formic acid decomposition [24].

![Figure 5.3](image)

**Figure 5.3.** CO concentration profiles for Au/C, Pd/C, and 30, 60, 150 and 300 sc% Pd-on-Au/C catalysts. Reaction conditions: 0.5 g catalyst, 23 °C, 1200 rpm stirring rate, 10 mL, 1 M formic acid.

5.3.4. *Effect of pH*

Various mixtures of formic acid and sodium formate ($\text{HCOOH} + \text{HCOONa}$) with a total of 1 M formate concentration were prepared and used for decomposition reaction to study the pH effect. Pure 7.1 M formic acid has a pH of 1.8, while adding more HCOONa, the pH of mixture gradually increases to the value of pure 7.1 M sodium formate ($\text{pH} = 9.1$).
Formic acid decomposition TOF is observed to have a strong dependence on the formic acid ratio (Fig. 5.4). With pure sodium formate, the TOF value is 4.6 h\(^{-1}\). This is much lower than those with certain percentage of HCOOH addition due to the lower concentration of active hydrogen from formic acid. The non-zero value of TOF, however, is probably due to the following reaction with a slower reaction rate: HCOONa + H\(_2\)O(l) = H\(_2\)(g) + NaHCO\(_3\), as observed by others. A HCOOH/(HCOOH + HCOONa) ratio of 0.67 gave the highest observed TOF, even more than pure formic acid. This can be concluded as the effects from both formic acid concentration and pH values. For one thing, sufficient concentration of formic acid species is required to generate hydrogen; for another, its concentration should not be too high such that its pH value is below which the active metals will be dissolved and deactivated. For this study, to minimize the above mentioned side reaction as well as reducing effect of formic acid at low pH, 1 M formic acid was used to carry out all catalytic reactions.
5.3.5. *Ex situ XAFS structures of as-synthesized catalysts*

0 min measurements were made before injecting formic acid, and were consistent with samples measured *ex situ*. For Au/C catalyst, a Au-Au coordination number (CN) of ~9.5 (Table 5.2) corresponds to an average NP size of ~4.3 nm based on TEM-EXAFS size correlation developed for supported Au materials [25]. Au atoms were all in metallic state with no evidence of oxidation. This result is consistent with our previous studies [12, 14, 16].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Treatment</th>
<th>Scattering path</th>
<th>CN (± 10%)</th>
<th>R, Å (± 0.02 Å)</th>
<th>DWF (× 10³ Å²)</th>
<th>E₀ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 min</td>
<td>Air RT</td>
<td>Au-Au</td>
<td>9.5</td>
<td>2.86</td>
<td>1.0</td>
<td>-0.6</td>
</tr>
<tr>
<td></td>
<td>H₂ 200 ºC</td>
<td>Au-Au</td>
<td>9.3</td>
<td>2.86</td>
<td>1.0</td>
<td>-1.0</td>
</tr>
<tr>
<td>5 min</td>
<td>Air RT</td>
<td>Au-Au</td>
<td>9.3</td>
<td>2.86</td>
<td>1.0</td>
<td>-0.3</td>
</tr>
</tbody>
</table>

60 sc% Pd-on-Au/C had coordination numbers similar to our previous results [12, 14], indicating a core-shell structure. A Pd-Pd CN value of 0.6 and Pd-O CN value of 0.9 means that the Pd atoms are in small 2-dimensional (2-D) ensembles and that 20% of those atoms are oxidized. This 0 min *in situ* result also matches with our previous structural model developed for 60 sc% Pd-on-Au NPs [12, 16]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Treatment</th>
<th>Scattering path</th>
<th>CN (± 10%)</th>
<th>R, Å (± 0.02 Å)</th>
<th>DWF (× 10³ Å²)</th>
<th>E₀ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 min</td>
<td>Air RT</td>
<td>Au-Au</td>
<td>9.1</td>
<td>2.85</td>
<td>0.0</td>
<td>-0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Au-Pd</td>
<td>2.3</td>
<td>2.78</td>
<td>0.0</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>H₂ 200 ºC</td>
<td>Au-Au</td>
<td>9.4</td>
<td>2.86</td>
<td>0.0</td>
<td>0.2</td>
</tr>
</tbody>
</table>
150 sc% Pd-on-Au/C catalyst at 0 min reaction also had a Au rich core and Pd rich shell, according to Table 5.4. Comparing to 60 sc% one, 150 sc% had larger Pd-Pd and Pd-O CN values (1.5, 1.3, respectively, Table 5.4), representing presence of large 2-D ensembles and higher fraction of 3-D ensembles with ~38% of total Pd oxidized.

**Table 5.4.** EXAFS fit parameters for 150 sc% Pd-on-Au/C samples on Au and Pd edges. Reaction conditions: 0.2 g catalyst, 23 °C, 0.5 mL, 0.5 M formic acid.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Treatment</th>
<th>Scattering path</th>
<th>CN (± 10%)</th>
<th>R, Å (± 0.02 Å)</th>
<th>DWF (× 10³ Å²)</th>
<th>E₀ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Au Edge</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 min</td>
<td>Air RT</td>
<td>Au-Au</td>
<td>8.8</td>
<td>2.85</td>
<td>0.0</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Au-Pd</td>
<td>2.4</td>
<td>2.78</td>
<td>0.0</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>H₂ 200 °C</td>
<td>Au-Au</td>
<td>8.7</td>
<td>2.85</td>
<td>0.0</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Au-Pd</td>
<td>2.5</td>
<td>2.78</td>
<td>0.0</td>
<td>2.9</td>
</tr>
<tr>
<td>5 min</td>
<td>Air RT</td>
<td>Au-Au</td>
<td>8.8</td>
<td>2.85</td>
<td>0.0</td>
<td>-0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Au-Pd</td>
<td>2.4</td>
<td>2.78</td>
<td>0.0</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>Pd Edge</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 min</td>
<td>Air RT</td>
<td>Pd-O</td>
<td>1.3</td>
<td>2.04</td>
<td>1.0</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pd-Pd</td>
<td>1.5</td>
<td>2.75</td>
<td>1.0</td>
<td>-3.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pd-Au</td>
<td>7.3</td>
<td>2.78</td>
<td>1.0</td>
<td>-6.0</td>
</tr>
<tr>
<td></td>
<td>H₂ 200 °C</td>
<td>Pd-Pd</td>
<td>2.0</td>
<td>2.75</td>
<td>1.0</td>
<td>-2.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pd-Au</td>
<td>7.8</td>
<td>2.78</td>
<td>1.0</td>
<td>-5.8</td>
</tr>
<tr>
<td>5 min</td>
<td>Air RT</td>
<td>Pd-O</td>
<td>1.2</td>
<td>2.05</td>
<td>1.0</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pd-Pd</td>
<td>1.3</td>
<td>2.75</td>
<td>1.0</td>
<td>-3.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pd-Au</td>
<td>6.2</td>
<td>2.78</td>
<td>1.0</td>
<td>-5.8</td>
</tr>
</tbody>
</table>
Different from 60 and 150 sc%, 300 sc% Pd-on-Au NP was highly oxidized (CN\textsubscript{Pd-O} = 2.6, 65%, Table 5.5) in air at room temperature. The core-shell structure of 300 sc% Pd-on-Au NPs is proved by a CN value of 8.6 for Au-Au scatter, a CN value of 2.4 for Au-Pd scatter and a CN value of 2.3 for Pd-Au scatter. At 200 °C \textsubscript{H2}, 300 sc% Pd-on-Au NPs were fully reduced and Pd had more Pd-Pd neighbors than Pd-Au, indicating a large 3-D ensembles on Au surface.

**Table 5.5.** EXAFS fit parameters for 300 sc% Pd-on-Au/C samples on Au and Pd edges. Reaction conditions: 0.2 g catalyst, 23 °C, 0.5 mL, 0.5 M formic acid.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Treatment</th>
<th>Scattering path</th>
<th>CN (± 10%)</th>
<th>R, Å (± 0.02 Å)</th>
<th>DWF (× 10\textsuperscript{3} Å\textsuperscript{2})</th>
<th>E\textsubscript{0} (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Au Edge</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 min</td>
<td>Air RT</td>
<td>Au-Au</td>
<td>8.6</td>
<td>2.85</td>
<td>0.0</td>
<td>-0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Au-Pd</td>
<td>2.4</td>
<td>2.78</td>
<td>0.0</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>\textsubscript{H2} 200 °C</td>
<td>Au-Au</td>
<td>8.5</td>
<td>2.85</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Au-Pd</td>
<td>3.1</td>
<td>2.78</td>
<td>0.0</td>
<td>4.1</td>
</tr>
<tr>
<td>5 min</td>
<td>Air RT</td>
<td>Au-Au</td>
<td>9.1</td>
<td>2.85</td>
<td>0.0</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Au-Pd</td>
<td>2.2</td>
<td>2.78</td>
<td>0.0</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>Pd Edge</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 min</td>
<td>Air RT</td>
<td>Pd-O</td>
<td>2.6</td>
<td>2.04</td>
<td>1.0</td>
<td>-1.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pd-Pd</td>
<td>1.1</td>
<td>2.75</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pd-Au</td>
<td>2.3</td>
<td>2.78</td>
<td>1.0</td>
<td>-2.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>\textsubscript{H2} 200 °C</td>
<td>Pd-Pd</td>
<td>6.5</td>
<td>2.75</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pd-Au</td>
<td>2.7</td>
<td>2.78</td>
<td>1.0</td>
<td>-4.1</td>
</tr>
<tr>
<td>5 min</td>
<td>Air RT</td>
<td>Pd-O</td>
<td>1.2</td>
<td>2.05</td>
<td>1.0</td>
<td>-0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pd-Pd</td>
<td>4.5</td>
<td>2.75</td>
<td>1.0</td>
<td>-1.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pd-Au</td>
<td>4.9</td>
<td>2.78</td>
<td>1.0</td>
<td>-2.8</td>
</tr>
</tbody>
</table>

The commercial Pd/C is fully reduced in \textsubscript{H2} at 200 °C (Table 5.6) and has a particle size of about 3-4 nm based on EXAFS-size relationship [25]. It has a typical Pd-Pd bond distance of 2.75 Å. The Pd/C in air is partially reduced, with ~40% metallic Pd and ~60% PdO. Generally, the smaller the Pd NP is, the higher the fraction of oxidized Pd. This is because at room temperature only the surface is oxidized, and for smaller NPs there is a higher fraction of Pd atoms.
Table 5.6. EXAFS fit parameters for Pd/C samples on Pd edge. Reaction conditions: 0.2 g catalyst, 23 °C, 0.5 mL, 0.5 M formic acid.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Treatment</th>
<th>Scattering path</th>
<th>CN (± 10%)</th>
<th>R, Å (± 0.02 Å)</th>
<th>DWF (× 10^3 Å^2)</th>
<th>E_o (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 min</td>
<td>Air RT</td>
<td>Pd-O</td>
<td>2.3</td>
<td>2.04</td>
<td>1.0</td>
<td>-5.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pd-Pd</td>
<td>3.5</td>
<td>2.74</td>
<td>1.0</td>
<td>-1.0</td>
</tr>
<tr>
<td></td>
<td>H_2 200 °C</td>
<td>Pd-Pd</td>
<td>8.6</td>
<td>2.75</td>
<td>1.0</td>
<td>0.2</td>
</tr>
<tr>
<td>5 min</td>
<td>Air RT</td>
<td>Pd-O</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pd-Pd</td>
<td>7.3</td>
<td>2.76</td>
<td>1.0</td>
<td>0.1</td>
</tr>
</tbody>
</table>

5.3.6. In situ XAS characterization during reaction

Au/C catalyst had no change in spectrum during reaction (Table 5.2), indicating no structural change for Au NPs. 60 sc% Pd-on-Au/C also had negligible change in either spectra (Figure 5.5a) or coordination numbers (Table 5.3). The percentage of oxidized Pd stayed 20% throughout reaction. 150 sc% Pd-on-Au/C had insignificant change in the coordination numbers for various absorber-scatterer (Table 5.4) except for Pd-O, indicating the core-shell structure of 150 sc% Pd-on-Au was not affected during reaction. However, XANES fitting indicates that the percentage of oxidized Pd dropped from 37.5% to ~20% after 5 min’s reaction and stayed ~20% after 30 min’s reaction. 300 sc% Pd-on-Au/C also had insignificant change in its coordination numbers (Table 5.5) but had a dramatic decrease in PdO%, from 62.5% for as-synthesized sample to ~18% after 5 and 30 min’s reaction. 150 and 300 sc% Pd-on-Au NPs are partially oxidized under in situ reaction conditions; however, the fraction of metallic Pd is higher than that for the catalyst ex situ in air only. Formic acid appears to partially reduce the surface Pd compared to as-synthesized samples.
Pd/C had a significant increase in coordination number of Pd-Pd scatter, representing a growth in particle size due to agglomeration. The percentage of PdO also decreased greatly from 60% to ~10% after 5 and 30 min’s reaction.
Figure 5.5. XAS spectra at the Pd K edge and the percentage of oxidized Pd for (a, b) 60 sc% Pd-on-Au/C, (c, d) 150 sc% Pd-on-Au/C, (e, f) 300 sc% Pd-on-Au/C and (g, h) Pd/C at 0, 5 and 30 min reaction times.

The reduction of PdO to metallic Pd observed for 150, 300 sc% Pd-on-Au/C and Pd/C is due to the reducing power of formic acid. Table 5.7 lists various oxidation-reduction potential (ORP) measured for different reaction conditions. The ORP value measured for air saturated H₂O is 298 mV. A positive value indicates an oxidative power while negative value represents a reductive power. 1 M formic acid in air saturated H₂O had an ORP value of 0 mV, indicating a neutral potential reaction medium. After replacing air with helium, the ORP value dropped down to -133 mV. Considering the pH of 1 M formic acid is ~2, this ORP value is enough to reduce PdO to Pd at room temperature, explaining our XAS observations. Furthermore, the addition of sodium formate into formic acid decreased its ORP value even more. With 0.01, 0.1 and 1 M sodium formate added into 1M formic acid, the ORP values were measured at -138, -158 and -224 mV, respectively.

It is also interesting to note that 150, 300 sc% Pd-on-Au/C and Pd/C catalysts still had ~10-20% PdO left after 5 and 30 min’s reaction. Possible reasons could be that some of those oxidized Pd are not on the surface, making formic acid hard to penetrate and reduce them, or that reaction time is not long enough to observe the rest being reduced.

Table 5.7. ORP values of various reaction conditions

<table>
<thead>
<tr>
<th></th>
<th>Air 1 M FA/air</th>
<th>1 M FA/He</th>
<th>1 M FA + 0.01 M SF/He</th>
<th>1 M FA + 0.1 M SF/He</th>
<th>1 M FA + 1 M SF/He</th>
</tr>
</thead>
<tbody>
<tr>
<td>ORP (mV)</td>
<td>298</td>
<td>0</td>
<td>-133</td>
<td>-138</td>
<td>-158</td>
</tr>
</tbody>
</table>

5.3.7. Correlation with kinetics results
Tedsee and co-workers extensively studied the structure-activity relationship of their Ag-Pd core-shell NPs catalyzed room temperature formic acid decomposition reaction. They concluded that both geometric effect (surface structure of the metal particle) and electronic effect (work function difference between two metals) are contributing to the observed enhanced activity with the highest TOF value of 192 h\(^{-1}\) for Ag@Pd/C (1:1) catalyst [24, 26, 27]. As to geometric effect, they identified two different binding modes for formate species on their metal surface. One is bridging binding of formate with two neighbor metal atoms, leading to the formation CO\(_2\) and H\(_2\) via dehydrogenation mechanism. Large terrace or ensemble sites are thought to be the ideal sites where metal atoms have sufficient neighbors for bridging binding of formate. Linear binding is another mode which is favored when surface unsaturated sites (adatoms, corners, steps, and kinks) are predominant, resulting in the formation of CO via dehydration pathway. The distribution of two modes is largely controlled by the surface geometry and particle size [32], giving rise to different catalytic activities and selectivities. As to electronic effect, Tedsee and co-workers calculated the work function difference for several bi-metal combinations (Rh, Ru, Au, and Pt) and found that Ag@Pd NPs had the largest work function difference (Fermi levels difference), which was concluded to favor the adsorption of formate species in a bridge mode. Other metals (Rh, Ru, Au, and Pt) as core had either too weak or too strong adsorption [56].

In our structural model, ex situ XAFS characterization confirmed the oxidation states and core-shell structures with different Pd ensemble formations for Pd-on-Au catalysts. In situ XAS revealed that core-shell structures of 60, 150 and 300 sc% Pd-on-Au NPs maintained while oxidized Pd species was reduced during reaction. Au NPs were metallic and had no change in structure throughout reaction. Au atom’s low affinity to formic acid in this Au NPs probably explains its inactivity. 30 sc% Pd-on-Au NPs had mostly scattered metallic Pd atoms, which
favor linear or multi-linear formate binding, leading to high CO ppm level. Nearly no activity was observed for 30 sc% Pd-on-Au NPs due to fast CO poisoning on the Pd atoms. 60 sc% Pd-on-Au NPs had mostly small 2-D Pd ensembles and few 1-D Pd atoms. Since small 2-D Pd ensembles, edge Pd atoms, scattered Pd atoms favor linear binding, it exhibited very small activity due to CO poisoning on those Pd atoms. 150 sc% Pd-on-Au NPs had mostly small 2-D Pd ensembles and few 1-D Pd atoms. Since small 2-D Pd ensembles, edge Pd atoms, scattered Pd atoms favor linear binding, it exhibited very small activity due to CO poisoning on those Pd atoms. 150 sc% Pd-on-Au NPs had mostly small 2-D Pd ensembles and few 1-D Pd atoms. Since small 2-D Pd ensembles, edge Pd atoms, scattered Pd atoms favor linear binding, it exhibited very small activity due to CO poisoning on those Pd atoms. 150 sc% Pd-on-Au NPs had mostly small 2-D Pd ensembles and few 1-D Pd atoms. Since small 2-D Pd ensembles, edge Pd atoms, scattered Pd atoms favor linear binding, it exhibited very small activity due to CO poisoning on those Pd atoms. 150 sc% Pd-on-Au NPs had mostly small 2-D Pd ensembles and few 1-D Pd atoms. Since small 2-D Pd ensembles, edge Pd atoms, scattered Pd atoms favor linear binding, it exhibited very small activity due to CO poisoning on those Pd atoms. 150 sc% Pd-on-Au NPs had mostly small 2-D Pd ensembles and few 1-D Pd atoms. Since small 2-D Pd ensembles, edge Pd atoms, scattered Pd atoms favor linear binding, it exhibited very small activity due to CO poisoning on those Pd atoms. 150 sc% Pd-on-Au NPs had mostly small 2-D Pd ensembles and few 1-D Pd atoms. Since small 2-D Pd ensembles, edge Pd atoms, scattered Pd atoms favor linear binding, it exhibited very small activity due to CO poisoning on those Pd atoms. 150 sc% Pd-on-Au NPs had mostly small 2-D Pd ensembles and few 1-D Pd atoms. Since small 2-D Pd ensembles, edge Pd atoms, scattered Pd atoms favor linear binding, it exhibited very small activity due to CO poisoning on those Pd atoms. 150 sc% Pd-on-Au NPs had mostly small 2-D Pd ensembles and few 1-D Pd atoms. Since small 2-D Pd ensembles, edge Pd atoms, scattered Pd atoms favor linear binding, it exhibited very small activity due to CO poisoning on those Pd atoms. 150 sc% Pd-on-Au NPs had mostly small 2-D Pd ensembles and few 1-D Pd atoms. Since small 2-D Pd ensembles, edge Pd atoms, scattered Pd atoms favor linear binding, it exhibited very small activity due to CO poisoning on those Pd atoms. 150 sc% Pd-on-Au NPs had mostly small 2-D Pd ensembles and few 1-D Pd atoms. Since small 2-D Pd ensembles, edge Pd atoms, scattered Pd atoms favor linear binding, it exhibited very small activity due to CO poisoning on those Pd atoms. 150 sc% Pd-on-Au NPs had mostly small 2-D Pd ensembles and few 1-D Pd atoms. Since small 2-D Pd ensembles, edge Pd atoms, scattered Pd atoms favor linear binding, it exhibited very small activity due to CO poisoning on those Pd atoms.

5.4. Conclusions

Pd-on-Au/C catalysts with various Pd surface coverages were tested for room temperature formic acid dehydrogenation. The most active catalyst had a calculated theoretical Pd surface coverage of 300 sc% with a TOF value of 123 h⁻¹, much more active than monometallic Au and Pd counterparts and literature values measured in similar conditions. Pd surface coverage played an important role in the reactivity, with a catalytic activity order of 30 sc% < 60 sc% < 150 sc% < 300 sc%. 300 sc% one had no apparent deactivation during 3 h reaction while 150 sc% one did. GC-TCD analysis of headspace gas indicated that H₂ to CO₂ ratio for all catalysts were 1.0, and that the CO concentration increased with decrease in Pd surface coverage. 300 sc% Pd-on-Au had no detectable amount of CO while 30 sc% one had the highest. Ex situ XAFS analysis matches with our previous structural model that Pd-on-Au catalysts had Pd-rich shell and Au-
rich core. *In situ* XAFS further discovered that oxidized Pd was partially reduced for 150 and 300 sc% Pd-on-Au and Pd/C while the core-shell structures of all Pd-on-Au catalysts were preserved. Electronic and geometric effects were proposed to explain the observed activity dependence on Pd surface coverage. Large 3-D Pd ensembles on 300 sc% Pd-on-Au NPs favor the dehydrogenation pathway of formic acid decomposition via bridging binding, while scattered Pd atoms as well as small 2-D Pd ensembles on Pd-on-Au NPs with lower surface coverages favor the dehydration pathway via linear binding, correlating to CO poisoning. Due to the tunability of surface Pd species via Pd surface coverage and Au particle size, the FA dehydrogenation activity should be further optimizable for higher TOF's.

### 5.5. Supplementary Information

**Table S5.1.** Comparison among different catalyst materials

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temperature</th>
<th>H₂ generation rate (mL/gₚₐ/min)</th>
<th>Initial TOF (h⁻¹)</th>
<th>Selectivity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/Al₂O₃</td>
<td>77 °C</td>
<td>n/a</td>
<td>n/a</td>
<td>100%</td>
<td>[5]</td>
</tr>
<tr>
<td>Pd-Au/C</td>
<td>92 °C</td>
<td>118</td>
<td>45</td>
<td>100%</td>
<td>[6]</td>
</tr>
<tr>
<td>Ru₃(CO)₁₂</td>
<td>75 °C</td>
<td>not given</td>
<td>102</td>
<td>100%</td>
<td>[2]</td>
</tr>
<tr>
<td>RuCl₂(benzene)₂</td>
<td>40 °C</td>
<td>not given</td>
<td>852</td>
<td>100%</td>
<td>[2]</td>
</tr>
</tbody>
</table>
Figure S5.1. Chromatography of a typical GC-TCD run. Detection of $O_2$ and $N_2$ was due to the mixture of air during injection.

5.6. References


Chapter 6

Recommendations for Future Work

6.1. Recommendations for future work

The concept of Pd surface coverage and the unique way that we precisely control our nanostructure guided this thesis work and also opens up new thoughts and directions for future researchers to follow. Several recommendations for future work are discussed below.

6.1.1. Modulating the catalysis for glycerol oxidation using bimetallic M-on-gold catalysts ($M=$Pt, Cu, Fe, Ni, Co, Zn)

Besides Pd and its combinations with Au, glycerol oxidation has been studied using other elements, resulting in different oxidation products. By using iron based homogeneous and heterogeneous catalysts, Pagliaro et al. reported one-pot oxidation of glycerol to ketomalonic acid [1]. Kimura et al. reported the efficient conversion of glycerol to dihydroxyacetone using Pd and Pt-Bi catalysts respectively [2]. Besides those reported glycerol derivatives from bimetallic oxidation catalysis, other chemicals such as 3-hydroxypropionic acid, 1,2-propanediol and 1,3-propanediol are of great industrial importance and interest for researchers. Intrigued by the enhanced activity from Pd-on-Au catalysts and different oxidation products from other metals, we come up with the following hypothesis: by depositing different metal atoms on the Au
surface, catalysis in glycerol oxidation can be modulated, resulting in different selectivities towards oxidation products. In the meantime, high catalytic activity can be maintained by the stabilization effect of Au on the metallic state of the metal.

Scheme 6.1 shows the possible way of synthesizing M-on-Au NPs (M=Pt, Cu, Fe, Ni, Co, Zn). Our 4 nm Au NPs synthesized from tannic acid-sodium citrate method can be used as starting solution, where aliquots amount of salt solutions can be added, mixed and subsequently reduced by H₂ or NaBH₄, depending upon the reactivity of metal M. ICP-OES, XPS and XAFS can examine whether this synthesis strategy is successful or not, i.e., whether M is truly reduced, and whether reduced M is truly on Au. Even before characterizations, batch reactions of glycerol oxidation using either colloidal suspensions or carbon supported forms can be tested to verify the effect of metal M. It will be interesting to see if Au still has the capability to stabilize some other metals (even non-noble) during glycerol oxidation; if metal M can act differently than Pd with respect to activity, selectivity and deactivation resistance; and if M surface coverage can modulate the catalysis. These results will extend our understanding in surface coverage effect of Au bimetallic systems.
6.1.2. Synthesizing ultra-small Pd-Au nano-clusters

It has been widely acknowledged that the size of Au NPs has a great effect on its catalytic activity. In an earlier study, we pushed the limit of tannic acid – sodium citrate method and successfully synthesized a series of Pd-on-Au NPs with Au core diameter from 3 nm to 20 nm [3, 4]. We have observed a significant size effect besides Pd surface coverage effect in HDC of TCE, where 7 nm Pd-on-Au NPs were shown to be the most active among those with 3, 7 and 10 nm Au cores [4]. However, our further understanding in Pd-Au catalysis and Pd surface coverage effect in the regime of even smaller PdAu nanoclusters is difficult due to the limitation of water phase synthesis.

Qian et al. has done tremendous work in the field of synthesizing and characterizing ultra-small Au nano-clusters with precise Au atom numbers [5, 6]. During our recent research, we supported Au$_{25}$(SR)$_{18}$ on activated carbon, followed by heating under H$_2$ at 200 ºC for 30 min,
then cooled to room temperature under He. We observed with EXAFS that Au-S bond was largely removed after heating, while the general structure of the Au clusters was maintained. The ability to remove such adsorbed surface ligands while maintaining the cluster structure shows promise for the Au cluster for catalytic applications either by itself or with the addition of other catalytic metals.

Scheme 6.2 exhibits the proposed strategy for synthesizing ultra-small PdAu nanoclusters. Au$_{25}$(SR)$_{18}$ is first synthesized based on the method from Qian et al., followed by addition of Pd precursor with an amount corresponding to a certain surface coverage: Pd$_x$Au$_{25-x}$(SR)$_{18}$. Then the PdAu nanoclusters can be immobilized on activated carbon and treated under hydrogen flow at 200 ºC for 30 min, followed by cooling under He to room temperature to remove excessive sulfur contents. Confirmation of this material’s nanostructure can be done through XAFS, XPS, XRD, etc. Research into these clusters would broaden our understanding of the Pd surface coverage effect to a much smaller dimensional regime which we have been unable to explore with the current synthesis method.
6.1.3 Low temperature methane direct oxidation to methanol using ultra small Pd-Au nanoclusters

Direct catalytic methane oxidation to methanol is a very useful but extremely challenging reaction due to the perfect symmetric tetrahedron structure of methane (Scheme 6.3). This reaction is extremely exothermic due to the breaking of the methane’s C-H bond (bond energy of 439 kJ/mol). The desired catalyst for such a reaction would perform at temperatures close to ambient, require no HCl, H₂SO₄, SO₃, or SO₂, use O₂, air, or H₂O₂ as the oxidant, have a high yield of CH₃OH, and would be resistant to H₂S poisoning.
Direct methane oxidation to methanol under mild conditions is very rarely reported in literature. Periana and co-workers used HgSO₄ and SO₃ to oxidize methane at 180 °C with a methane conversion of 50% and a yield of 43% [7]. Fujiwara *et al.* used CF₃CO₂H as solvent, K₂S₂O₈ as oxidant and CaCl₂, Pd(OAc)₂/Cu(OAc)₂ and Mg as different catalysts at ~80 °C, reporting a TON <1 h⁻¹ [8-10]. Bell *et al.* reported activity at 65 °C using CF₃SO₃H and CaCl₂ as catalysts with SO₂ and K₂S₂O₈ as oxidants [11]. Sen *et al.* reported the catalytic activity of PdCl₂ at 90 °C using (CF₃CO)₂O as solvent [12, 13]. Hutchings and coworkers tested AuPd/TiO₂ catalysts with H₂O₂ as oxidant at 50 °C and achieved 12% selectivity to methanol and a TOF value of 6.9 h⁻¹ [14].

As shown in our glycerol study (Chapter 2-3), the combination of Pd and Au can activate O₂ very efficiently. Initial experiments would test our existing Pd-on-Au NPs catalysts for low temperature (<100 °C) water phase methane oxidation using O₂. In literature, Pd, Cu, Ni, and In all showed some capability to activate CH₄. We can further test M-on-Au NPs catalysts as described in Section 6.1.1. Additionally it has been reported that ultra-small Au clusters are able to activate CH₄ at very low temperature [15]. This suggests that the PdAu nano-clusters...
described in Section 6.1.2 also have the potential to be an efficient catalyst for low temperature methane oxidation.

6.2. References


